Factors controlling the retention and release of dissolved organic carbon in upland organo-mineral soils

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Abstract

Soils play a significant role in the movement of Dissolved Organic Carbon (DOC) within a catchment and are a major source of DOC to surface waters. Recent DOC increases in some surface waters in Europe and North America could be indicative of changes in soils leading to greater export of DOC. Organo-mineral soils have the ability to act as both sources and sinks for DOC due to the presence of a large organic layer as well as mineral horizon(s). However, the role of these soils in the movement of DOC within catchments requires further research. This study investigated the factors controlling the sorption and release of DOC in organo-mineral soils. Firstly, the sorptive properties of DOC leached from organic horizons beneath *Calluna vulgaris* (heather), *Molinia caerulea* (grass) and *Picea sitchensis* (forest) were investigated using a batch study and three isotherm models. The forest exhibited greatest adsorption to the mineral soil but released DOC with a high specific ultra-violet absorbance (SUVA). Both the heather and grass showed no net adsorption but released DOC with a lower SUVA. Secondly, the Langmuir isotherm was used to derive sorption parameters for 20 mineral soils collected from 11 UK upland sites. The sorption parameters showed no differences by soil type (gleysol or podzol) or by horizon (A, B, E). The maximum sorption capacity (Q_{max}) was greater for soils beneath graminoids than for soils beneath forest or shrubs. The amorphous forms of aluminium (Al_o) were the most significant predictor of Q_{max}. However, the occurrence of adsorption was controlled by soil pH; adsorption increased with increasing soil pH. The most significant control on desorption within the soils was Al_o. Iron content was not a major contributor to sorption within these soils. Thirdly, a column study was carried out to determine the effect of soil solution retention time on the adsorption of DOC to mineral soil. Sorption equilibrium was reached within 24 hours which would suggest that in soils prone to waterlogging most DOC sorption would occur in 24 hours. Additionally it was observed that there is a fixed sorption equilibrium concentration which differs only by DOC source. The work of this thesis suggests that vegetation cover could be used to manage DOC export in soils. The work here also suggests that the recovery of organo-mineral soils from previous acid deposition is likely to be having the effect of enhancing adsorption in the mineral horizons. However, as mineral horizons recover beyond their optimum pH for adsorption then it is likely that greater release of DOC from the mineral horizons will occur and increases in DOC will be observed in the catchments.

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1 Introduction

1.1 Research Overview

Dissolved organic carbon (DOC) is a complex mixture of molecules that are derived from the degradation of plant and soil material or from root exudates (Kalbitz et al., 2000; Leenheer and Croué, 2003). Over the last few decades there have been observed increases in the concentrations of DOC in surface waters in the UK, other parts of Europe and North America (Evans et al., 2005; Monteith et al., 2007). The observed DOC increases have far reaching implications for water treatment, acidity, metal mobility, water transparency and aquatic ecology. In the UK, upland catchments are a major source of potable water and increasing DOC is a source of financial and operational concern for water companies. DOC can impact on water transparency by giving waters a characteristic brown colour. The colour of potable waters is regulated in the UK with the current standard being 20 mg/L on the platinum-cobalt (Pt/Co) scale (The Drinking Water Inspectorate, 2009). DOC rich waters can also be problematic to treat since they can form carcinogenic disinfection by products (DBP) such as trihalomethanes (THMs), haloacetic acids (HAAs) when waters are treated with chlorine (Singer, 1999). The current standard for THMs in UK potable waters is 100 µg/L (The Drinking Water Inspectorate, 2009). Therefore management strategies to minimise the export of DOC to surface waters would assist water companies in meeting national standards for water quality.

Soils play a significant role in the movement of DOC within a catchment and are a major source of DOC to surface waters (Figure 1.1). At catchment scale the main control on DOC release to surface waters is the size of the soil carbon pool (Aitkenhead et al., 1999; Hope et al., 1997); therefore the release of DOC is greatest from areas with high proportions of peat and organo-mineral soils. The main source of DOC is in the organic rich horizons (Dalva and Moore, 1991) , while the mineral horizons with their clay minerals, and oxides of iron and aluminium have the capacity to bind DOC (Jardine et al., 1989). In the UK the largest increases in surface water DOC concentrations have been observed in the uplands where peat and organo-mineral soils dominate. To date more research has focused on the factors controlling the production, mobility and export of DOC from peat soils (Clark et al., 2012; Freeman et al., 2004; Freeman et al., 2001b; Worrall et al., 2002). In comparison, the organo-mineral soils are not well researched with respect to their contribution to catchment DOC dynamics, particularly variability between soil types in capacity to sorb DOC and their sensitivity to the quantity and chemical reactivity of DOC inputs. UK upland organo-mineral soils typically are vegetated by a variety of vascular plants including low shrubs, acid grassland, and occasionally forests (Holden et al., 2007; Reed et al., 2009). Predicted temperature increases (Jenkins et al., 2009), as well as, increasing carbon dioxide levels, water table changes and declining acid deposition could lead to an increase in vascular plants in the UK uplands (Ritson et al., 2014b). Whilst a number of studies have explored the sorptive properties of DOC leached from the O-horizon of forest soils (Chorover and Amistadi, 2001; Dalva and Moore, 1991; Guggenberger and Zech, 1992; Guggenberger and Zech, 1993; Kaiser et al., 2002), few studies have considered the influence of DOC leached from O-horizons dominated by non-forest vegetation. Knowledge of how non-woody plants influence the production and sorption of DOC in upland catchments would be useful in predicting and managing the impacts of the increased DOC export to waters. This would also be instructive to hydrochemical modellers interested in land management scenarios.

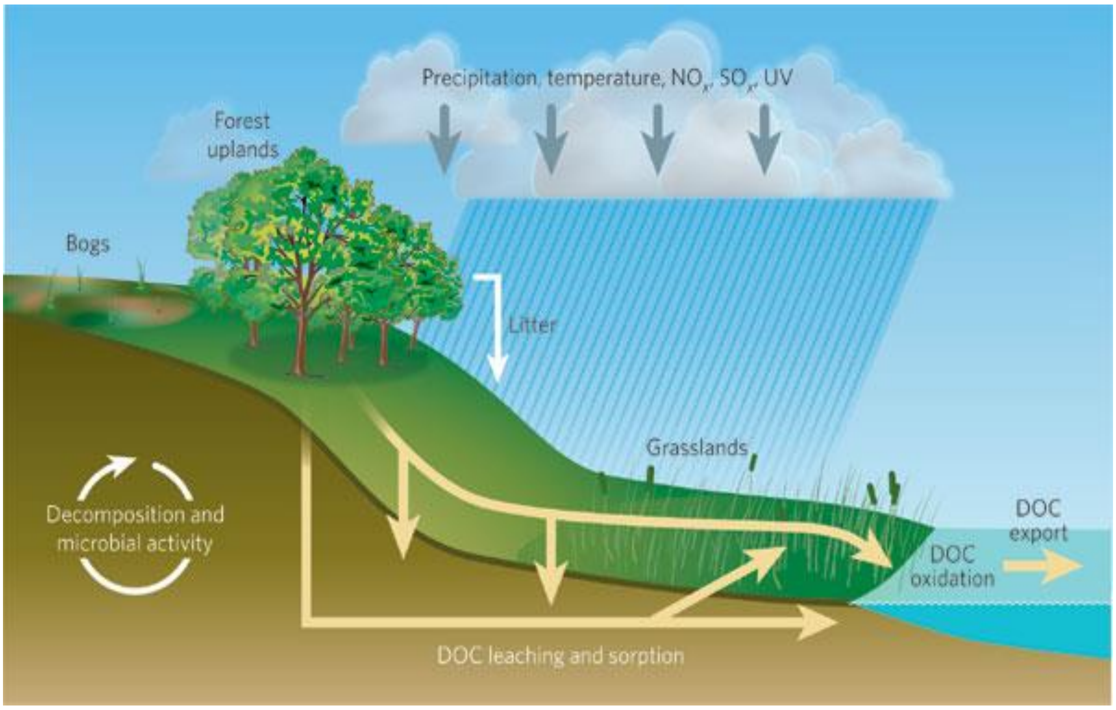


Figure 1.1. Passage of dissolved organic carbon (DOC) through the landscape. (Roulet and Moore, 2006)

The increase in surface water DOC concentrations has also raised concerns about the stability of soil carbon stores (Bellamy et al., 2005). Using data from the National soil inventory for England and Wales for the period 1978-2003, Bellamy et al. (2005) found that the soils lost carbon at a rate of 0.6% per year. The carbon lost has been suggested to be due to the destabilization of soil carbon as a result of climate change (Bellamy et al., 2005). The surface water DOC increases could also be due to mineral soils having a reduced capacity to retain DOC due to sorption sites being saturated. However, this theory has not been explored or investigated for mineral or ogano-mineral soils within the UK. Other theories for the rising DOC in surface waters include changes in: atmospheric deposition (Evans et al., 2006); hydrological export (Hongve et al., 2004) and land management (Armstrong et al., 2012; Clutterbuck and Yallop, 2010).

The rising DOC concentrations and the implications for water quality have been a stimulus for intensive research into the reasons for these increases. Significant advances have been made with regards to the production and movement of DOC in peat soils (Clark et al., 2012; Freeman et al., 2004; Freeman et al., 2001b; Worrall et al., 2002) and forested catchments (Borken et al., 2011; Chorover and Amistadi, 2001; Dalva and Moore, 1991; Guggenberger and Zech, 1993; Vanguelova et al., 2010) . However, with the mixture of woody and non woody plants present in the uplands as well as the prevalence of organo-mineral soils in these areas there is a need for greater research on the role of non woody plants and organo-mineral soils on the DOC dynamics in upland catchments. It would be of great value to know if sorption properties of organo-mineral soils differ between soil types or by different horizons within the soil profile. Additionally, knowledge of the capacity of these soils to retain carbon and the properties which control sorption behaviour would facilitate better land management practices to minimise the release of DOC from these soils. Isotherm models such as the initial mass isotherm and the Langmuir isotherm have been used to model sorption parameters of soils in Canada (Kothawala et al., 2008), Belgium (Vandenbruwane et al., 2007) and the US (Jardine et al., 2006). However, such studies have not been done on UK organo-mineral soils and to do so would be useful in the prediction of the behaviour of DOC in catchments dominated by organo-mineral soils.

1.2 Aim and Objectives

1.2.1 Aim:

This research seeks to expand the knowledge of the factors that influence the retention and release of DOC within UK Upland organo- mineral soils.

1.2.2 Objectives:

1. Determine the role of dominant vegetation cover on DOC sorption in organo-mineral soils.

2. Determine the capacity of upland organo-mineral soils to retain DOC.

3. Determine the soil properties which control the adsorption and desorption of DOC in UK organo-mineral soils.
4. Assess how the retention time of soil solutions affects DOC sorption within organo-mineral soils.

1.3 Research Approach

To fulfil the aim and objectives described in section 1.2, soils were collected from sites across the uplands of England and Wales (Table 1.1) and a combination of batch and column studies were carried out in the laboratory. To fulfil objective one, a batch study was used to analyse the sorption properties of DOC leached from organic horizons beneath forest, heather and grass. The sorption properties of the three DOC sources were compared using three isotherm models: the linear initial mass isotherm; a modified Langmuir isotherm using the initial mass of DOC added and a modified Langmuir isotherm using the mass of DOC in the equilibrium solution. To fulfil objectives two and three, 20 mineral soils were collected from 11 sites and a batch study was carried out. The modified Langmuir isotherm with equilibrium solution concentration was used to model sorption parameters of the soils including the maximum sorption capacities (objective two). Statistical models were used to determine and describe the dominant controls on DOC sorption within the soils (objective three). To fulfil objective four, the influence of soil solution retention time was determined using a column study which assessed the sorption behaviour over a period of 120 hours of DOC collected from peat beneath heather and grass.

1.4 Thesis Structure

The thesis comprises six chapters. Chapter two presents a review of the relevant literature and sets the global context of this PhD in terms of carbon cycling, the factors controlling soil as a source and sink of DOC and highlights the research gaps and inconsistencies within the literature. Chapter three presents the results from a batch experiment that investigates the sorptive properties of DOC extracted from organic soils beneath heather, grass and forest vegetation. Chapter four presents the results from an experiment that examined whether UK upland soils are saturated or close to saturation with organic carbon and the soil properties which influence sorption in these soils. The results from an experiment that investigated the influence of increased retention time of DOC solution on adsorption are presented and discussed in chapter five. Chapter six presents a summary of the main research findings, their implications and suggestions for future research

Table 1.1. Details of the UK upland sites studied in the investigation of the research objectives of this thesis

Site	Grid location	Elevation (m)	Soil classification	Geology	Research objectives
Coalburn, Kielder Forest, Northumberland	N 55°05’29.53 W 002°29’26.94	300	stagnohumic clay loam (Gill and McIntosh, 2001)	sandstones and shales (Gill and McIntosh, 2001)	1,2 and 3
Wye, mid-Wales	N 52°27’45.84 W 003°44’23.04	470	peaty podzol (Monteith and Evans, 2005)	shale, gritstone (Monteith and Evans, 2005)	2 and 3
Hafren, mid- Wales	N 52°28’32.64 W 003°42’09.92	390	peaty podzol (Monteith and Evans, 2005)	shale, gritstone (Monteith and Evans, 2005)	2 and 3
Carleton Moor, Craven District, North Yorkshire	N 53^{o} 55.502’ W 002^{o} 03.693	340	Stagnopodzol (Soil survey of England and Wales, 1976)	millstone grit (British Geological Survey, 2016a)	2 and 3
Elslack , Craven District, North Yorkshire	N 53^{o} 55. 772 W 002^{o} 05.049	291	Stagnopodzol (Soil survey of England and Wales, 1976)	sandstone (British Geological Survey, 2016b)	2 and 3
Levisham, Ryedale, North Yorkshire	N 54^{o} 19.907’ W 000^{o} 42.972’	259	stagnopodzol (Soil survey of England and Wales, 1976)	sandstone (British Geological Survey, 2016c)	2 and 3
Dalby forest, Pickering, North Yorkshire	N 54^{o} 37.330 W 000^{o} 37.917	253	iron pan stagnopodzol (Ordinance Survey, 1976)	Sandstone (Wilson et al., 2001)	2 and 3
Nidderdale, North Yorkshire	N 54^{o} 09.625 W 001^{o} 54.450	384-418	Cambic stagnohumic gley (Soil survey of England and Wales, 1976)	millstone grit (Chapman et al., 2010)	2 and 3
Etherow, South Pennines	N 53^{o} 29.479 W 001^{o} 49.479	337	peaty podzols (Patrick et al., 1995)	millstone grit (Patrick et al., 1995)	2 and 3
Crowden , Derbyshire	N 53^{o} 29.946 W 001^{o} 53.209	337	stagnopodzol (Soil survey of England and Wales, 1976)	sandstone and shale (Blundell et al., 2013)	2 and 3
Marsden Moor, Huddersfield, West Yorkshire	N 53^{o} 36’ 19.9 W 001^{o} 57’ 51.9	293	stagnohumic gley (Soil survey of England and Wales, 1976)	sandstone and shale (Blundell et al., 2013)	2, 3 and 4

2 The retention and release of DOC from soils: A literature review.

2.1 Introduction: definition and current interest in DOC

Dissolved organic carbon (DOC) refers to a mixture of simple and complex organic molecules dissolved in natural waters such as ground water, soil and sediment pore waters, oceans, lakes, estuaries and other surface waters (Thurman, 1985). It is further operationally defined as the organic carbon passing through a 0.45 micrometre filter (Thurman, 1985). Within the last 20 years significant increases in DOC concentrations in surface waters have been observed in parts of Europe and North America (Burns et al., 2006; Clutterbuck and Yallop, 2010; Couture et al., 2011; de Wit et al., 2007; Evans et al., 2005; Freeman et al., 2001a; Hongve et al., 2004; Monteith et al., 2007). DOC within a surface water body may have originated from autochthonous sources or may have been transported from land based sources with surface water runoff or through the transport of ground water (Aitkenhead-Peterson et al., 2003; Bertillson and Jones, 2003). Increases in DOC within a catchment can be cause for alarm due to the known negative associations of DOC. DOC is comprised in part of organic acids, which means it has the ability to influence water acidity. DOC can form complexes with metals and influence the mobility and toxicity of metals in the ecosystem; this can be problematic when it complexes with heavy metals (Weng et al., 2002). The heavy presence of organic matter can lead to discolouration of water, which can affect light penetration and hamper the activity of phototrophs. During drinking water treatment processes, DOC in water can interact with disinfecting agents to form carcinogenic by products making it challenging to treat DOC rich waters (Sharp et al., 2006). The latter is of great concern, especially in the UK where potable water is sourced from a number of carbon rich catchments.

As water moves through the soil profile there is the potential for DOC to be adsorbed by mineral horizons. Previous research has shown that along a soil profile DOC concentrations in soil solution of subsurface mineral horizons were often less than the DOC concentrations in soil solution of surficial organic horizons (Borken et al., 2011; Grieve, 1990; McDowell and Likens, 1988; McDowell and Wood, 1984; Sawicka et al., 2016). For example, McDowell and Wood (1984) observed that the concentration of DOC in soil water collected in B horizons was less than that collected in the A horizons, in their study of soil waters collected in the Hubbard Brook catchment located in New Hampshire, USA. Similarly, Sawicka et al. (2016) in their study of nine sites across the UK also observed that DOC in soil solution collected in subsurface mineral horizons was often less than the DOC concentration of solutions collected in organic horizons. The reduction in DOC concentration is usually attributed to the adsorption of DOC by the mineral layers as it passes through the soil profile (Borken et al., 2011; Grieve, 1990; McDowell and Likens, 1988; McDowell and Wood, 1984; Sawicka et al., 2016). Furthermore, the adsorption of DOC by mineral horizons can regulate the quantity and composition of DOC that is exported to surface waters (McDowell and Likens, 1988; McDowell and Wood, 1984). McDowell and Wood (1984) observed that stream waters draining the Hubbard Brook experimental catchment were within 1 mg/L of DOC concentrations observed in soil waters collected in the B horizon of soils within the catchment. This indicates that sorption of DOC by mineral horizons can play a significant role in the export of DOC to surface waters. It is possible that observed DOC increases in catchments where mineral and organo-mineral soils are prevalent could be reflective of changes in the ability of mineral horizons to retain DOC. Studies of long term data for upland catchments in the UK have shown increasing DOC trends in B horizons of forests (Sawicka et al., 2016) and grassland/moorland sites (Sawicka et al., 2016; Stutter et al., 2011). The observations of Sawicka et al. (2016) and Stutter et al. (2011) would also seem to suggest that observed DOC increases could be reflective of temporal changes in the ability of mineral soil horizons to retain DOC.

2.2 Composition of DOC

Humic substances make up 50-75% of DOC and are responsible for giving DOC rich waters that characteristic ‘tea’ colour (Thurman, 1985). Humic substances are a mixture of aromatic and aliphatic hydrocarbon structures (Leenheer and Croué, 2003; vanLoon and Duffy, 2005). Although this mixture may vary by DOC source and a complete molecular characterisation of DOC has not been achieved, there are still a number of functional groups which have been identified as the cause of many of the properties of DOC. Some of these groups include amides, alcohols, carboxyl, ketones and quinones. Table 2.1 summarises these functional groups and some of the key properties of DOC which have been attributed to each.

Table 2.1 Summary of key functional groups found in DOC and the properties conferred due to their presence (adapted from Steinberg, 2003).

Type of Compound	Functional groups	Attributable properties
Aromatic	Phenols, alkylaromatics, quinones	Absorbs UV radiation. Initiates photoreactions such as photomineralisation Aromaticity can be predictor of heavy metal binding Responsible for adsorption to clay particles Controls change in humic substance quality as it passes through soils
Ionic	Carboxyl, phenolic hydroxyl amino	Reduces hydrophobicity and increases water solubility of humics Carboxyl and phenolic groups responsible for metal ion complexation
Aliphatic	Carbohydrates, amino acids	Decreases strength of aromatic properties. Act as substrates for biodegradation Acid polysaccharides involved in metal binding in colloids

Soil humic substances may be further divided into humic acid, fulvic acid and humin based on pH dependent precipitation. Fulvic acid constitutes the largest portion of humic substances in DOC due to its higher proportion of carboxylic and hydroxyl functional groups. Fulvic acids are also lower molecular weight compounds ranging from 800-2000 Daltons while humic acids are larger than 2000 Daltons (Thurman, 1985).

In the case of aquatic humic substances, these are often subdivided into hydrophilic acids and hydrophobic humic substances based on adsorption to hydrophobic resins (Steinberg, 2003; Thurman, 1985). The most often used resin for this separation is the Amberlite XAD-8 resin which has been shown to have a high sorptive capacity for humic substances and a good recovery of sorbed substances once eluted with a base (Goslan, 2003; Chow, 2006). The hydrophobic fraction can contain aliphatic carboxylic acids, aromatic carboxylic acids and phenols, while the hydrophilic fraction may be comprised of polyfunctional organic acids and aliphatic acids (Goslan, 2003).

2.3 DOC and the carbon cycle

Carbon in the form of DOC is transferred from terrestrial to aquatic and then to marine ecosystems thereby forming a significant component of the global carbon cycle (Moore, 1998). However, flux through the aquatic continuum (soil waters, inland waters and the ocean) is not the only way in which DOC contributes to the cycling of carbon. Most of the dissolved organic matter produced on land is not transported to aquatic systems instead it is mineralised or retained by soils (Kaiser and Kalbitz, 2012). McDowell and Likens (1988) in their study of the movement of DOC within the Hubbard Brook catchment in the USA, observed that DOC concentrations and fluxes decreased with passage of soil solution from the forest floor (28-37.5 mg/L; 20130 kg/km^2 yr^{-1}) through the mineral horizons (2.96 mg/L; 1720 kg/km^2 yr^{-1}). DOC concentrations similar to that of soil waters collected in the B horizons were observed in Bear Brook (3.13 mg/L) and Mirror lake (2.01 mg/L), which are surface waters draining the Hubbard Brook catchment (McDowell and Likens, 1988). The study by McDowell and Likens (1988) indicates that a large amount of the DOC produced is not exported to surface waters but is instead retained by mineral horizons. The DOC that is transported to inland waters will undergo further processing within that aquatic ecosystem. It is estimated that collectively inland waters receive 2.7 petagrams (Pg) C yr^{-1}, of which 0.6 Pg C yr $^{-1}$ is buried in sediments, 1.2 Pg C yr^{-1} is mineralised and 0.9 Pg C yr^{-1} is transported to oceans (Battin et al., 2009). Therefore a large amount of carbon, and by inference DOC, entering inland water bodies is not transported to the oceans. Within carbon cycle models the DOC entering the ocean is often represented as riverine flux (Figure 2.1). Dai et al. (2012) estimate DOC transport from rivers of the world to oceans are 0.17- 0.21 (Pg) yr^{-1} and Schlesinger and Bernhardt (2013) report the fluxes to be 0.4 Pg yr^{-1} (Figure 2.1). Although differences exist among estimates of DOC flux in the literature, when compared to other processes within the global carbon cycle (Figure 2.1) all estimates of the contribution of DOC fluxes from rivers to oceans seem small. As such the significance of DOC to the carbon cycle can be lost if this is the main means by which the contribution of DOC to the carbon cycle is measured. However, within the terrestrial environment DOC plays a major role in the carbon budget of many ecosystems as evidenced by the internal movement and processing of carbon in soils and inland waters which leads to a reduction in DOC export to oceans (Moore, 1998).

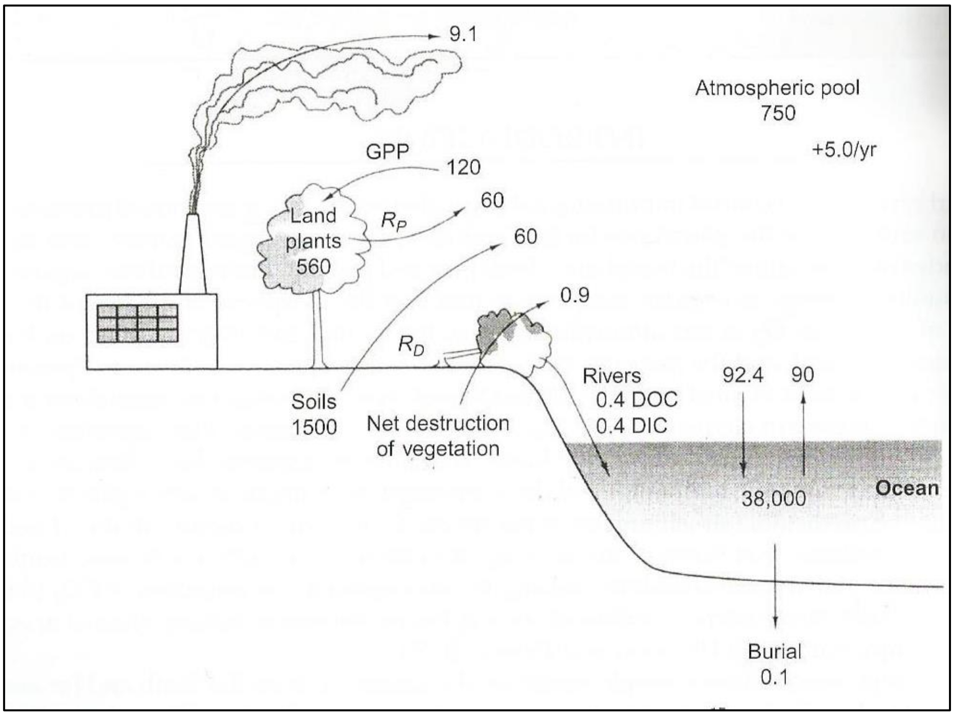


Figure 2.1 Global carbon cycle with carbon pools and fluxes. Estimates of carbon pools are in units Pg C and fluxes are in units Pg C/ yr (Schlesinger and Bernhardt, 2013, p. 420).

In purporting that the transfer of DOC from land to freshwaters and then to marine systems is a significant pathway in the carbon cycle, it is important to note that researchers have found differences in the chemical quality and composition of the DOC in each of these systems (Coble, 1996; Malcolm, 1990; Meyers-Schulte and Hedges, 1986). Studies by Coble (1996) using excitation – emission spectroscopy suggest that marine humic substances are chemically different to those in freshwaters. Malcolm (1990) in comparing terrestrial, freshwater and marine DOC found significant compositional differences. Soil fulvic acids were the most aromatic, marine fulvic acids the most aliphatic and stream fulvic acids the most phenolic (Malcolm, 1990). These differences may be due to the reactivity of DOC and reflect its involvement in a number of biological and geochemical reactions within each ecosysytem. Compositional differences could also be due in part to differences in autochthonous sources of DOC which may vary across ecosystems. A lack of extensive molecular characterisation of DOC (Kim, 2003), which would allow for the better understanding and tracking of the fate of terrestrial DOC as it moves through the various ecosystems could be a hindrance to deciphering why there is variation in its composition and by inference its reactivity between ecosystems.

2.4 Factors influencing DOC production in and export from soils

2.4.1 Temperature

A number of studies have shown a positive relationship between temperature and DOC production (Freeman et al., 2001a; Moore et al., 2008; Moore and Dalva, 2001). Moore and Dalva (2001) in examining soils and plant tissues found that the rate of DOC release at 22^{O}C was an average of 2.4 times greater than at 4^{O}C. Freeman et al. (2001a) conducted peat soil warming experiments in the range 2-20^{O}C and found that the increased temperatures resulted in increases in the release of DOC. The temperature sensitivity of DOC also seems to vary under aerobic and anaerobic conditions with increased sensitivity observed under aerated conditions (Clark, 2005). Two explanations were noted for the temperature dependence of DOC production: i) DOC production occurs by the action of microbes and increased temperature will lead to increased microbial activity and increased DOC production (Worrall et al., 2004); ii) with temperature increases there is the possibility from increased drawdown of the water table leading to a bigger zone of oxidation and increased DOC production (Worrall et al., 2004).

2.4.2 Hydrological changes

The transport of DOC is dependent on its production and discharge (Tranvik and Jansson, 2002). Therefore, increased concentrations of DOC as a result of increased production on land does not mean transport to water bodies will increase (Tranvik and Jansson, 2002). Eimers et al. (2008) used long term data (1980-2001) to investigate the influence of sulphate concentrations on DOC patterns in a wetland influenced catchment located in Ontario, Canada. The data utilised by Eimers et al. (2008) included continuous measurements of stream discharge at a v-notch weir located at the outflow of the sub-catchment and chemical analyses of grab samples of stream water taken at the weir. It was observed that a negative relationship existed between daily stream flow and DOC concentration (Eimers et al., 2008). The inter-annual patterns observed by Eimers et al. (2008) further exemplify the importance of hydrological flow to the transport of DOC (Eimers et al., 2008), maximum DOC concentrations occurred in the summer when stream flow was lowest, the DOC concentrations then decreased through late fall when stream flow increased, stabilized in late winter when runoff was relatively low, showed slight decreases again in April at the height of spring runoff before increasing again in May. Within the subcatchment PC1 snowmelt occurs in the spring and the volume of stream discharge associated with the snowmelt accounts for over 50% of the annual runoff (Eimers et al., 2008). The observed negative relationship between daily stream flow and DOC concentration was driven by processes occurring in the spring (Eimers et al., 2008).

Changes in rainfall patterns or storm events can alter DOC export to streams (Evans et al., 2005). Storm events can shift dominant flow paths with runoff in organic horizons being favoured over transport through and subsequent adsorption by mineral subsoils (Evans et al., 2005; Kalbitz et al., 2000). In Norway, Hongve et al. (2004) found that DOC increases in lakes monitored from 1983, were most likely due to periods of increased rainfall changing the flow path from vertical flow through mineral horizons to more subsurface flow through organic horizons. It is thought that the change towards increased flow through upper soil horizons in storm events also leads to a shift in the composition of the DOC exported from soils. Typically the hydrophobic fraction of DOC is preferentially adsorbed to mineral soils (Kaiser et al., 1996). However, with the shift towards increased flow during periods of high intensity rainfall, less sorption to mineral surfaces will occur and there will be a greater export of the hydrophobic acids (Hongve et al., 2004).

In anaerobic peats, droughts and the following rewetting cycle can impact on DOC production and export (Evans et al., 2005). Increased DOC is produced in the drought induced aerated soil and this is then flushed during the rewetting cycle (Evans et al., 2005, Evans et al., 2006).

2.4.3 Changes in Atmospheric Deposition

Several studies have suggested that declining atmospheric deposition of sulphur is a significant driver in the increased export of DOC from soils to water bodies (Clark et al., 2011; Evans et al., 2006; Evans et al., 2012; Monteith et al., 2007; Sawicka et al., 2016). Evans et al. (2006) observed that in the UK acid waters monitoring network (AWMN), which consists of 11 lakes and 11 streams in acid sensitive regions of the UK, there were significant increases in DOC within the period 1988-2003. It was noted that the DOC increases corresponded to decreasing concentrations of sulphate and marine ions at almost all of the AWMN sites (Evans et al., 2006).

Evans et al. (2006) therefore proposed that changes in sulphur deposition and changes in sea salt loading are significant drivers in the export of DOC to water bodies. Similar suggestions have been made by Monteith et al. (2007) who examined time series data for the period 1990- 2004 for 522 lakes and streams in Northern Europe and North America. Increasing DOC trends were observed in 363 of the water bodies examined by Monteith et al. (2007). Monteith et al. (2007) found that the relative change in the DOC (DOC change per year as percentage of site median) was strongly and inversely related to the change in both the sulphate and chloride concentrations of the waters (n=522). The concentrations of sulphate and chloride ions in surface waters of North America and Northern Europe are generally correlated with the concentrations of these ions in deposition (Monteith et al., 2007). Linkages have also been made between decreasing sulphur deposition and increasing DOC in soil solution in other studies (Borken et al., 2011; Sawicka et al., 2016). Sawicka et al. (2016) observed that at three UK grassland sites (Moorhouse, North Pennines; Glensaugh, Scotland and Sourhope, Scotland) DOC in organic soil solutions increased significantly over the period 1993-2000. These increases coincided with periods of the sharpest decreases in sulphate in the soil solutions and sharpest reductions in dry deposition of sulphate. Similarly, Borken et al. (2011) observed that DOC increases in soil solutions of forest sites in Germany were correlated with decreasing sulphate concentrations in soil solutions.

It has been suggested that the changes in atmospheric deposition affect soil organic matter solubility by changing the acidity of the soils or the ionic strength of the soil solutions (Monteith et al., 2007). Acid deposition (sulphate) and sea salt (chloride) can affect both processes (Monteith et al., 2007). Some researchers say that DOC adsorption in soils is favoured by decreasing pH (Gu et al., 1994; Münch et al., 2002; Sposito, 1984). However, decreasing acid deposition and sea salt loadings can result in pH increases (Monteith et al., 2007). The pH increases then result in increased organic matter solubility (Ekström et al., 2011) and the possibility for greater DOC export. The decline in atmospheric deposition of sulphate and chloride could also have the effect of lowering the concentration of multivalent ions in solution thereby affecting the ionic strength of the solution. Since increasing ionic strength of soil solution was shown to reduce DOC flux (Evans et al., 1988; Tipping and Hurley, 1988), Monteith et al. (2007) proposed that a decreasing ionic strength should lead to increased DOC flux. The theory of a relationship between DOC increases and sulphur and sea salt deposition seems to be supported by laboratory and field experiments in which increases in acidity and ionic strength resulted in decreases in DOC in soil solution (Clark et al., 2011; Evans et al., 2012). Clark et al. (2011) conducted batch experiments in which they treated peat soils and the organic horizons of organo-mineral soils from seven sites in the UK with two treatment solutions; i) sulphuric acid to represent an input of acidity and ii) a neutral sea salt solution to represent inputs from marine sulphate and to adjust ionic strength. It was observed that DOC release decreased from all soils with the addition of both treatment solutions. The response varied by soil type with soils rich in exchangeable aluminium and low in base saturation, such as the organo-mineral soils, showing greater sensitivity to the treatments (Clark et al., 2011).

Changing nitrogen deposition has also been suggested as a driver of increasing DOC concentrations in surface waters (Findlay, 2005; Sleutel et al., 2009).Findlay (2005) observed that during the period 1988-2003, concentrations of DOC in the Hudson River in New York had doubled. The observed increase in DOC was attributed to declining acidity due to decreased sulphur deposition and to nitrogen deposition (Findlay 2005). Nitrogen deposition in the Hudson River catchment had been sustained during the study period (1988-2003) (Findlay 2005). Sleutel et al. (2009) in their analysis of soil solutions collected in forests in Flanders, Belgium observed a positive relationship between dissolved organic nitrogen (DON) and DOC collected in forest floor leachate and in mineral horizons. The effect of nitrogen deposition on DOC release seems to be supported by the work of Pregitzer et al. (2004) who observed an increase in DOC export following the addition of nitrogen (3 g N m^{-2} yr^{-1}) for eight years to soils in Hardwood forests in Michigan, USA. It has been proposed that the increased nitrogen leads to a reduction in the activity of oxidative enzymes in the soils which results in incomplete degradation of lignin (Findlay, 2005; Pregitzer et al., 2004). The decreased decomposability (less mineralisation) of the carbon results in more intact phenolic compounds which could be potentially exported and hence result in the increased DOC export (Findlay, 2005).

2.4.4 **Vegetation cover**

Vegetation cover can influence the quality and quantity of DOC produced and exported from soils. Plant species can be categorized by differences in their functional types or functional traits (Yang et al., 2015). A plant functional type (PFT) refers to a group of functionally similar plants (plant species with similar roles in ecosystem processes that respond similarly to environmental factors) (Box, 1996; Yang et al., 2015). The classification of PFTs may be based on similarities in morphology, physiology or geophysical characteristics (Box, 1996; Yang et al., 2015). While categorizing vegetation by PFT has proven useful in the prediction of vegetation distribution, the use of PFT is deemed problematic when predicting ecosystem functions or carbon cycling (Van Bodegom et al., 2012; Yang et al., 2015). This is due to the existence of greater differences within PFTs than among PFTs (Yang et al., 2015). Furthermore, the features used to define PFTs are fixed and so do not consider adaptation to the environment (Van Bodegom et al., 2012;

Yang et al., 2015). It is important to consider adaptation to the environment when assessing the mechanisms involved in the cycling of water, carbon and other nutrients between the land and the atmosphere (Van Bodegom et al., 2012). Recent research has therefore moved away from the PFT to categorising vegetation based on functional traits (FT). FTs are morphological, physiological and phenological traits that indirectly affect plant health by their effects on growth, reproduction or survival of the plant (Yang et al., 2015). The ways in which plants take in and process carbon and the influence plants have on soil properties are largely determined by plant functional traits (FTs) (De Deyn et al., 2008; Dorrepaal, 2007). Consideration of the plant functional trait, relative growth rate, provides a good example of how differences in FTs might affect the carbon dynamics within an ecosystem. Soil carbon is mainly the product of decaying plant tissue, with root exudates also making a small but significant contribution (De Deyn et al., 2008). Plants which have a high growth rate usually have greater photosynthetic capacity than slow growing plants (De Deyn et al., 2008). Fast growing plants also have a shorter lifespan, lower dry matter content (such as leaf dry matter) and lower concentrations of carbon in their organs (De Deyn et al., 2008). However, due to the high photosynthetic capacity of fast growing plants and their short lifespans, fast growing plants have the potential to input greater amounts of carbon to the soil than slow growing plants (De Deyn et al., 2008).

Plant functional traits can also influence the composition of carbon and by extension carbon decomposability, as well as, carbon loss from, and immobilisation within soils (De Deyn et al., 2008). A good example of how differences in FTs might affect the carbon composition within an ecosystem is a comparison of litter production in forest with that of grasslands. In long lived woody plants as seen in forests, most of the carbon is distributed in organs for structural support and the resulting litter debris is mostly tough, dense and not easily degraded, resulting in a chemically complex organic carbon pool within the soil (De Deyn et al., 2008; Kögel-Knabner, 2002). Similarly shrub litter is of low decomposability (De Deyn et al., 2008). Conversely in fast growing, short-lived plants such as grasses most of the carbon is distributed to photosynthetically active structures of low density and high nutrient quality which can be easily decomposed (De Deyn et al., 2008). Additionally in grasslands the large rhizosphere makes a greater contribution to carbon inputs to the soils via root decay and root exudates (Stevenson and Cole, 1999). The DOC produced in the rhizosphere is mostly low molecular weight compounds (van Hees et al., 2005) which are more readily degraded by microbes. Thus in grasslands there is the potential for faster mineralisation of carbon leading to the production of DOC of lower concentration as well as the production of DOC less complex in character. It should be noted that although the rhizosphere is larger in grasslands, root exudates do play a significant role in the production and breakdown of carbon in all ecosystems. The labile DOC produced by root exudates is thought to increase microbial growth and activity in the rhizosphere (Kuzyakov, 2002). This increased microbial activity facilitates the decomposition and mobilization of higher molecular weight soil organic matter (Kuzyakov, 2002).

Root products can also enhance carbon retention in soils through their interaction with soil minerals. Leaching of DOC through the soil column is one way by which root products may come into contact with soil minerals. In addition, plant traits such as root depth, root branching and the root exudates can increase the possibility of retention by soil minerals (De Deyn et al., 2008). Deeper roots tend to be found in woody species such as trees (~7 m) and shrubs (~5.1 m) than in grasses and herbs (~2.6 m) (Canadell et al., 1996; Jackson et al., 2000). The overlying vegetation can therefore determine where in the soil profile the root products are released and by inference increase or decrease the possibility of their contact with mineral horizons.

These differences in carbon processing based on plant functional types may be of great significance in explaining differences in the quality and quantity of DOC produced in UK uplands. The UK uplands are typically vegetated by low shrubs, acid grasslands and occasionally are afforested (Holden et al., 2007; Reed et al., 2009). Data collected for 41 sites in the UK with varying vegetation covers showed that DOC in soil pore waters increased in the order moorland > woodland > heathland > grassland (van den Berg et al., 2012). Another UK study looking at the influence of vegetation cover on DOC produced in peatlands found that sites dominated by the moorland shrub *Calluna vulgaris* had the highest DOC concentrations while the grass species *Molinia* and *Sphagnum* moss dominated sites had the least (Armstrong et al., 2012). While studies have clearly shown that the concentration of DOC can vary with dominant vegetation cover, the effects of vegetation cover on the quality of DOC produced and its retention to and release from mineral horizons is not well understood. There are a few studies which have looked at long-term data for catchments with different types of vegetation (Camino-Serrano et al., 2014; Monteith et al., 2015; Sawicka et al., 2016). Camino-Serrano et al. (2014) analysed soil solution data for the period 1988-2012 for several catchments across the world, including 311 forest and 26 non forest habitats on mineral soils. Consistently higher concentrations of DOC were observed in soil solutions collected beneath forest than in solutions collected beneath non-forest habitats (Camino-Serrano et al., 2014). Sawicka et al. (2016) analysed long term data for soil solutions collected beneath forests and grasslands in the UK. In the study by Sawicka et al. (2016) soil solutions collected in the B horizons of the forests showed increasing DOC trends while those collected in the B horizons of the grasslands showed variability in their trends. The grassland site at Sourhope, Scotland showed a decreasing DOC trend while an increasing DOC trend was observed at the grassland site in Glensaugh, Scotland (Sawicka et al., 2016). This might suggest that prolonged inputs of DOC from a particular vegetation source will affect the soil's ability to retain DOC from that source. Contrary to this is the finding by Monteith et al. (2015) of no significant difference in DOC concentrations in surface waters of forest and moorland dominated catchments in the UK.

2.5 Soil as a source and sink for DOC

Soil is the main source of DOC to rivers in the UK uplands and soil properties have a major influence on aquatic DOC. It is known that a major source of DOC to streams is the most carbon rich soils in the catchment (Hope et al., 1997; Palmer et al., 2005; Worrall et al., 2002). These carbon rich soils occur in areas where precipitation is greater than evapotranspiration. Therefore, to date, research on DOC concentrations in surface waters has focussed on the factors controlling DOC production in, and export from, peat soils (Freeman et al., 2004; Worrall et al., 2002). While peats may be a major source of DOC to surface waters there are other categories of organic soils such as organo-mineral soils which are commonly found in areas where surface water DOC concentrations are increasing. The export of DOC from peat soils is mainly via near surface flow due to low hydraulic conductivity in lower layers limiting vertical flow (Holden and Burt, 2003). This is in contrast to organo-mineral soils where descending horizons are more permeable and adsorption to mineral surfaces can restrict DOC transport to surface waters (Worrall et al. 2002).

The organic matter content of soils may range from less than 1% for very young soils to 95% in some deep peats (Simpson, 1983). Soil organic content (prospective DOC) and its mineral properties (potential DOC binding sites) greatly influence the export of DOC. The study by Tipping et al. (1999) is a good illustration of variability of DOC export based on soil type. By leaching intact soil cores from three UK upland Moorland soils, Tipping et al. (1999) discovered that DOC concentration increased in the order: peaty gley>>brown earth>micro-podzol. This result was explained by the higher organic matter content of the peaty gley and the larger mineral horizon of the micro-podzol and brown earth (Tipping et al., 1999). Soils described in the study by Tipping et al. (1999) were classified using the soil survey for England and Wales classification system. Nelson et al. (1992) also found that soil type had a large influence on the amount of DOC exported; they showed that in two adjacent catchments with similar land use, climate, vegetation and topography, the amount of DOC exported to streams was significantly different, with higher export observed in the catchment with a higher percentage of sandy mineral soils. Furthermore the authors found DOC adsorption capacities were a function of soil clay contents and specific surface area (Nelson et al., 1992). Thus it can be surmised that the greater the organic content of the soil, the greater its potential as a DOC source and the greater the soil clay and/or mineral oxide content, the greater the potential to sorb DOC and thus act as a sink.

2.6 UK upland organic soils

2.6.1 Classification of organic soils

Organic soils are distinguished from other soil types based on the depth and organic matter content of the O-horizon (Joint Nature Conservation Committee, 2011). Within the United Kingdom there are differing definitions of organic soil types based on these two soil properties (Figure 2.2). For example, in England and Wales organo-mineral soils are defined as having an organic matter content of no less than 20% and an organic horizon of depth within the range 10-40 cm; soils with O-horizon depths greater than 40 cm are defined as peat (Joint Nature Conservation Committee, 2011). The Scottish classification defines organo-mineral as having an O-horizon depth between 10 and 50 cm; for O-horizon depths above 50 cm the soil is considered to be peat. Additionally under the Scottish classification organo-mineral soils should have more than 20 % organic matter while peats should have more than 60 % organic matter (Joint Nature Conservation Committee, 2011; Scottish Executive Environment and Rural Affairs Department, 2007). In Northern Ireland the soils should have no less than 40% organic matter in their surface horizon and a horizon thickness of no less than 40cm before it can be categorised as an organic soil (Figure 2.2) (Joint Nature Conservation Committee, 2011).

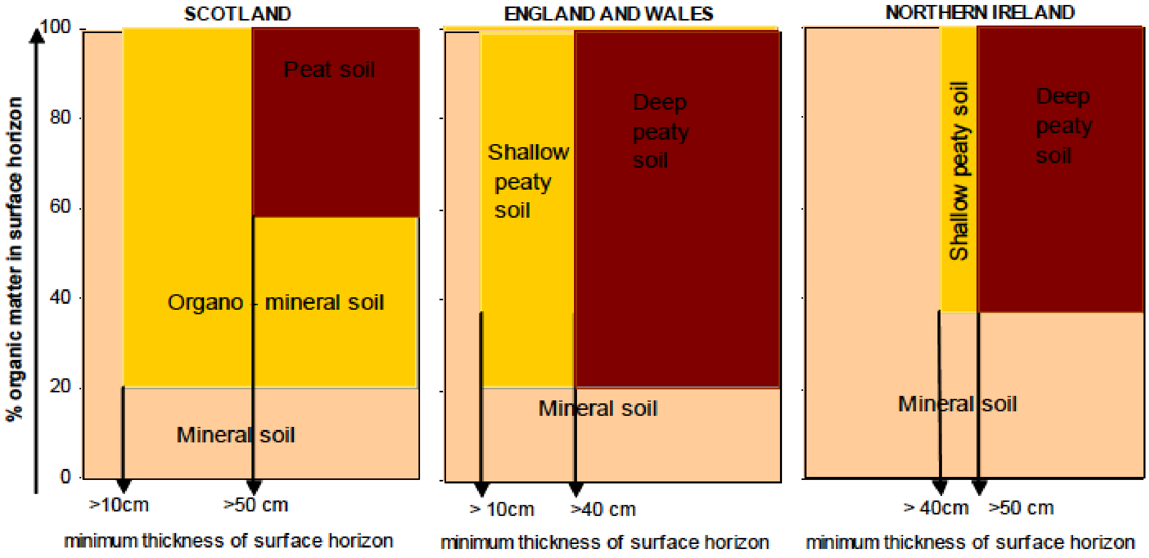


Figure 2.2 Minimum depth and percentage organic matter content used to differentiate between mineral, organo-mineral (peaty) and peat soils in Scotland, England and Wales (Joint Nature Conservation Committee, 2011, p.6)

2.6.2 Location of organic soils in UK

In England and Wales organic soils are distributed across approximately 11% of the land and cover 15719 km^2 of land area; organo-mineral soils cover 11130 km^2 and peat occupies the remaining 4589 km^2 (Holden et al., 2006). In Northern Ireland organic soils cover 24.6 % (3483 km^2) of which peaty soils (organo-mineral soils) cover approximately 1417 km^2 and peat covers approximately 2064 km^2 (Joint Nature Conservation Committee, 2011). In Scotland these soils are distributed across a greater percentage (>65.9 %) of the total land area (Scottish Executive Environment and Rural Affairs Department, 2007). Across the UK, organic soils occur predominantly in upland areas (Figure 2.3), where high rainfall, low summer temperatures, low rates of evapotranspiration, impermeable substrate and low relief result in periods of prolonged water logging (Holden et al., 2006; Jarvis et al., 1984). Under these waterlogged conditions organic matter decomposition is restricted and the partially decomposed material accumulates at the soil surface (Holden et al., 2006; Jarvis et al., 1984). The general relationships between soil types, climate, slope and elevation are shown in Figure 2.4.

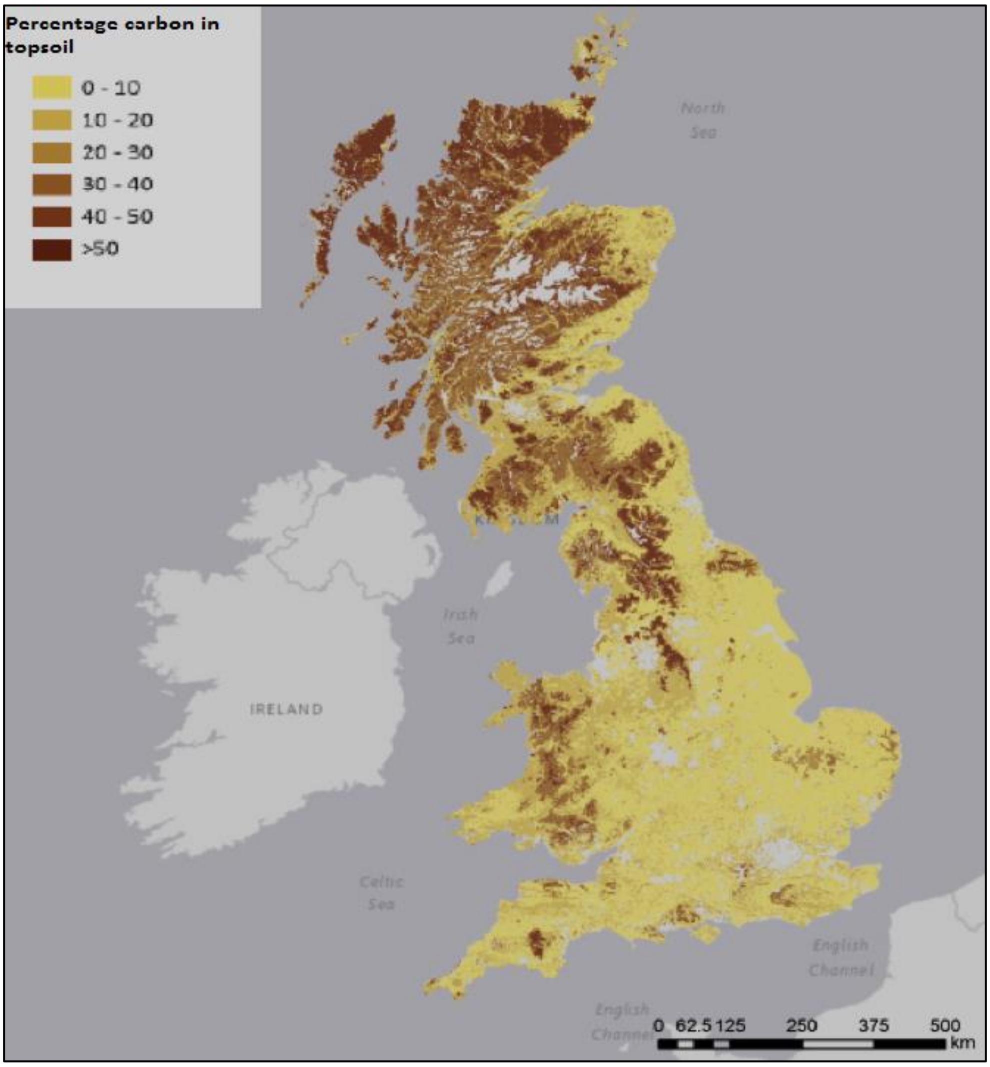


Figure 2.3 Carbon content (%) of upper soil horizons of soils in England, Wales and Scotland. (Source: Model estimates of topsoil properties [Countryside Survey] © Database Right/Copyright NERC – Centre for Ecology & Hydrology. All rights reserved. Contains British Geological Survey materials © NERC 2014. Contains Ordnance Survey data © Crown copyright and database right 2007.)

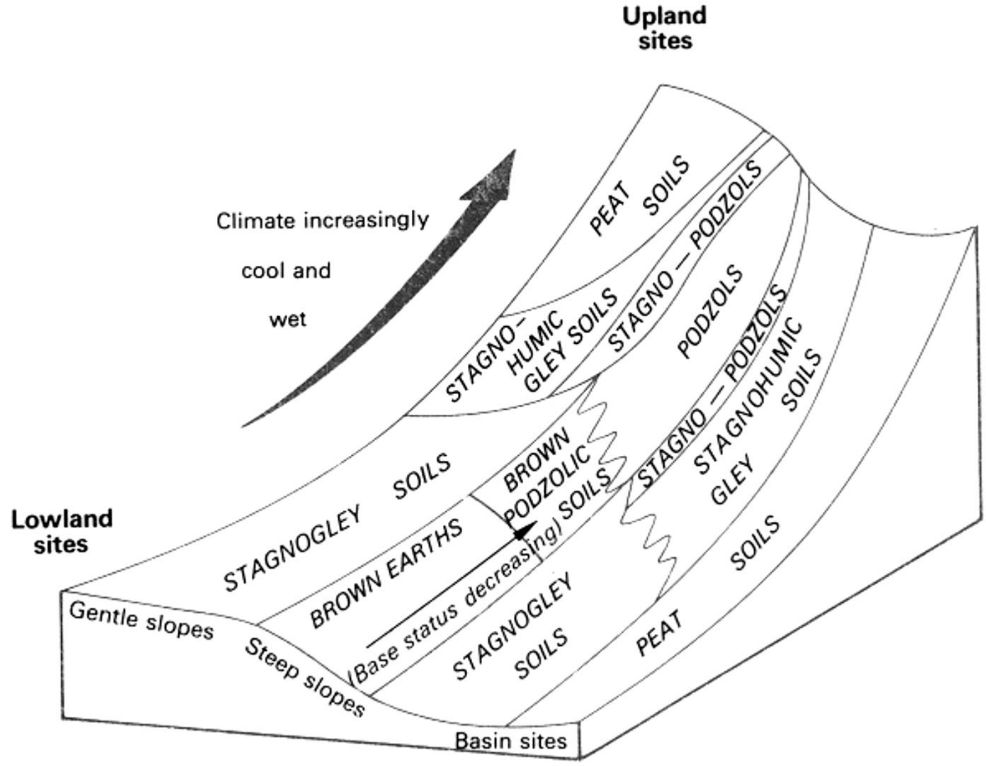


Figure 2.4.Relationships between soils, climate and relief (Jarvis et al., 1984, p. 49)

2.6.3 Upland organo-mineral soils

The major organo-mineral soils are gleys, stagnohumic gleys, humic podzols and stagnohumic podzols. Stagnohumic gleys and stagnohumic podzols are the most abundant organo mineral soils in England and Wales covering 5420 km^2 and 3566 km^2 respectively (Holden et al., 2006). Similarly, in Scotland peaty gleys and peaty podzols are the most abundant organic soils covering 17156.7 km^2 and 12240.40 km^2 respectively (Scottish Executive Environment and Rural Affairs Department, 2007). In Northern Ireland organo-mineral soils cover just 1417 km^2 of the land (Joint Nature Conservation Committee, 2011)

Stagnohumic gley soils typically have an organic horizon > 15cm, are not freely drained and are susceptible to seasonal waterlogging caused by high rainfall and low permeability of subsoil (Avery, 1980; Holden et al., 2006). Waterlogging results in the reduction, mobilisation and removal or relocation of iron compounds within the soil which causes the development of a gleyed mineral horizon (Jarvis et al., 1984). In these soils the gleyed subsoil has a prominent mottled appearance (Jarvis et al., 1984). A typical stagnohumic gley soil is shown in figure 2.5 and figure 2.6 shows a close up of the mottled subsoil of the gleysol.

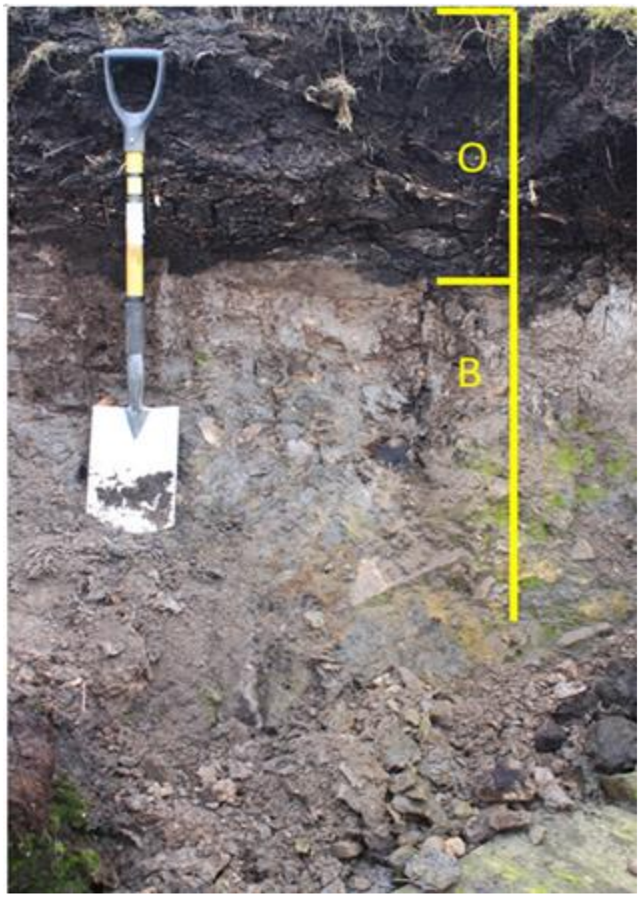


Figure 2.5 Photo of a stagnohumic gley sampled in Nidderdale, North Yorkshire (Northeast England). Shown are the organic horizon (O) and a mineral B horizon (B).

Figure 2.6. Photo of the mottled subsoil horizon of a stagnohumic gley sampled in Nidderdale, North Yorkshire (Northeast England)

The stagnopodzols are characterised by a periodically wet, bleached subsurface horizon overlying an iron enriched horizon (Avery, 1980). The organic horizon typically does not exceed 40 cm (Avery, 1980). Unlike the stagnogleys these soils overly a more freely draining mineral horizon. A typical stagnopodzol is shown in figure 2.7.

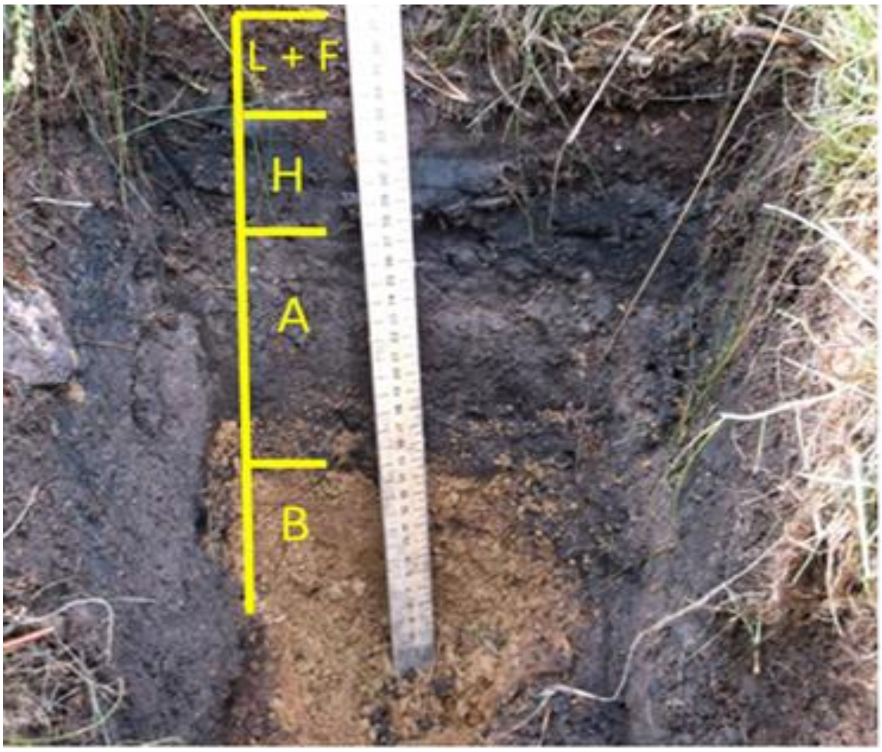


Figure 2.7. Photo of a stagnopodzol in Elslack forest, Craven District, North Yorkshire. Shown are the Litter and Fermented horizons (L+F), the Humic horizon (H), a mineral A horizon (A) and a mineral B horizon (B).

2.6.4 The influence of organo-mineral soils on the behaviour of DOC in UK upland catchments

The thick upper organic layer of organo-mineral soils is a great potential source of DOC. Within these soils the permeability is greater than in saturated peats and therefore there is greater potential for downward flow. The underlying mineral horizons offer greater potential for the adsorption of DOC. These organo-mineral soils are likely to have an impact on the amount and composition of DOC reaching UK upland surface waters and, therefore, need further investigation. Chapman et al. (2010) in their study of stream water colour in the Upper Nidd catchment showed that the largest increase in water colour over a 20 year period occurred in catchments with a larger proportion of flow coming from the mineral horizons. The Upper Nidd catchment is located in the North East of England; the major soil types include peats on the upper slopes and organo-mineral soils on the lower slopes (Chapman et al., 2010). The major organo-mineral soils within the Upper Nidd catchment are cambic stagnohumic gleys (Soil survey of England and Wales, 1976). From the work of Chapman et al. (2010) it can be inferred that these organo-mineral soils do indeed have a major influence on DOC within a catchment. Recent studies by Stutter et al. (2011) and Sawicka et al. (2016) using time series data have shown an increasing long-term trend in soil solution DOC concentration for a humus iron podzol located at Glensaugh, Northeast Scotland. Sawicka et al. (2016) also observed increasing temporal trends for two forests planted on organo-mineral soils; one site at Llyn Brianne, Wales was on an imperfectly drained gleysol while the other site, Ladybower in the Upper Derwent Valley of Derbyshire, England, was on a well-drained cambic podzol. The observed increases in soil solution DOC of organo-minerals with time at some upland sites could suggest that the ability of these soils to retain DOC is changing and possibly leading to a greater export of DOC to surface waters. Very few studies exist which have examined DOC dynamics within the subsoil horizons of UK upland organo-mineral soils. Those studies that have done so (Sawicka et al., 2016; Stutter et al., 2011) seem to suggest that the behaviour of DOC within these organo-mineral soils might provide an explanation for the recent increases observed in upland surface waters. However, further research is needed to determine the processes controlling the retention and release of DOC in organo-mineral soils. Without a better understanding of the processes controlling DOC retention and release within these soils, it is difficult to predict or model future DOC changes and their subsequent impact on drinking water treatment and quality, freshwater biota and the carbon cycle.

2.7 DOC sorption

Adsorption is the accumulation of a chemical substance at the common boundary between two phases which are in direct contact with each other (Sposito, 2004). In the context of this thesis it is the accumulation of molecules of organic carbon at the interface between soil solution/DOC and particles of mineral soil. Within the literature several processes have been identified as possible mechanisms for the adsorption of DOC to mineral soil surfaces. These mechanisms include adsorption via physical forces (Jardine et al., 1989), cation bridging (Kerr and Eimers, 2012), anion exchange (Jardine et al., 1989) and ligand exchange (Kaiser and Guggenberger, 2000; Tipping, 1981). Due to the complex mineralogical structure of soils, a mineral soil may have more than one type of DOC binding site. This may result in more than one mechanism of adsorption occurring for the adsorption of DOC to that soil's surface. This was seen by Jardine et al. (1989), who deduced that anion exchange and physical adsorption due to favourable entropy changes were the mechanisms by which DOC adsorbed to the soils they tested. The mechanism of DOC adsorption is controlled by the soil properties, solution chemistry and environmental factors, thus changes in these factors may result in a shift in the dominant mechanism of DOC sorption in a given soil.

2.7.1 Mechanisms of DOC adsorption to mineral soils

2.7.1.1 *Ligand Exchange*

Several researchers have identified ligand exchange as the dominant mechanism for DOC sorption to soil minerals (Gu et al., 1994; Kothawala et al., 2012; Tipping, 1981). This mechanism involves the replacement of a hydroxyl or water group on the mineral soil surface by an organic functional group of the DOC (Sanderman et al., 2014). In ligand exchange a strong covalent bond is formed between the organic anion and the mineral surface (McGrath et al., 2014). Due to the strength of these bonds substances bonded in this way do not easily desorb (McGrath et al., 2014). Ligand exchange occurs predominantly at the edge of terminal hydroxyl groups of variable charged minerals (McGrath et al., 2014) and so would most likely be favoured in soils with high metal oxide content.

2.7.1.2 *Electrostatic forces (Anion and cation exchange)*

Anion exchange reactions are ion exchange reactions in which negatively charged ions are attracted to sites of positive charge on the soil's surface and are held there by weak electrostatic forces. Mineral sub-soils may exhibit some positive charge due to the positively charged surfaces of clay and the metal oxides especially under slightly acidic conditions. Under slightly acidic conditions exposed hydroxyl groups may become protonated resulting in a positive charge at the soil's surface (Stevenson, 1994). This facilitates the formation of an electrostatic bond between the soil and the negatively charged organic anion. Jardine et al. (1989) deduced that anion exchange accounted for approximately 25% of the total DOC adsorbed by a B horizon soil sampled in Oakridge Tennessee USA. This was deduced by saturating the soil with SO_4^{2-} ions to occupy all of the anion exchange sites prior to batch adsorption experiments. Following saturation of anion exchange sites with SO_4^{2-} it was observed that the amount of DOC adsorbed was reduced compared to experiments in which there was no prior addition of SO_4^{2-} (Jardine et al., 1989). Ussiri and Johnson (2004) also suggested anion exchange as the most likely mechanism of DOC sorption to five mineral soils which they tested in a batch study. Ussiri and Johnson (2004) used soils from five horizons E, Bh, Bs1 Bs2 and C with pHs ranging from 3.8 to 4.5 and DOC solutions at pHs 3, 4 and 5. These researchers observed that the equilibrium pH of the solution either decreased or remained unchanged. From this they suggested electrostatic attraction between negatively charged carboxyl groups and positively charged soil surfaces was the likely mechanism of adsorption.

2.7.1.3 *Cation Bridging*

Cation bridging is when a divalent or polyvalent cation forms a bridge between negatively charged groups of the DOC molecule and negatively charged sites on the soil's surface (Sanderman et al., 2014). Kerr and Eimers (2012) have shown that cation bridging can be a significant mechanism for DOC binding with divalent and polyvalent cations being the major cations involved in this binding mechanism. Kerr and Eimers (2012) conducted batch sorption experiments in which they varied the solution Ca^{2+}, Na^{+}, pH and SO_4^{2-} content. These experiments were conducted in the presence and absence of soil to determine the contributions of adsorption and flocculation. It was noted that the amount of DOC adsorbed to soil increased with increasing Ca^{2+} while the addition of Na^{+} had no effect. Furthermore in the absence of soil some DOC was removed by flocculation for two of the treatments with Ca^{2+}. However, the amount removed by this method was less than seen in treatments with soil. This led these researchers to suggest that divalent and polyvalent cations formed bridges between the DOC and soil surface.

2.7.1.4 *Physical Adsorption*

Jardine et al. (1989) and Vance and David (1992) both suggested that DOC adsorption to the mineral soils in their experiments was due to physical adsorption. In both studies temperature had a miniscule effect on DOC adsorption and so it was determined that the adsorption reactions were driven by favourable entropy changes and not by enthalpy. No other studies were found which suggest physical adsorption due to favourable entropy change as the mechanism of DOC sorption.

2.7.2 Factors influencing DOC sorption in soils

2.7.2.1 *Pre-existing Soil Organic Matter*

Several studies show that with increasing amounts of pre-existing soil organic matter, the amount of DOC adsorbed decreases (Jardine et al., 1989; McDowell and Wood, 1984; Moore et al., 1992; Ussiri and Johnson, 2004). It was found that the removal of organic carbon from a B-horizon high in indigenous organic carbon prior to conducting batch adsorption experiments resulted in an almost four fold increase in adsorption of added DOC (Jardine et al., 1989). Furthermore, Jardine et al. (1989) saw the release of DOC in the A horizon soils without the removal of the indigenous carbon which they took as evidence that the pre-existing soil carbon impeded adsorption of added DOC. Ussiri and Johnson (2004) found that soil horizons with the least amount of soil organic carbon strongly retained DOC while those with the most indigenous carbon showed little or no adsorption for DOC. It has been proposed therefore that the soil carbon potentially blocks active binding sites limiting the amount of DOC that can be adsorbed (Kaiser and Guggenberger, 2000).

This limitation of adsorption by pre-existing soil organic matter (SOM) would seem to imply that at some point soils will become saturated with carbon and will no longer adsorb DOC, resulting in greater export from soils to surface waters. This raises the question of whether soils have a maximum adsorption capacity and whether some soils are at or are approaching that capacity. Few researchers have sought to investigate this theory. Of those that have, views on the relationship between maximum DOC capacity and existing SOM is conflicting. Kothawala et al. (2009) found that statistically pre-existing soil carbon had no influence on the maximum DOC capacity of soils; this study included 52 mineral soils from 17 soil orders across Canada. What is consistent throughout all the research is that soil carbon did affect the point at which DOC adsorption and release are equal, which is known as the null point. Inputs of DOC to the mineral horizon which are less concentrated than the null point would result in net desorption from soil while inputs of DOC which are more concentrated than the null point would result in net adsorption.

2.7.2.2 *Metal Oxides*

Aluminium (Al) and iron (Fe) oxides and hydroxides in soils also influence DOC sorption (Jardine et al., 1989; Moore et al., 1992). A study looking at twelve acid sub-soil horizons suggested that in these soil horizons there are amorphous or poorly crystalline phases present which are involved in carbon stabilization (Mikutta et al., 2006). These researchers also found Fe hydroxides and oxides to be more effective in carbon protection than the Al hydroxides because of their large positively-charged surface area (Kaiser and Guggenberger, 2000; Kaiser and Guggenberger, 2003). This relationship is further supported by a Canadian study on DOC sorption in a variety of soil orders and horizon types which showed that the soils' maximum adsorption capacities for DOC could be predicted based on the amount of Fe and Al in poorly crystalline phases (Kothawala et al., 2009). Furthermore, the observation by Gu et al. (1994) that a large portion of the DOC bound to Fe oxides is irreversibly bound seems to support the theory of finite sorption capacity.

2.7.2.3 *Clay minerals*

Clay minerals have also been shown to be involved in the sorption of DOC to mineral soils (Feng et al., 2005; Jardine et al., 1989; Kahle et al., 2004; Singh et al., 2016). Jardine et al. (1989) and Singh et al. (2016) observed that after treating soils to remove the Fe and Al oxides, DOC was still adsorbed to the soils. This was attributed to the remaining soil clay minerals (Jardine et al., 1989; Singh et al., 2016). The contribution of the clay minerals to DOC adsorption in soils is still uncertain; Kaiser and Zech (2000) observed a decrease of between 41-85% in adsorption of DOC to mineral soils after the removal of the metal oxides. This would suggest that although the remaining clay minerals are capable of retaining DOC in some soils they are poor sorbents compared to the Al and Fe oxides. There are two types of clays, expanding and non-expanding clays (Stevenson, 1994). Expanding clays are able to swell when exposed to a liquid thereby providing both internal and external surfaces for the adsorption to take place (Stevenson, 1994) . Contrarily non expanding clays do not swell and so have a smaller surface area than expanding clays (Stevenson, 1994). Singh et al. (2016) in comparing the adsorption of DOC to clay minerals observed that the expanding smectitic clays had a greater adsorption capacity for DOC than the non-expanding kaolinitic clays. The clay minerals have been shown to differ in their preference for specific organic compounds. Feng et al. (2005) observed that sorption of aliphatics was preferred by kaolinite, while montmorillinite favoured the sorption of aromatic carbon.

2.7.2.4 *Soil solution cations and anions*

The presence of multivalent cations such as Ca^{2+}, Fe^{3+} and Al^{3+} in soil solution, can affect the affinity of dissolved organic matter for soil surfaces. Kerr and Eimers (2012) found that increasing Ca^{2+} in solution led to increased DOC adsorption while the monovalent Na^{+} had no effect. The authors attributed this to a greater affinity of polyvalent cations for cation exchange sites in soils and also to the formation of cation bridges (Kerr and Eimers, 2012). In another study, it was observed that the addition of cations to soil solution increased the sorption of humic acid to the surfaces of illite, kaolinite or montmorillonite in the order Al > Ca > Mg > K, Na (Varadachari et al., 1991). This supports Kerr and Eimers (2012) theory of greater affinity of polyvalent cations possibly due to a smaller hydrated radius and increased charge.

In the case of anions, SO_4^{2-} or PO_4^{3-} compete with DOC for adsorption to mineral soils and their presence leads to reductions in the amount of DOC adsorbed (Gu et al., 1994; Vance and David, 1992). PO_4^{3-} seems to be the stronger of the anions with regards to the displacement and suppression of DOC adsorption (Kalbitz et al., 2000; Qualls, 2000). When

PO_4^{3-} adsorbs to mineral soils its spatial arrangement on the soil's surface hinders the adsorption of organic matter and it also shields the soil surface due to charge repulsion of the negatively charged organic carbon (Mikutta et al., 2007). It is not expected that interference from PO_4^{3-} would be a major problem in carbon rich soils as these generally have low amounts of phosphates unless fertilised. However SO_4^{2-} may be an influencing factor as many soils in western Europe and North America would have been subjected to high rates of sulphate deposition in previous decades (Palmer et al., 2013).

2.7.2.5 *pH*

There are discordant views on the role of pH in the adsorption of DOC. The majority of studies show that DOC export in organic soils is positively correlated to pH (Kalbitz et al., 2000). However when adsorption in mineral soils is assessed there are conflicting results within the literature. For some there was an optimum solution pH at which DOC sorption reached a maximum, for pHs above and below this optimum value DOC sorption decreased (Jardine et al., 1989; Ussiri and Johnson, 2004). Some researchers observed increased DOC sorption as solution pH decreased between solution pH and DOC sorption. For Jardine et al. (1989) the optimum solution pH for sorption of DOC onto a B horizon soil was 4.5 while for Ussiri and Johnson (2004) the optimum pH was 4 for adsorption to B and C horizon soils sampled along the soil profile at a single location. Kennedy et al. (1996) also observed greater adsorption of DOC to B and C horizon soils at lower pHs (pH 3 and pH 4.5). The increased adsorption to B and C horizon at low pH may be due to increased positive charge on the oxides facilitating the attraction and adsorption of the negatively charged organic functional groups in DOC. While at higher pHs the mineral surface becomes negatively charged leading to repulsive forces between the soil minerals and the negatively charged DOC (Jardine et al., 1989).

Kennedy et al. (1996) also experimented with E, O and A horizon soils and observed that there were no pH effects on the amount of DOC adsorbed by E horizons while the O and A horizons showed only a very small pH effect at the highest concentration of DOC tested. This could be due to a reduction in the oxides in these horizons. Vance and David (1992) also noted no effect of soil solution pH on DOC sorption when they tested B horizon soils.

Research is therefore suggesting that pH is a major control on the adsorption of DOC in the horizons high in mineral oxides, while it plays less of a role in adsorption in the upper organic and eluvial horizons. However with studies such as that of Vance and David (1992) showing no effect of pH in B horizon soils it would be useful to further investigate the effects of pH in a wider range of mineral soils.

2.7.2.6 *Retention time of soil solution*

As mentioned in section 2.5, for some organo-mineral soils such as stagnohumic gleys the permeability is low and they may become saturated during periods of high rainfall (McRae, 1988) . During the times of saturation the DOC will have a longer contact time with soil mineral horizons, but there is very little information available which examines how an increased DOC retention time may affect adsorption in mineral horizons. There have been studies which mention reduced retention time as a result of storm flow events leading to diminished adsorption to forest mineral soil (Hongve et al., 2004; Kaiser and Guggenberger, 2005) (see section 2.4.1.2). Based on this one might assume that the reverse is also true, and an increased retention time leads to an increased adsorption of DOC but no studies exist to support this. Furthermore, if we consider that in the UK carbon rich soils are often seen in areas of higher precipitation and low evapotranspiration, it is likely that contact time does affect carbon retention.

2.8 Adsorption Isotherms

The sorption of DOC can be modelled using adsorption isotherms (Kothawala et al., 2008; Lilienfein et al., 2004; Vandenbruwane et al., 2007). The adsorption isotherm describes the relationship between the concentration of the DOC in solution and the amount of DOC adsorbed on the soil after equilibrium at constant temperature. The initial mass isotherm and the Langmuir isotherm are often used to model the adsorption of DOC to soil.

2.8.1 Initial mass isotherm

The initial mass isotherm is based on the existence of a linear relationship between the amount of DOC adsorbed to the soil or released to the solution and the original mass of DOC added (Kothawala et al., 2008). It is described by the following equation:

$$RE = m \cdot X_i - b \tag{1}$$

Where *RE* (mg/kg) is the amount of DOC adsorbed or desorbed and X_i (mg/kg) is the initial mass of DOC in the solution. The partition coefficient m (unitless) is given by the slope of the line and is a measure of the fraction of total reactive DOC that is adsorbed by the soil (Pengerud et al., 2014). The amount of adsorbent desorbed into solution at a starting concentration of 0 mg C/kg is given by the parameter b (mg/kg) and it corresponds to the intercept of the line with the y axis.

The partition coefficient is used to calculate the distribution coefficient K_d (m^3/kg) which is a measure of the affinity of the DOC for the soil. In equation (2) V (m^3) is the volume of solution and M (kg) is the mass of the soil used in the experiments.

$$K_d = \frac{m}{1-m} \cdot \frac{V}{M} \qquad (2)$$

The reactive soil pool (*RSP*) is the quantity of pre-existing soil organic carbon that readily exchanges with DOC in the solution under the experimental conditions and is measured in mg C / kg soil (Nodvin et al., 1986; Pengerud et al., 2014).

$$RSP = \frac{b}{1-m} \qquad (3)$$

2.8.2 **Limitations of the initial mass isotherm**

The initial mass isotherm has the advantage of accounting for any pre-existing carbon which can potentially be desorbed in adsorption experiments. However, this model is based on a linear adsorption relationship between DOC and the soil, which would imply that mineral soils will have an infinite capacity for DOC sorption. Limited DOC sorption by pre-existing soil carbon and competing anions (section 2.6.2), as well as the apparent irreversibility of the sorption of some forms of DOC, would suggest that the soil's capacity for DOC is not infinite. Therefore as soils begin to reach that point of saturation the initial mass isotherm would not accurately describe the sorption relationship. Evidence in the literature also shows that DOC sorption is linear at low concentrations but becomes curvilinear at higher inputs of DOC (Vandenbruwane et al., 2007).

2.8.3 **Langmuir isotherm**

The Langmuir isotherm (Eq 4) has also been used to model adsorption of solutes to soil, where Q_{max} (mg/kg) is the maximum adsorption capacity; k (kg soil/ mg DOC) is the binding affinity and X_f (mg/kg) the final equilibrium concentration.

$$RE = \frac{Q_{max} \cdot k \cdot X_f}{1 + k \cdot X_f} \qquad (4)$$

In its classic form Eq (4) does not have a desorption term to account for any pre-existing soil carbon with the potential to desorb into solution. Lilienfein et al. (2004) added a desorption parameter b (mg/kg) to account for any pre-existing soil organic matter which desorbs at low DOC concentrations, Eq (5).

$$RE = \frac{Q_{max} \cdot k \cdot X_f}{1 + k \cdot X_f} - b \tag{5}$$

Lilienfein et al. (2004) and Vandenbruwane et al. (2007) have shown that the modified Langmuir equation with final equilibrium concentration is a better model for DOC adsorption to mineral soils than the initial mass isotherm. However, Kothawala et al. (2008) observed that the desorption term when used with the final equilibrium concentration was of no real value. Instead they proposed the use of the modified Langmuir equation with the initial mass of DOC (X_i) so that the desorption term b would be truly reflective of the behavior of the soil when no DOC is added. The modification of the Langmuir equation described by Kothawala et al. (2008) is shown in Eq (6).

$$RE = \frac{Q_{max} \cdot k \cdot X_i}{1 + k \cdot X_i} - b \tag{6}$$

2.8.4 Limitations of the Langmuir isotherm

Two key assumptions of the Langmuir equation are: i) the adsorbent has a fixed number of identical sites for adsorption resulting in monolayer coverage of the adsorbent by the adsorbate and ii) adsorption is reversible (Sparks, 2003). However as shown in section 2.6 there can be multiple sites for adsorption of DOC within a mineral soil due to the complex mineralogy of some soils. Additionally some sorption mechanisms involve strong chemical bonds which may result in the DOC being irreversibly bound. Therefore the adsorption of DOC to mineral surfaces may defy the assumptions which are intrinsic to the Langmuir isotherm leading to flawed estimates of the sorption parameters Q_{max} and k.

2.8.5 Usefulness of sorption isotherms in modelling DOC sorption to mineral surfaces

Despite their limitations, the parameters derived from the initial mass isotherm and the Langmuir isotherm have been used to compare the sorption of DOC from different sources (Jagadamma et al., 2012) or DOC sorption to different mineral soils (Kothawala, 2009; Mayes et al., 2012). Such comparisons allow for the determination of soil types which have a greater affinity for a particular DOC substrate or the type of DOC that is most likely to be adsorbed by a particular soil. As some studies have suggested that soils have a finite capacity for DOC sorption, comparisons of sorption parameters among soils and DOC sources would allow the identification of sites and soils which are most likely to become saturated with carbon faster. An understanding of these differences between soils in their carbon sorption and carbon saturation state could aid stakeholders to consider and put in place mitigating measures to limit DOC export to surface waters as a result of soil saturation.

2.9 Summary

- The production of DOC and its export from soils is influenced by several factors including temperature (Freeman et al., 2001a; Moore et al., (2008); Moore and Dalva (2001); see Section 2.4.1), hydrological changes (Tranvik and Jansson (2002); Eimers et al., (2008); see Section 2.4.2), acid deposition (Monteith et al., (2007); Evans et al., (2012); see Section 2.4.3) and dominant vegetation cover (van denBerg et al., (2012); Armstrong et al., (2012); see Section 2.4.4). Of these the role of vegetation cover in the production and export of DOC has not been widely studied and properly understood. A few studies show differences in the concentration of DOC exported from organic soil horizons based on vegetation cover (Armstrong et al., 2012; Sawicka et al., 2016; van den Berg et al., 2012) but even fewer explore the effect of vegetation cover on the quality of DOC released.
- Organo-mineral soils can act as both a source and a sink for DOC (see Section 2.5). These soils have large organic horizons which can act as a DOC source (see Section 2.6). Sorption in these soils is determined by a mixture soil and environmental properties (see Section 2.7). Due to differences in soils characteristics and sorption mechanisms, some soils may have the capacity to retain more DOC than others and so would take longer to reach their saturation point. Few studies have sought to determine and compare the affinity for DOC and the maximum sorption capacity of different mineral soils or which factors are most likely to control DOC sorption affinity and capacity in these soils (Jardine et al., 1989; Kothawala et al., 2008; Kothawala et al., 2009; Mayes et al., 2012).
- In the UK organo-mineral soils can be found predominantly in the uplands and at sites where DOC increases have been observed (see Section 2.6). Vegetation cover and mineral soil types at these sites are variable (Holden et al., 2006; Sawicka et al., 2016), leading to differences in DOC quality and possibly its subsequent interaction with mineral soils (Sawicka et al., 2016; Stutter et al., 2011). However, in the UK there has been a greater emphasis placed on researching DOC dynamics in peats (Armstrong et al., 2012; Freeman et al., 2001a; Freeman et al., 2004; Worrall et al.,

2002) and so the role of organo-mineral soils in the retention and release of DOC in the UK uplands has not been adequately researched is not fully understood.

2.10 Research gaps

This literature review has highlighted a need for further research in the following areas

- There needs to be a better understanding of the role of vegetation cover in the adsorption and release of DOC in minerals soils (see Section 2.4.4). This would allow upland land managers to make informed decisions on land management strategies to best minimise DOC export to surface waters.
- The maximum sorption capacity of these mineral soils needs to be further studied (see Sections 2.7.2.1; 2.7.2.2; and 2.7.2.3). If these soils do have a maximum capacity to retain carbon then knowledge of that capacity and the current state of saturation would be useful in identifying sites which are more likely to export greater amounts of DOC due to a saturated state.
- To better predict and model the sorption of DOC in organo-mineral soils there needs to be greater research on the soil and catchment properties which influence sorption (see Sections 2.7.2 and 2.8).
- Further research is needed on the role of soil solution retention time in the sorption of DOC to organo-mineral soils (see Section2.7.2.6).This is especially pertinent since the pre-dominant organo-mineral soils, stagnohumic gleys, are prone to seasonal waterlogging resulting in an extended soil solution retention time(see Section 2.6) .

Research in the above areas would aid with predicting the behaviour of DOC and managing the impacts of increasing DOC export in upland catchments.

3 Comparison of the composition and adsorptive properties of dissolved organic carbon extracted from organic horizons beneath three different types of vegetation

3.1 Introduction

This chapter investigates whether there are differences in the composition and adsorptive properties of dissolved organic carbon leached from surface peat developed under different types of vegetation.

Vegetation is a major contributor to the production of DOC, with possible input sources being canopy leaching, litter and root exudates (Guggenberger and Zech, 1994; Hansson et al., 2010; Wickland et al., 2007; Kalbitz et al., 2000). There have been conflicting views on the similarities of DOC composition sourced from different parts of the plant. Hansson et al. (2010) determined that the DOC production rate from Norway spruce varied between the spruce needles and roots, with roots producing DOC more slowly, however the composition based on the degree of aromaticity of the DOC was found to be similar from both sources. Guggenberger and Zech (1994) also studied DOC production from Norway spruce and found variations in the composition of DOC from canopy through fall and forest floor leachate. It had been assumed that forest floor leachate represented inputs from plant litter (Kalbitz et al., 2000), however it was later shown that this leachate was a mixture of fresh litter and older more decomposed organic matter in organic soil horizons (Park and Matzner, 2003). Therefore leachate from the forest floor is representative of sources of organic carbon at various stages of decomposition.

To date most of the research on vegetation influence on DOC production and export within soils has focused on soils from forest habitats (Kaiser et al., 2001a; McDowell and Likens, 1988). In collecting soil solution from beneath coniferous and hardwood tree species in Adirondack Park, New York, researchers found that there were significant differences in DOC concentration but no significant differences in the composition based on the analysis of DOC fractionated into hydrophobic and hydrophilic fractions (Cronan and Aiken, 1985). Others such as Gough et al. (2012) found significant differences in both the quantity and composition of DOC after comparing DOC extracted from organic soils beneath different tree species; European beech, Norway spruce, Japanese larch and Scots pine. They found that the composition of DOC, as measured with Specific UV Absorbance (SUVA), and the proportion of the hydrophobic and hydrophilic fractions varied with tree species. The

Spruce had the highest mean SUVA (7.0 ± 0.99 L/mg/m) and the least amount of hydrophobic acids (38%); while the Larch had the lowest SUVA (1.2 ± 0.36 L/mg/m) and the highest percentage (50%) of hydrophobic acids. Of the few studies that have investigated DOC from different vegetation types, including non-woody plants, the focus has been on the variation in DOC concentration and flux (Buckingham et al., 2008; Roberts et al., 2009; van den Berg et al., 2012; Armstrong et al., 2012) rather than DOC composition. With the exception of Buckingham et al. (2008) who were limited by insufficient data, all these studies demonstrated that vegetation type has a strong control on DOC concentration. Armstrong et al. (2012) examined soil pore waters taken from different plots at a single site in the UK. They compared plots dominated with *Calluna*, sedges, *Sphagnum* and *Molinia* and found that the pore waters from the *Calluna* plots had the highest mean DOC concentration while those from the *Molinia* plots had the lowest. Van den berg et al. (2012) in a UK multisite study of grasslands, heathlands, woodlands and moorlands also found that soil pore waters from grasslands had the lowest DOC concentration while soil pore waters from moorlands had the highest.

Although not stated directly, there are a number of observations made within the literature that suggest that vegetation type is likely to control the composition of DOC produced. In peatlands, plants differ in important characteristics such as litter decomposability and association with fungi, which in turn affects the C balance (Limpens et al., 2008) and also DOC production. A column study using peat from a Canadian peat bog found that different plant species differ in the rate and degradability of their root exudates and that the vegetation type controlled the allocation of C within the peat column (Crow and Wieder, 2005). Sanderman et al. (2008) in comparing DOC from vegetation with the underlying soil organic matter found that there was a greater difference in the chemical characteristics of DOC from the grassland vegetation and its underlying soil carbon than in that of the forest vegetation and soil. This study by Sanderman et al. (2008) also indicates that differences in DOC character between vegetation types could be leading to sorptive differences when the different sources of DOC bind to mineral soil. However, this is an area of research which has mostly been overlooked in the literature and as such more studies are needed which investigate the impact of catchment vegetation cover on DOC composition and sorptive behaviour.

It is possible that compositional differences in DOC produced from different vegetation types leads to differences in how the DOC binds to soil. Most studies have examined the sorptive properties of DOC based on differences in the soil properties and have often utilised a single dissolved organic matter (DOM) solution and several soil horizons (Kothawala et al., 2009; Lilienfein et al., 2004; Moore et al., 1992; Pengerud et al., 2014; Turunen and Moore, 2003). Studies that used more than one DOM solution have seen differences in their adsorption to mineral soil horizons (Moore and Matos, 1999; Rennert and Mansfeldt, 2003). Moore and Matos (1999) showed that DOC derived from seven different plant and soil sources led to differences in the way the DOC was adsorbed to a single mineral soil. The DOC sources investigated included fresh maple leaves, old maple litter, mosses and lichens, a fibrisol (histosol), the O and A horizons of a brunisol (cambisol) and a commercial humic acid. When the adsorption of these DOC sources was modelled using the linear initial mass isotherm, it was found that there were differences in the sorption characteristics derived from the initial mass isotherm of the seven vegetation sources. Furthermore, it was observed that fractionation of the DOC solutions into humic, hydrophobic and hydrophilic fractions led to the discovery of weak relationships between the DOC chemistry and the sorption parameters. This supports the hypothesis that DOC composition influences its sorptive behaviour but there is a need for more research comparing DOC from other habitats. Furthermore, since organic soils are known to be major sources of DOC (Hope et al., 1997; Tipping et al., 1999) greater research is needed to determine how differences in vegetation cover affects the composition and sorptive properties of DOC produced in organic soil horizons.

In the UK uplands, heathland and unimproved grasslands dominate the vegetation types (Averis et al., 2004). The dwarf shrub *Calluna vulgaris* typically dominates on acidic peaty soils (Armstrong et al., 1997; Milne et al., 2002). While the grass species *Nardus stricta* and *Molinia caerulea* usually dominate on slightly less acidic upland soils and at higher altitudes (Armstrong et al., 1997; Milne et al., 2002). *N. stricta* typically thrives on drier soils while *M.caerulea* can grow on wetter soils (Armstrong et al., 1997). Within the last century the uplands have also been sites of the large scale planting of coniferous trees (Reed et al., 2009), and the two most commonly used conifers are lodgepole pine (*Pinus contorta*) and sitka spruce (*Picea sitchensis*) (Averis et al., 2004). Forest soils, especially soils under conifers, are usually more acidic than adjacent moorland soils (Harriman and Morrison, 1982; Sawicka et al., 2016). Since several studies have suggested that DOC adsorption is favoured at low pH (Clark et al., 2011; Evans et al., 2006; Evans et al., 2012; Kennedy et al., 1996; Monteith et al., 2007), it might be expected that greater sorption would be exhibited by forest soils. Contrary to this is the finding by Sawicka et al. (2016) in which they observed an increasing DOC trend in subsoil solution collected under four UK forest; with the greatest increases occurring in solutions collected under two coniferous forests.

However, Sawicka et al. (2016) also observed a decreasing DOC trend in a deciduous forest and in a grassland. The differences in DOC trends among the different habitats were attributed to differences in the catchment soils; the decreasing sorption with time in the coniferous forest was due to the lighter mineral texture of the soils at these sites compared to the heavy clay mineral texture of the soils at the grassland and deciduous forest sites (Sawicka et al., 2016). Soil properties are known to be major controls in the sorption of DOC (Jardine et al., 1989; Kothawala et al., 2009; Mayes et al., 2012; Vandenbruwane et al., 2007). However, it could be possible that the DOC produced under the different vegetation covers were a contributing factor to the differences in DOC trend among the different habitats observed by Sawicka et al. (2016). If sorption of the forest derived DOC was initially more favourable due to its acidic nature, then over a prolonged period sorption sites may eventually become saturated. Thus the increase in DOC over time may reflect a reduction in sorption capacity. Furthermore it is likely that different types of vegetation will produce soil organic matter of differing phenolic contents and by inference different hydrophobicity, this can result in differences in the decomposition rates and adsorption/desorption properties of the DOC (Clark et al., 2010; Stutter et al., 2011)

Vegetation types which produce DOC that exhibits less retention by mineral soil horizons may result in greater loss of DOC to surface waters. Thus it might be possible to further explain DOC trends within a catchment based on the dominant vegetation type and the tendency of its DOC to be adsorbed by mineral soils or be exported. Further research is therefore needed in comparing the retention of DOC sourced from different vegetation types to mineral soils.

This study sought to determine the extent to which compositional differences in DOC sourced from organic soil beneath three vegetation types typically found in UK uplands affects the ability of the DOC to bind to mineral horizon soil. Soils were sourced from beneath *Molinia caerulea* (grass), *Picea sitchensis* (forest) and *Calluna vulgaris* (heather) as these vegetation types are typical of the UK uplands (Armstrong et al., 1997; Averis et al., 2004; Milne et al., 2002). The specific research questions were:

- Are there compositional differences in the DOC extracted from the organic horizon beneath each vegetation type?
- Are there differences in the way the DOC from each vegetation source binds to a common mineral soil?
- Which components of DOC are preferentially adsorbed by the mineral soil?

3.2 Methods

This study investigated the existence of compositional differences in DOC leached from organic horizons beneath *Molinia caerulea* (grass), *Picea sitchensis* (forest) and *Calluna vulgaris* (heather), and whether the DOC leached from these three organic horizons differed in their adsorption to mineral soil. DOC was obtained by soaking each organic horizon in an artificial rain solution. The DOC obtained from each source was then characterised based on its fractionation into hydrophobic and hydrophilic fractions, as well as other chemical properties such as pH and specific ultra violet absorbance at 254 nm (SUVA). Sorption experiments were conducted with each DOC source and a single common mineral soil. The mineral soil used was chosen from the least disturbed site to be representative of the site's natural state prior to changes in vegetation under new land management regimes. Leachates were characterised for SUVA and pH. The leachate DOC concentrations were used to construct isotherms to describe and compare the sorption behaviour of each DOC source.

3.2.1 Site and soil sampling

For this study, the Coalburn catchment in Kielder forest, Northumberland was selected due to the presence of a number of areas with differing vegetation types (Figure 3.1) occurring on soils developed from a common parent material. Selecting a single site meant that the soils would have developed under similar climatic and environmental conditions. The locations of each sampling point are given in Table 3.1. Coalburn is dominated by raw oligo-fibrous peat soils of the Winterhill and Longmoss series (Lawes Agricultural Trust, 1983). Also present in the catchment are cambic stagnohumic gley soils of the Wilcocks 1 series (Lawes Agricultural Trust, 1983; Robinson, 1999). These soils have developed on boulder clay (Birkinshaw et al., 2014). Prior to the 1970s, vegetation in the catchment was dominated by *Molinia* grass and peat bog species such as *Eriophorum* spp., *Calluna vulgaris* spp., *Sphagnum* moss spp., *Plantago* and *Juncaceae* (Birkinshaw et al., 2014; Robinson, 1999). In 1973 the Forestry Commission began planting the area with *Picea sitchensis* (Sitka Spruce) and some *Pinus contorta* (Lodegepole Pine) (Mounsey, 2000). Approximately 90% of the catchment was planted with trees, and natural moorland vegetation occupies the remaining 10% of the catchment (Mounsey, 2000). For this study, O-horizon soil samples were taken from beneath *Picea sitchensis* (henceforth referred to as forest), *Molinia caerulea* (henceforth referred to as grass) and *Calluna vulgaris* (henceforth referred to as heather). The forested and grassland sites were underlain by stagnohumic gleys with a considerable peaty O-horizon (20-40 cm); the heather site was a short distance away and was underlain by a somewhat deeper surface peat horizon (Table 3.1). Samples from all sites were collected on November 30th 2012. However the O-horizon soil beneath the grass collected on that date yielded DOC of very low concentration (21.65 ± 0.75 mg/L) which when subsequently diluted would not yield the volumes or concentrations of DOC solutions needed for sorption experiments. Coalburn was revisited on March 21st 2013 and O-horizon samples were taken from beneath another nearby grassland site (see Table 3.1).

Soil samples were taken from the organic horizon beneath each type of vegetation and the first mineral horizon (Ah) beneath the grassland site sampled on November 30th 2012 (Table 3.1). The mineral soil was sampled beneath the grassland because this was considered to be representative of the site's natural state prior to changes in vegetation under new land management regimes. Samples were placed in zip-locked bags and upon returning to the laboratory they were placed in cold storage at 4°C until needed for analysis.

Figure 3.1 The vegetation habitats present within the Coalburn catchment, heather moorland with grassland in the foreground (left), Sitka Spruce forest and grassland (right).

Table 3.1 Description of sites and horizons sampled in the Coalburn catchment of Kielder Forest, Northumberland.

Vegetation cover	Location	Date sampled	Horizon sampled	Horizon depth
Heather	55° 7' 41''N 2° 30' 45''W	30th November 2012	O	>1m
Forest	55° 5' 48''N 2° 28' 55''W	30th November 2012	O	20cm
Grass	55° 5' 50''N 2° 28' 49''W	30th November 2012	O	40cm
			A	> 8cm
Grass	55° 5' 29''N 2° 29' 20''W	21st March 2013	O	24cm

3.2.2 Experimental Approach

3.2.2.1 *Soil preparation and characterisation*

The mineral soil was oven dried at 40°C, gently crushed and passed through a 2 mm sieve. For the organic soils any obvious live vegetation and roots were handpicked from the soil. All soils were then characterised based on pH, moisture content, organic matter content by the loss on ignition method (LOI) and carbon and nitrogen content using a combustion analyser. Mineral soils were also analysed for amorphous Al and Fe and organically bound Al and Fe using acid ammonium oxalate and pyrophosphate extractions respectively. All soil analyses were done in triplicate. Method detection limits where stated were calculated as three times the standard deviation of the blanks (Van Reeuwijk, 1998). The blanks used for each method's limit of detection were the pooled blanks from all sections of this thesis.

Using the method of Bascomb (1974), the pH of the dried mineral soil was measured first in water then in 0.01 M Calcium Chloride ($CaCl_2$) solution using a ratio of 1:2.5 w/v. The pH was measured using a Mettler Toledo MPH 225 glass electrode pH meter. For organic soils the pH in water and 0.01 M $CaCl_2$ were measured using the method of Robertson et al. (1999), which entailed the use of field moist soil samples in a ratio of 1:2 w/v. The moisture content of the soils was determined by drying the soil at 105°C and the organic matter content by the loss on ignition method of combusting the oven dried soils in a furnace at 500°C overnight (Rowell, 1994). To determine soil carbon and nitrogen, soils were analysed using a Eurovector EA combustion analyser. The combustion analyser has a detection limit of 0.2 µg.

For the mineral soils, amorphous Fe and Al were extracted by shaking one gram of the < 2 mm fraction with 0.2 M acid ammonium oxalate (50 ml) in the dark for 4 hours. The organically bound Fe and Al were extracted by shaking one gram of the < 2mm fraction with 0.1 M sodium pyrophosphate (100 ml) for 16 hours (van Reeuwijk, 2002). The extracts were analysed using inductively coupled plasma-optical emission spectroscopy (ICP-OES). The method detection limits for the ammonium oxalate extractions were: Al = 0.06 mg/L and Fe = 0.03 mg/L. The detection limits for the pyrophosphate extractions were: Al = 0.03 mg/L and Fe = 0.05 mg/L.

3.2.2.2 *Removal of pre-existing carbon from the mineral soil*

Organic carbon already bound to the mineral soil has been shown to reduce the adsorption of DOC (Moore et al., 1992). To minimise the effect of any reduced sorption capacity due to pre-existing soil carbon, the pre-existing soil carbon was removed. This was done using an adaptation of the method of Kaiser et al. (2002). Five grams of soil was shaken with 50 ml of alkalinised (pH 8) 0.1M sodium hypochlorite (NaOCl) on a horizontal shaker for six hours at 25^{o}C. The suspension was then centrifuged at 2500 rpm for 30 minutes and the supernatant decanted. The process was repeated five times; following the fifth treatment the soil was washed with deionised water. To ensure that there was no residual available chlorine left to react with the DOC that would be added, the wash water was colorimetrically analysed for free chlorine using Hach free chlorine powder pillows. The Hach free chlorine method uses N,N-diethyl-p-phenylenediamine (DPD indicator) to test for the presence of hypochlorus acid or hypochlorite ion. These ions react with the indicator to produce a magenta colour which is proportional to the chlorine concentration (Hach, 2000). The method has an estimated detection limit of 0.0003 mmol/L (Hach, 2000). Chlorine in wash water samples was less than 0.0003 mmol/L.

The solid residue was removed from the centrifuge tubes, placed on plastic trays and dried in an oven at 40^{0}C for 2 days. The remaining soil carbon was quantified by analysis of triplicate samples from the pooled residue using a Eurovector EA combustion analyser. The percentage carbon removal was determined to be 63%.

3.2.2.3 *DOC Extraction*

The solution used to extract DOC from the O horizon was synthesized to mimic the precipitation chemistry at Kielder (Table 3.2), hereafter referred to as artificial rain solution. The artificial rain solution was made by dissolving sodium chloride, magnesium sulphate and calcium sulphate in deionised water followed by the addition of 0.1M hydrochloric acid to adjust pH (Table 3.3). The target pH was 5.39. From the rainfall data (Table 3.2) it can be seen that potassium (K^+) and nitrite (NO_2^-) were present in very low concentrations in the Kielder rain; therefore for expediency these ions were excluded from the artificial rain.

Using a modification of the methods of Jones and Willett (2006) and Moore et al. (1992), soil from each organic horizon was soaked in the artificial rain at ambient room temperature for 14 days using a soil mass to rain volume ratio of 1:2. The leachate was separated from the soil by sieving through a plastic mesh. The leachate was then filtered under suction, first using a glass fibre filter with nominal pore size 1.2 µm, followed by a 0.7 µm glass fibre filter and finally filtered using a 0.45 µm pre washed cellulose nitrate filter.

Table 3.2 Average (1993-1997) rainfall chemistry at Coalburn [Adapted from Mounsey (2000)]

Ion	Mean (meq/L)
Ca^{2+}	0.0254
Mg^{2+}	0.0268
Na^+	0.0979
K^+	0.0078
Cl^-	0.1445
SO_4^{2-}	0.0515
NO_3^-	0.0264
NO_2^-	0.0005
NH_4^+	0.0334

Table 3.3. Compounds used to synthesize extracting solutions representative of rain at Coalburn.

Compound	Purpose	Quantity (mmol)	Mass or volume
NaCl	Supplies all Na^+ and some Cl^- ions	0.0979	5.73 mg/L
$MgSO_4$	Supplies all Mg^{2+} and some SO_4^{2-}	0.0134	1.61 mg/L
$CaSO_4.2H_2O$	Supplies remaining SO_4^2 and Ca^{2+}	0.0124	2.13 mg/L
NH_4NO_3	Supplies all the NH_4^- and some NO_3^-	0.0264	2.11 mg/L
HCl	Used to adjust the pH and supply additional Cl^-	0.0466	0.47ml/L of 0.1M

3.2.2.4 *DOC Quantification*

All DOC solutions were analysed for organic carbon content by thermal oxidation using an Analytik Jena Multi N/C 2100S analyser. This equipment uses a differential method to calculate total organic carbon (TOC) in a sample. The total dissolved carbon (TC) is determined by digestion of both organic and inorganic carbon and subsequent detection of the carbon dioxide released. The total inorganic carbon (TIC) from carbonates, hydro-carbonates and free carbon dioxide is measured in a separate TIC reactor. The TIC is subtracted from the TC to give the quantity of TOC in the sample. Since all solution samples analysed in this study were filtered to <0.45 μm, TOC was assumed to equate to DOC. Each batch of analyses included the use of a certified reference material (VKI WW4A) and a standard prepared with the commercially available TIC (1000 ± 10 mg/L, Fluka product 12003-250ML-F) and TOC (1000 ± 10 mg/L, Fluka product 76067-250ML-F) standard solutions. The method detection limit was determined to be 0.25 mg/L using the method of Van Reeuwijk (1998).

3.2.2.5 *DOC fractionation*

The original DOC extracts were fractionated using the method of Aiken et al. (1992). Specifically for this study, each of the three DOC extracts was diluted to an approximate concentration of 10 mg /L using the artificial rain solution. The diluted sample (500 ml) was acidified to pH 2 using hydrochloric acid and subsequently pumped from the top of the column packed with the DAX 8 resin. A flow rate of 4 mL/min was used (Chow, 2006). The hydrophilic effluent was collected and stored at 4°C. Elution of the sorbed hydrophobic fraction was carried out by pumping 120 ml of 0.1 M sodium hydroxide through the column. Figure 3.2 shows the set up of the equipment. Each fraction was analysed for DOC concentration using the Analytik Jena Multi N/C 2100S analyser as described in section 3.2.2.4.

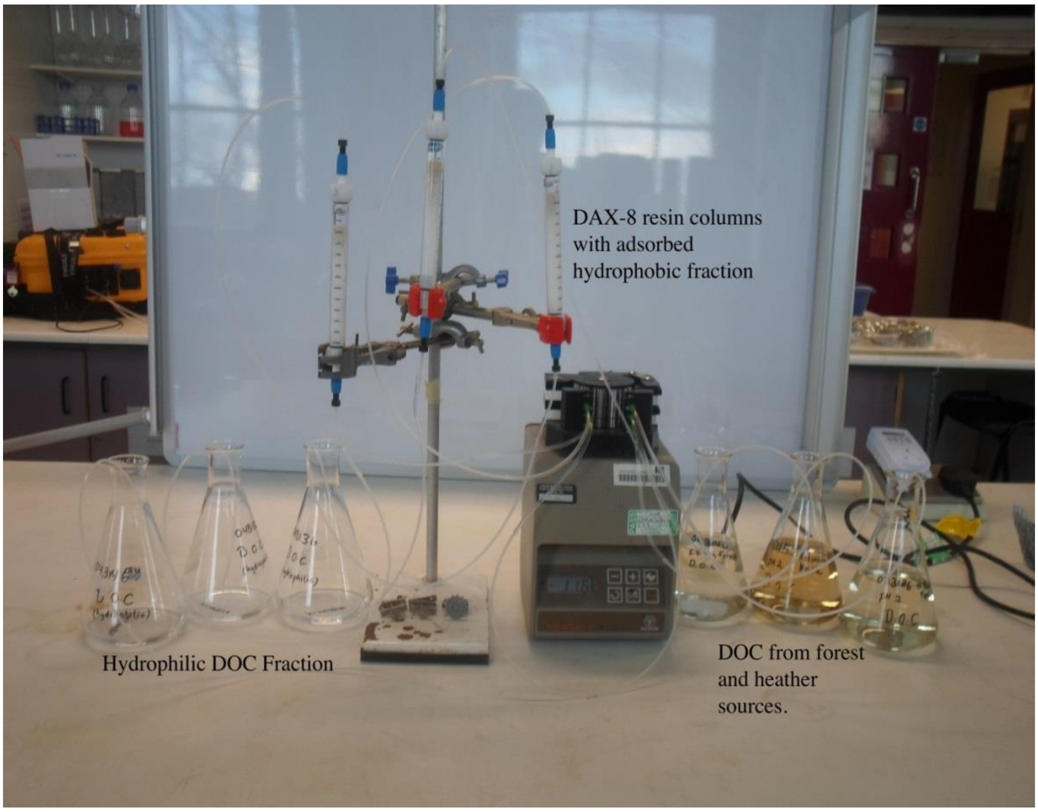


Figure 3.2. Fractionation of dissolved organic carbon with DAX-8 resin

3.2.2.6 *Ultra Violet Visible Spectroscopy.*

Samples were analysed for UV–Vis with a Jasco V-630 double beam spectrophotometer at wavelength 254 nm using 10 mm and 2 mm quartz cells (2 mm was used where samples exceeded the instrument range). SUVA was determined for all samples by dividing the absorbance by the sample DOC concentration.

3.2.2.7 *Batch experiment*

The forest and heather DOC extracts were diluted using the artificial rain solution to produce seven solutions with DOC concentrations ranging from 5 to 49 mg/L. These concentrations are similar to those observed in the literature for upland forested sites in the UK and within the range recorded for moorland sites. For example, Van den Berg et al. (2012) reported DOC concentrations of 10.2 mg/L to 46.13 mg/L for woodlands and 25.53 and 74.86 mg/L for moorlands in the UK. The grass extract was diluted to give six DOC solutions ranging from 4.5 to 31 mg/L. The volume and concentration of the leachate obtained limited the production of a DOC solution of higher concentration. However the range used is similar to the range of concentrations recorded in the literature for grassland sites in the UK uplands, 2.48 mg/L to 29.49 mg/L (van den Berg et al., 2012). At the Coalburn site average annual DOC concentrations of soil solution from the O-horizon beneath Sitka Spruce forest have been reported to be in the range 6.05 mg/L to 12.15 mg/L for the period 2002-2005 (Buckingham et al., 2008). The DOC concentrations given by Buckingham et al. (2008) for the Coalburn site fell within the range of concentrations for each DOC source used in these experiments. A 1:10 soil mass:solution volume ratio is often reported in the experimental protocol of batch studies which have looked at DOC sorption to mineral soils (Kothawala et al., 2008; Kothawala et al., 2009; Moore et al., 1992; Pengerud et al., 2014; Ussiri and Johnson, 2004; Vance and David, 1992; Vandenbruwane et al., 2007). It has also been shown that the release of DOC from soils varies with soil mass : solution volume ratio (Kaiser et al., 2001b). Therefore to be able to compare with the existing literature, a 1:10 soil mass:solution volume ratio was used in this study. Twenty millilitres of solution was added to 2 g of soil in 50 ml centrifuge tubes. Five replicates were prepared for each DOC solution as well as blanks containing no DOC (only artificial rain). The tubes were gently shaken by hand then laid flat on a horizontal shaker and gently shaken for 24 hours in an incubation fridge set to 4^{o}C. Twenty-four hours has been shown to adequate time for sorption equilibrium to be reached between mineral soils and DOC in batch experiments (Moore et al., 1992; You et al., 1999). After being shaken for 24 hours, samples were filtered under suction using pre-washed 0.45 µm cellulose nitrate filters. Filtered samples were analysed for DOC concentration as described in section 3.2.2.4 and SUVA as described in section 3.2.2.6. The difference between the DOC concentration at time 0 and the DOC concentration after 24 hours was used to calculate the mass of DOC adsorbed or desorbed by the soil (mg/kg).

3.2.2.8 *Statistical analysis*

The significance of the difference in SUVA between the pre adsorption and post adsorption solutions were analysed in SPSS version 22 using a paired t test.

3.2.2.9 *Isotherms*

The sorption of DOC was modelled using the initial mass isotherm and the Langmuir isotherm as modified by (Lilienfein et al., 2004) and (Kothawala et al., 2008) (see section 2.7).

The initial mass isotherm expresses the amount of DOC adsorbed or desorbed (RE) as a linear function of the initial concentration of DOC (X_i) in units of mass (mg/kg) (Moore et al., 1992). It is described by (Eq 1) below:

$$RE = m \cdot X_i - b \tag{1}$$

The partition coefficient m is given by the slope of the line and is a measure of the fraction of total reactive DOC that is adsorbed by the soil (Pengerud et al., 2014). The amount of adsorbent desorbed into solution at a starting concentration of 0 mg C/kg is given by the parameter b and it corresponds to the intercept of the line with the y axis.

The partition coefficient was used to calculate the distribution coefficient K_d which is a measure of the affinity of the DOC for the soil. In (Eq 2) V is the volume of solution and M is the mass of the soil used in the experiments.

$$K_d = \frac{m}{1-m} \cdot \frac{V}{M} \tag{2}$$

The reactive soil pool (*RSP*), shown in (Eq 3), was also calculated. This is the quantity of native soil organic carbon that readily exchanges with DOC in the solution under the experimental conditions (Nodvin et al., 1986; Pengerud et al., 2014).

$$RSP = \frac{b}{1-m} \tag{3}$$

Langmuir isotherm

The modified Langmuir isotherms described by Lilienfein et al. (2004) (Eq 4) and Kothawala et al. (2008) (Eq 5) were used to account for the soil carbon which remained (37 %) after pretreatment of the mineral soil to remove pre-existing soil carbon. The Langmuir equation expresses a relationship between the amount of organic carbon adsorbed (RE) and the equilibrium DOC concentration (X_f), the binding affinity (k) and the maximum absorption capacity of the soil to retain carbon (Q_{max}). The studies by Lilienfein et al. (2004) and Kothawala et al. (2008) both modified the Langmuir isotherm by adding a desorption term (b) to account for any native soil carbon with the potential of it to be desorbed. Lilienfein et al. (2004) modified the classic Langmuir equation which uses the equilibrium solution concentration (X_f). However Kothawala et al. (2008) determined that any desorption term derived from using the equilibrium solution concentration was of no real value and further modified the equation by using the initial solution concentration (X_i) instead of the final solution concentration (X_f).

$$RE = \frac{Q_{max} \cdot k \cdot X_f}{1 + k \cdot X_f} - b \tag{4}$$

$$RE = \frac{Q_{max} \cdot k \cdot X_i}{1 + k \cdot X_i} - b \qquad (5)$$

Model fitting and performance

The initial mass isotherm was fit using simple linear regression. The two modified Langmuir isotherms could not be linearly transformed so these were fit iteratively using the Levenberg-Marquardt algorithm in the statistical software SPSS 22.0. The performances of the models were evaluated using the root mean square error (RMSE), the coefficient of residual mass (CRM) and the model efficiency (EF).

The RMSE is an estimate of the variance of the residual error; smaller values indicate a better fit of the model. The CRM assesses the difference between the observed and predicted values and can indicate if there is a bias in the model towards one of these (Kothawala et al., 2008; Vandenbruwane et al., 2007). The EF assesses the fit of the data to the model with a value of 1 describing a perfect fit (Kothawala et al., 2008).

3.3 Results

3.3.1 Properties of the organic soil horizons.

The organic horizon soils ranged in pH from 3.76 to 5.36 when measured in water, with the organic horizon collected from beneath forest being most acidic while the grass was the least acidic (Table 3.4). The organic horizon beneath the heather had the highest carbon content (51.9 ± 0.1%), and organic horizon beneath the grass the least (5.8 ± 0.1%).

3.3.2 Properties of the DOC extracts

Concentration of DOC extracted was highest in the heather (170.6 mg/L), followed by the forest, (157.4 mg/L), and then the grass (55.3 mg/L). The forest extracted DOC was most acidic (pH = 4.87) and the grass DOC the least (pH = 5.93) (Table 3.5). SUVA increased in the order heather (6.02 L m/mg) > forest (5.39 L m/mg) > grass (4.37 L m/mg).

Analysis of the distribution of the organic fractions relative to the total DOC recovered shows the two fractions to be similarly distributed for the grass and the heather while the DOC from the forest produced less hydrophobic carbon than the other types of DOC (Figure 3.3).

From the extracted DOC, diluted solutions were prepared as follows: heather DOC (5.20 mg/L to 49.30 mg/L); grass (4.50 mg/L to 30.90 mg/L); forest (5.20 mg/L to 42.10 mg/L) (Table 3.6). The SUVA for the solutions was generally of the order heather>forest>grass (Table 3.6), thus the SUVA order observed in the concentrates (Table 3.5) was maintained despite differences of up to 1 L m/mg between diluted samples of the same DOC extract.

Table 3.4 Properties of the organic horizon soil collected beneath forest, grass and heather in the Coalburn Catchment. Standard error of the mean given in brackets, n = 3.

Property	Forest	Grass	Heather
Soil pH_{H2O}	3.76 (0.0)	5.36 (0.0)	4.27 (0.0)
Soil pH_{CaCl2}	3.06 (0)	4.39 (0.0)	3.03 (0.0)
Organic Matter %	35.82 (2.8)	10.66 (0.5)	96.48 (0.2)
Carbon %	12.9 (0.2)	5.8 (0.1)	51.9 (0.1)
Nitrogen %	0.68 (0.0)	0.45 (0.0)	1.49 (0.0)
C/N ratio	18.9 (0.1)	12.9 (0.1)	34.8 (0.1)

Table 3.5 Properties of DOC extracted from O horizon soil beneath forest, grass and heather collected from the Coalburn Catchment.

Property	Forest	Grass	Heather
DOC Concentration (mg/ L)	157.4	55.3	170.6
pH	4.87	5.93	5.21
Conductivity (µS/ cm)	117	106	104
$SUVA_{254}$ (L m/mg)	5.39	4.37	6.02

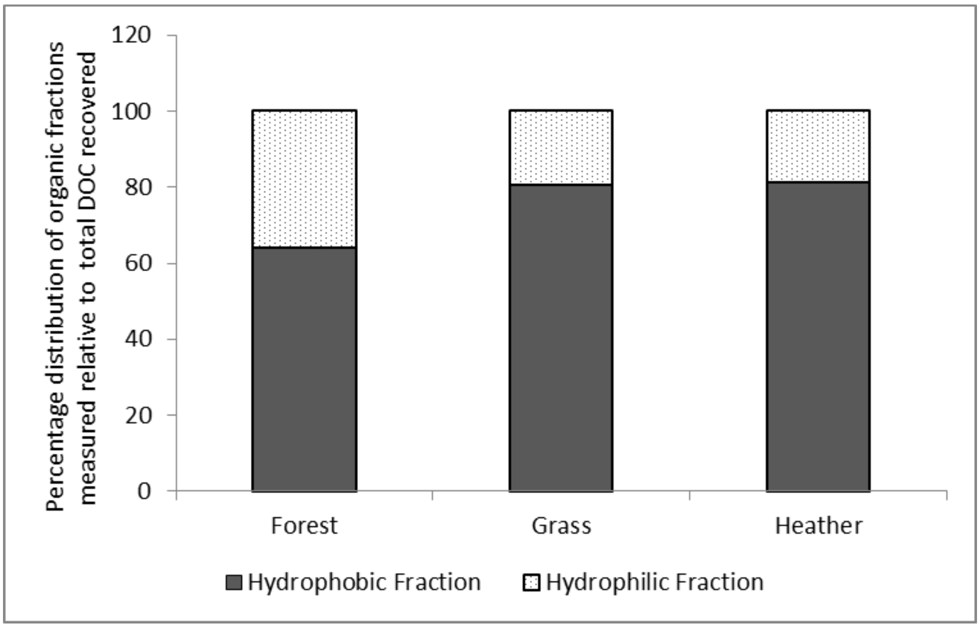


Figure 3.3 Percentage recoveries of the hydrophobic and hydrophilic DOC fractions for the three vegetation types measured as a percentage of the total DOC recovered.

Table 3.6. Concentrations and specific UV absorbance at 254 nm for the range of DOC solutions used in the adsorption experiments

Forest		**Grass**		**Heather**	
Concentration (mg/L)	$SUVA_{254}$ (L m/mg)	Concentration (mg/L)	$SUVA_{254}$ (L m/mg)	Concentration (mg/L)	$SUVA_{254}$ (L m/mg)
5.20	5.83	4.50	4.23	5.20	5.80
11.10	4.83	10.30	3.95	11.00	5.36
15.40	4.68	16.00	4.16	16.20	5.96
24.60	4.43	21.50	4.12	21.40	5.69
27.80	4.78	26.70	4.19	25.30	5.51
31.70	5.04	30.90	4.41	30.90	5.44
42.10	4.83	-	-	49.30	5.38

3.3.3 Properties of the mineral soil.

The 19400 mg/kg carbon in the mineral soil was reduced to 7100 mg/kg after treatment with sodium hypochlorite (Table 3.7). Therefore a 63% reduction in soil carbon was achieved. This value was lower than that achieved by Kaiser et al. (2002) who obtained between 77 to 95% carbon removal.

Table 3.7. Properties of the mineral soil. Standard error of the mean given in brackets, n = 3.

Property	Measurement
Nitrogen (mg/kg)	800 (0.00)
Carbon (mg/kg)	19400 (333)
Carbon after NaOCl treatment (mg/kg)	7100 (100)
C/N	23.83 (0.25)
Organic Matter (%)	4.28 (0.40)
pH $_{H2O}$	4.64 (0.03)
pH $_{CaCl2}$	3.61 (0.00)
Al_p	1.01 (0.01)
Al_o	1.53 (0.04)
Fe_p	2.36 (0.05)
Fe_o	5.65 (0.20)
Texture	Sandy loam

3.3.4 Batch Experiment: Interaction between the soil and DOC solutions

In the forest batch experiments desorption was seen at low concentrations of treatment DOC but at concentrations above 200 mg/kg adsorption was observed (Figure 3.4). For the range of concentrations used in this study, the heather and grass batch experiments exhibited only desorption with the extent of net desorption generally decreasing with increasing concentration of added DOC (Figures 3.5, 3.6 and 3.7). Visual inspection of the data from the grass batch experiments showed that the data points at 214.8 mg/kg and 266.5 mg/kg of added carbon deviated substantially from the other data points (Figure 3.5). The deviation of these two points led to negative slopes in all three isotherm models for DOC from this source. There was no rationale for this behaviour based on the soils used or the sites studied and no precedent for this behaviour was found in the literature. Therefore, the data points at 214.8 mg/kg and 266.5 mg/kg of added grass DOC were considered to be experimental artefacts (outliers) and were removed from the dataset. Reanalysis of the data without these data points resulted in a positive slope for all three isotherm models (Figure 3.6).

3.3.4.1 *Efficiency of fitted models*

The CRM is zero (Table 3.8) for all models indicating that there is no systematic bias towards either the observed or predicted values. The RMSE and the EF indicated that the Langmuir initial mass isotherm is the best fit for the forest and grass DOC while the heather DOC seems to be better fitted by the linear initial mass isotherm (Table 3.8). Although the Langmuir initial mass isotherm (Langmuir X_i) had the best measures of modelling efficiencies for the grass extracted DOC, the RMSE was still high (12.75 ; Table 3.8) and the EF low (0.56 ; Table 3.8) indicating that this isotherm model might not best explain the adsorption behaviour of the DOC extracted from the grassland. Removal of the possible outliers at 214.8 mg/kg and 266.5 mg/kg of added carbon sourced from beneath grass resulted in improved fits for all isotherm models tested (Table 3.8). The RMSE error for the Langmuir X_i decreased from 12.75 to 5.15 after the removal of outliers. The RMSE of the Langmuir model with final mass (Langmuir X_f) decreased from 17.78 to 5.14 and the RMSE of the linear model also decreased; dropping from 18.79 to 6.92. The EF values increased with the removal of the outliers (Table 3.8). The removal of the outliers in the data also resulted in similar measures of model efficiency for the Langmuir X_i and Langmuir X_f (Table 3.8). Based on the similar model efficiencies both Langmuir models were equally acceptable as the best fit model for DOC from this source.

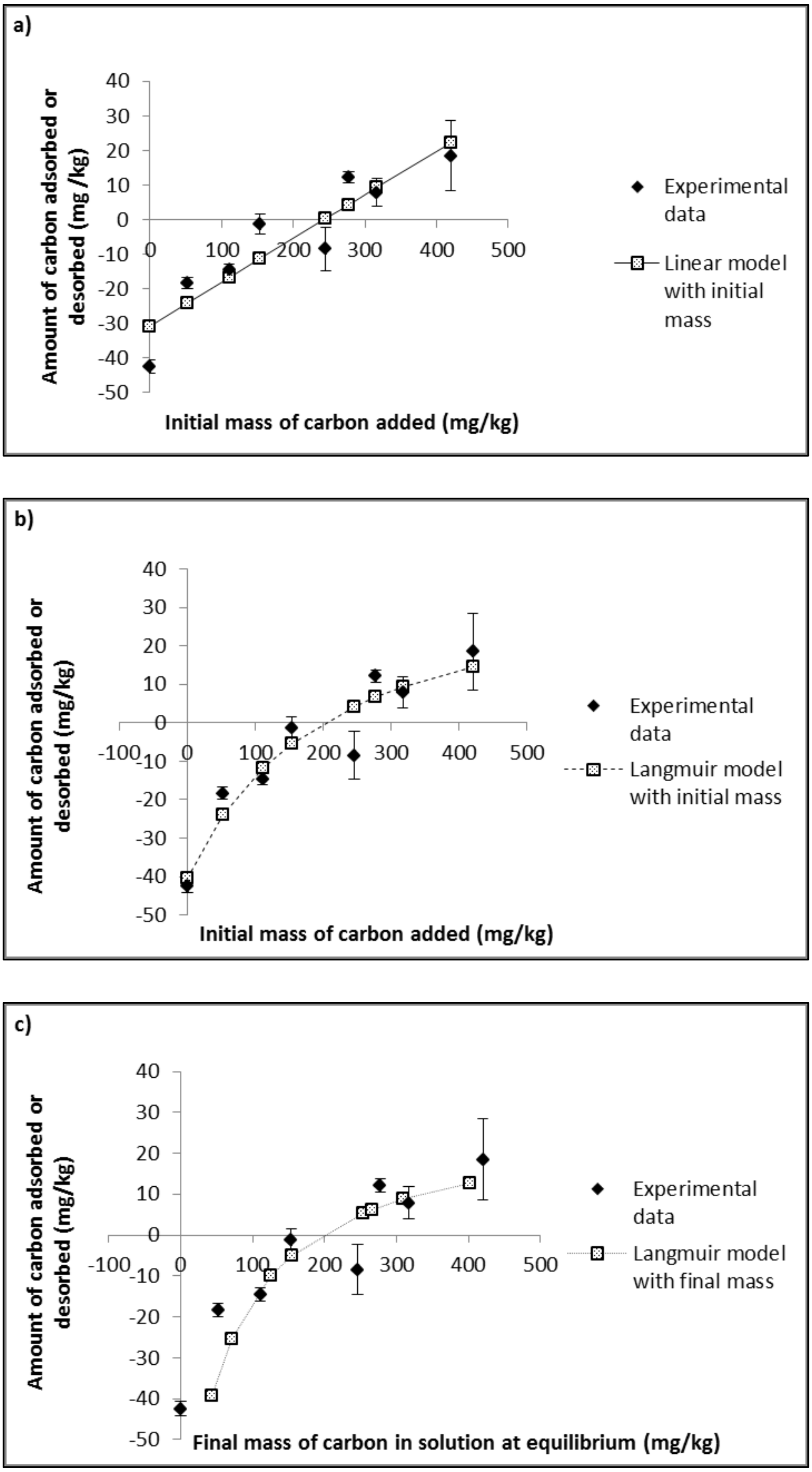


Figure 3.4. Comparison of the three isotherm approaches used to describe the adsorption to mineral soil of DOC sourced from an organic horizon beneath a forest. a) Linear initial mass isotherm for the b) Langmuir model with initial mass of carbon added, c) Langmuir Isotherm with final mass of carbon at equilibrium

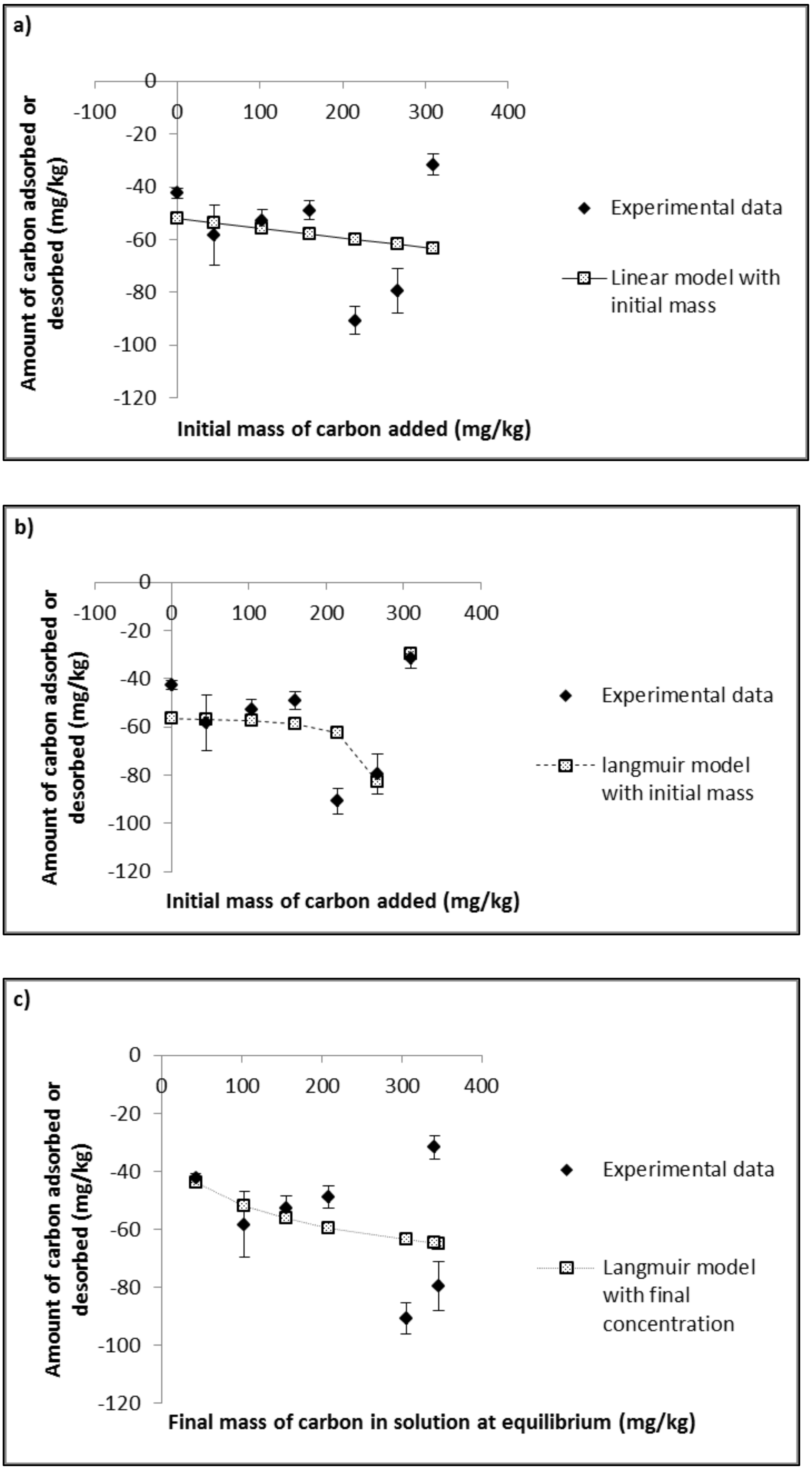


Figure 3.5. Comparison of the three isotherm approaches used to describe the adsorption of DOC sourced from an organic horizon beneath grass to mineral soil (figures include all data points). a) Linear initial mass isotherm, b) Langmuir Isotherm with initial mass of carbon added, c) Langmuir Isotherm with final mass of carbon at equilibrium

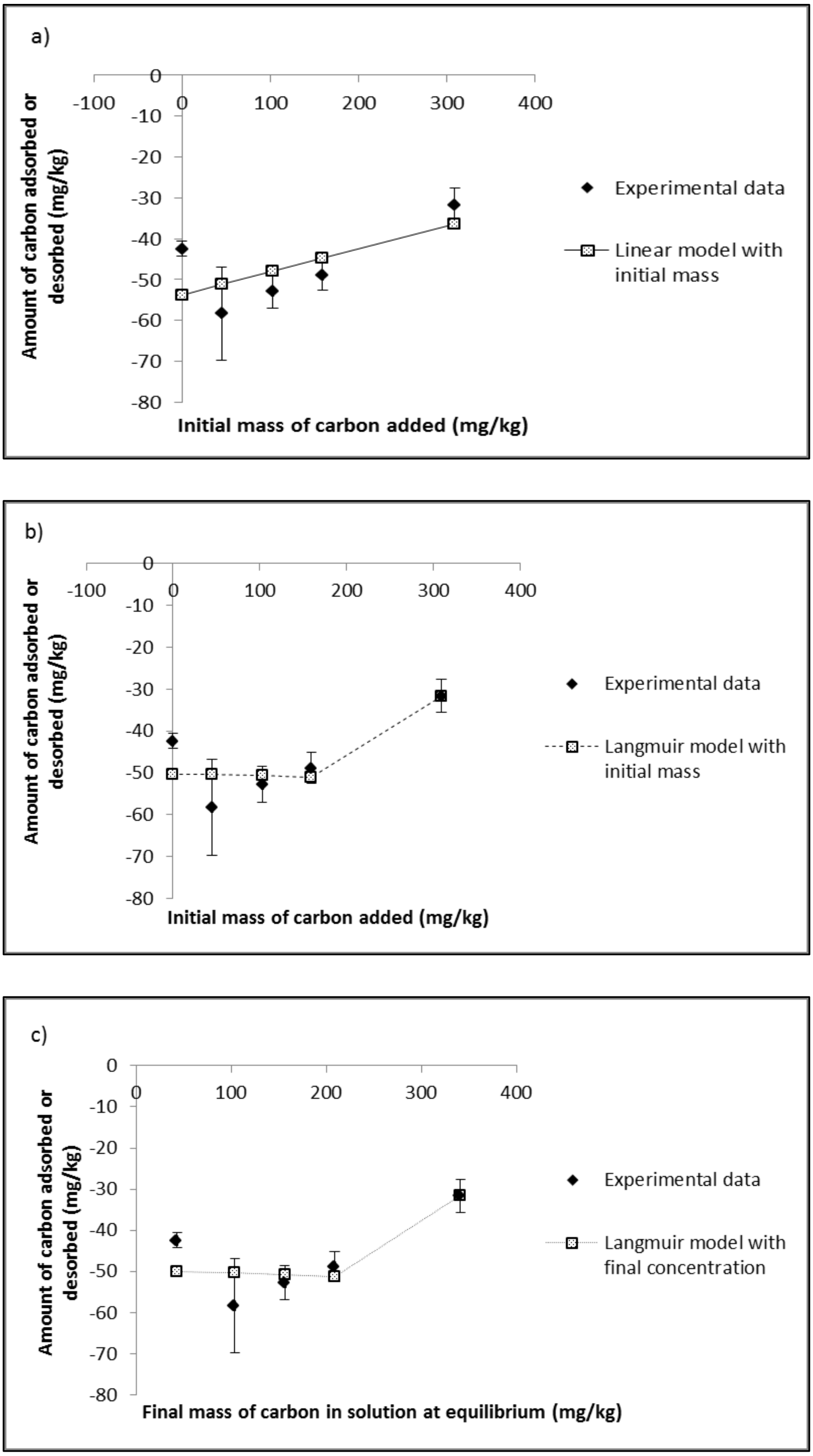


Figure 3.6. Comparison of the three isotherm approaches used to describe the adsorption of DOC sourced from an organic horizon beneath grass to mineral soil after outliers in data set have been removed. a) Linear initial mass isotherm, b) Langmuir Isotherm with initial mass of carbon added, c) Langmuir Isotherm with final mass of carbon at equilibrium

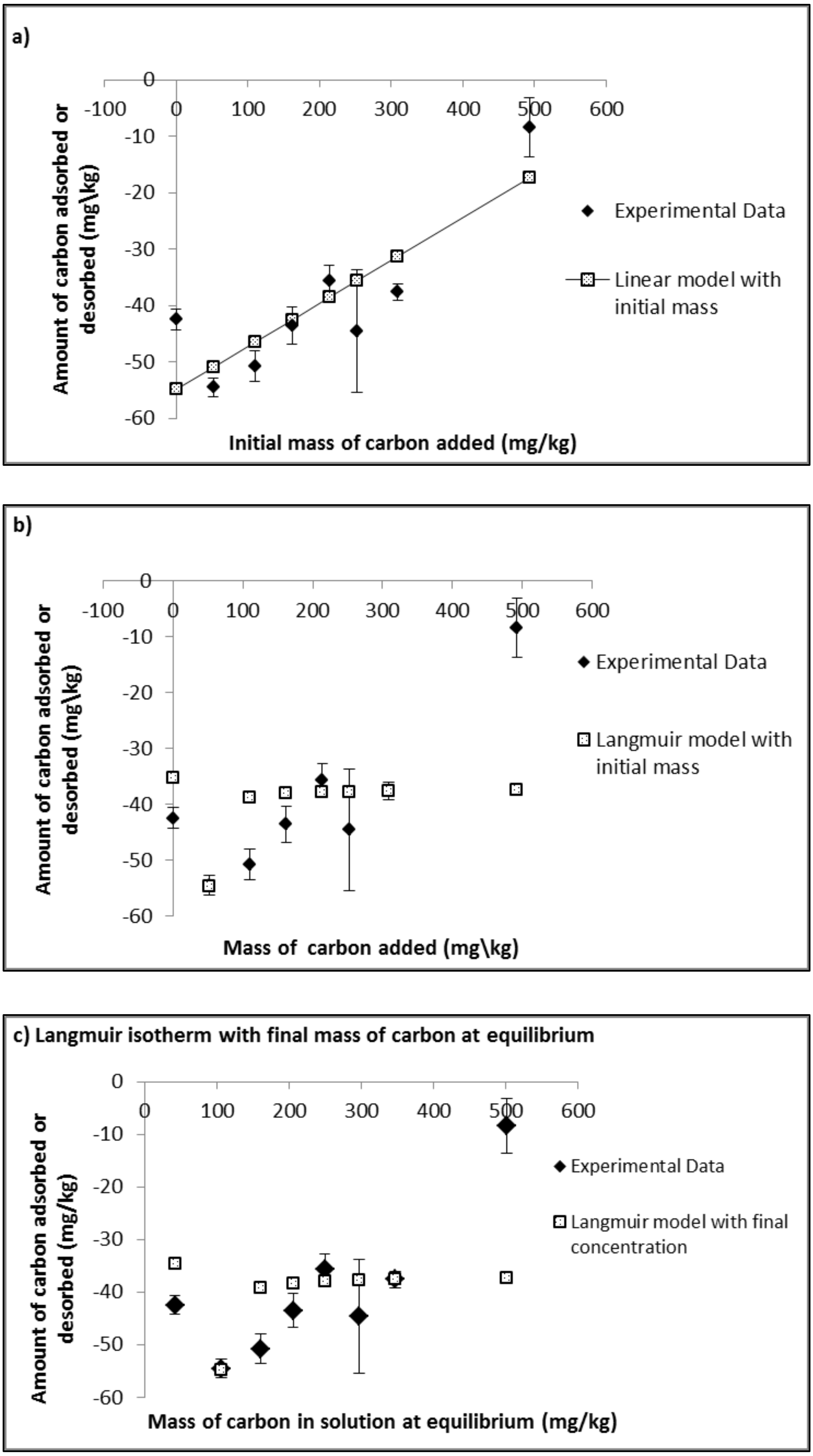


Figure 3.7.Comparison of the three isotherm approaches used to describe the adsorption of DOC sourced from an organic horizon beneath heather to mineral soil. a) Linear initial mass isotherm, b) Langmuir isotherm with initial mass of carbon added, c) Langmuir isotherm with final mass of carbon at equilibrium

Table 3.8. Measures for the model efficiencies for the three isotherm models applied to the three DOC sources

Vegetation	Isotherm Model	RMSE	EF	CRM
Forest	Langmuir initial mass	5.78	0.90	0
	Langmuir final mass	6.69	0.87	0
	Linear initial mass	7.35	0.84	0
Grass (all data)	Langmuir initial mass	12.75	0.56	0
	Langmuir final mass	17.78	0.14	0
	Linear initial mass	18.79	0.004	0
Grass (outliers removed from data)	Langmuir initial mass	5.15	0.69	0
	Langmuir final mass	5.14	0.69	0
	Linear initial mass	6.92	0.43	0
Heather	Langmuir initial mass	11.86	0.19	0
	Langmuir final mass	11.81	0.20	0
	Linear initial mass	7.03	0.72	0

3.3.4.2 *Adsorption characteristics based on the isotherm models*

Desorption term

The modelled desorption estimates (b) for all the extracts and all isotherm models were theoretically possible. However, for the forest solutions, the Langmuir model with initial concentration most accurately modelled the desorption term (Figure 3.4b). The estimated value was 40.29 mg /kg while the experimental value was 42.48 mg /kg.

Null point

The null point is the equilibrium DOC concentration (X_f) or the initial concentration of added DOC (X_i) at which there is no net change in adsorption or desorption of DOC. For the forest the linear isotherm and modified Langmuir with final concentration produced significantly higher null points than the Langmuir with the initial concentration (Table 3.9). The null points for all three isotherms occur between 200 and 300 mg /kg of added final carbon (Figure 3.4). Using all data for the grass (including the two outliers) negative null points were observed for the Linear isotherm (-1405.40 mg/kg; Table 3.9) and the Langmuir isotherm with final DOC concentration (-73.46 mg/kg; Table 3.9). A negative null point is theoretically impossible and so would indicate that these models are not suited to describing the adsorption behaviour of the grass DOC. However, with the removal of the two outlier points the null points for grass DOC derived from the three isotherm models are all theoretically possible (linear = 959.68 mg/kg ; Langmuir X_i = 337.65 mg/kg; Langmuir X_f = 339.15 mg/kg; Table 3.9). For the heather the null point was much higher in the linear initial mass isotherm than in the other two models (Table 3.9).

Table 3.9. Sorption characteristics derived from the linear initial mass isotherm, Langmuir plotted with the initial concentration X_i and Langmuir plotted with the final concentration X_f for DOC soil extracts taken from beneath different vegetation types. (Linear isotherm: m is the regression coefficient, b the intercept, Kd the distribution coefficient and RSP the reactive soil pool. Langmuir: K is a measure of the binding affinity, b is the desorption term, and Q_{max} the maximum adsorption capacity. Np in all instances refers to the null point/ the point at which there is no net change in adsorption or desorption. R^2 is the correlation coefficient.)

	Linear		Langmuir X_i		Langmuir X_f	
Forest	M	0.123	K	0.005	K	0.015
	b (mg/kg)	30.76	b (mg/kg)	40.285	b (mg/kg)	82.646
	Np (mg/kg)	250.08	Np (mg/kg)	19.54	Np (mg/kg)	194.23
	Kd m^3/kg (10^{-3})	1.4	Q_{max}(mg/kg)	81.528	Q_{max} (mg/kg)	111.015
	RSP	35.07	R^2	0.901	R^2	0.868
	R^2	0.84				
Grass (complete dataset)	M	-0.037	K	-0.003	K	0.006
	b (mg/kg)	52.001	b (mg/kg)	56.383	b (mg/kg)	34.96
	Np (mg/kg)	-1405.4	Np (mg/kg)	345.43	Np (mg/kg)	-73.46
	Kd m^3/kg (10^{-3})	-35	Q_{max}(mg/kg)	1.974	Q_{max} (mg/kg)	-44.52
	RSP	50.145	R^2	0.156	R^2	0.142
	R^2	0.04				
Grass (outliers removed from dataset)	M	0.056	K	-0.003	K	-0.003
	b (mg/kg)	53.74	b (mg/kg)	50.342	b (mg/kg)	50.010
	Np (mg/kg)	959.68	Np (mg/kg)	337.65	Np (mg/kg)	339.15
	Kd m^3/kg (10^{-3})	5.9	Q_{max}(mg/kg)	0.594	Q_{max} (mg/kg)	0.741
	RSP	56.93	R^2	0.685	R^2	0.686
	R^2	0.431				
Heather	M	0.076	K	-0.021	K	-0.010
	b (mg/kg)	54.84	b (mg/kg)	35.25	b (mg/kg)	35.64
	Np (mg/kg)	721.5	Np (mg/kg)	45.02	Np (mg/kg)	96.26
	Kd m^3/kg (10^{-3})	0.82	Q_{max}(mg/kg)	-2.04	Q_{max} (mg/kg)	-1.384
	RSP	59.35	R^2	0.191	R^2	0.198
	R^2	0.72				

Q_{max}

Of all the vegetation types only the Q_{max} of the DOC extracted from the forest soil could be feasibly estimated (Table 3.9). None of the Langmuir models were a good fit for the heather DOC. A narrower range of concentrations was used for the grass DOC, and within that range a negative binding affinity was observed with the linear model (Kd = -35×10^{-3} m^3 /kg ; Table 3.9) and with the Langmuir model with initial concentration (K = -0.003; Table 3.9). This would indicate that adsorption of this DOC to the soil is not favoured and therefore estimates of the Q_{max} using the DOC range of this experiment are unreliable. Removal of the two outlier points resulted in a positive binding affinity for the linear model (5.9×10^{-3} m^3 /kg; Table 3.9). However, both Langmuir isotherm models had a negative binding affinity (K) of -0.003 and low estimates of Q_{max} (Langmuir Xi = 0.594 mg/kg; Langmuir Xf = 0.741 mg/kg; Table 3.9). Even with the removal of the outliers, sorption of grass DOC is still not favoured and the estimates of Q_{max} seem unrealistic.

3.3.5 Post adsorption SUVA

Significant decreases in the SUVA of the solution were seen for the grass (t (5) = 8.605, p< 0.001) and the heather (t (6) = 2.576, p = 0.042) after adsorption to mineral soil (Table 3.10 and Figure 3.7). For the forest soil most of the solutions show DOC increases post adsorption, however the increases were not statistically significant.

Table 3.10. DOC concentration and change in SUVA after batch adsorption experiments

Forest		Heather		Grass	
Concentration (mg/L)	Change in SUVA (L m/mg)	Concentration (mg/L)	Change in SUVA (L m/mg)	Concentration (mg/L)	Change in SUVA (L m/mg)
7.04	0.25	10.66	-1.71	10.33	-0.63
12.56	0.40	16.08	-1.04	22.65	-1.61
15.53	1.53	20.56	-1.27	27.50	-1.64
25.45	0.13	24.97	-0.79	31.15	-1.47
26.58	-0.08	29.77	-0.53	37.58	-1.24
30.91	-0.58	34.67	-0.24	44.41	-1.59
40.25	-0.27	50.14	0.55		

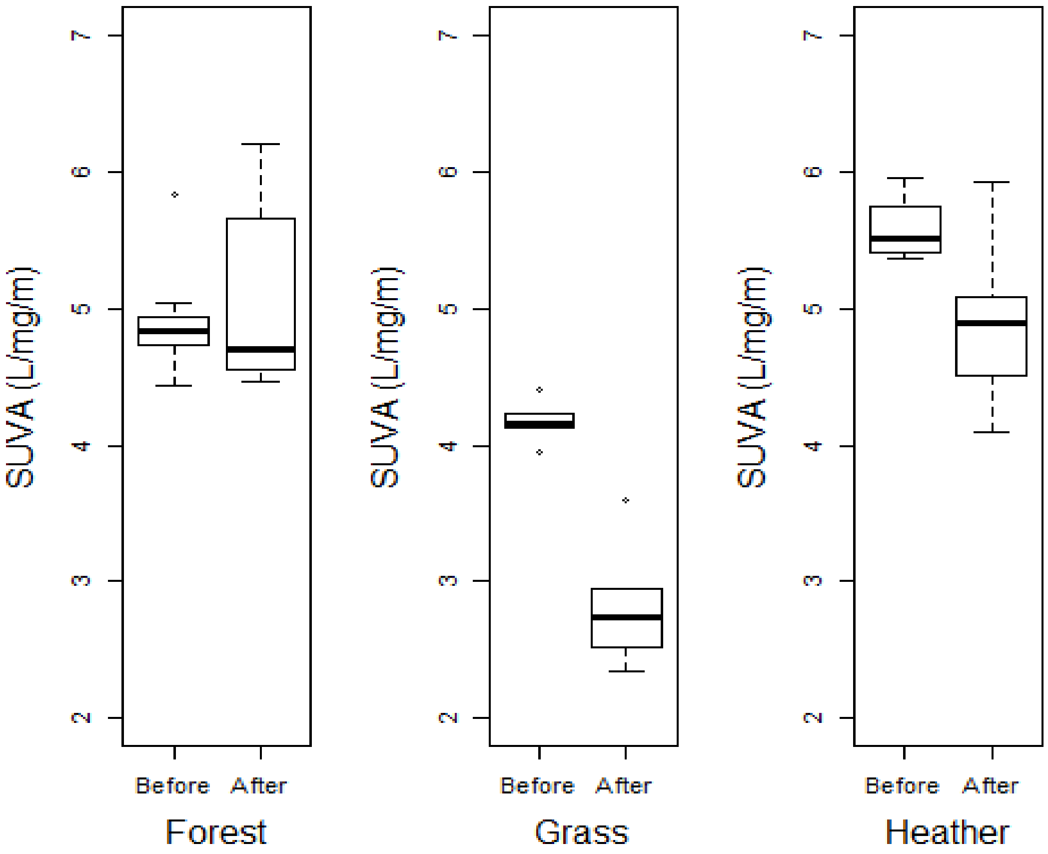


Figure 3.8 Boxplots comparing the pre and post adsorption SUVA$_{254}$ character of solutions obtained from O horizon soil beneath Forest, Grass and Heather. The line in the middle of the box represents the median value, the top of the box represents 75% of the distribution and the bottom of the box represents 25% of the distribution. The lower whisker represents 10% of the distribution and the upper whisker represent 90% of the distribution. Points on the graphs represent outliers which are below or above 1.5 x the interquartile range.

3.4 Discussion

The research described in this chapter shows that vegetation cover influences the quality of DOC produced in O-horizon soils and the sorption of that DOC to mineral soils. The research here also provides additional evidence that vegetation cover does influence the quantity of DOC produced from O-horizon soils. These main findings and their implications for upland land management in the UK will be further discussed in subsequent sections.

3.4.1 Vegetation cover influences the quantity and chemical characteristics of DOC leached from organic horizons

The three organic horizons differed both in the amount and composition of DOC produced. The heather produced DOC with the highest carbon content (170.6 mg/L) and the grass produced DOC with the least carbon content (55.3 mg/L). This was a reflection of the original carbon content of the soil, since the heather moorland soil also had the highest carbon content (51.9 ± 0.1 %) and the grassland soil the least (5.8 ± 0.1 %). Using SUVA as a proxy for aromaticity it was observed that the DOC produced from the three organic horizons also differed in their chemical properties. The DOC extracted from O-horizon soil beneath heather was most aromatic (6.02 L m/mg), followed by the DOC extracted from O-horizon soil beneath forest (5.39 L m/mg) and the DOC from the grass (4.39 L m/mg) was the least aromatic.

Differences in the amount and composition of extractable DOC among vegetation types may be explained by differences in the mode of production of the carbon substrate in the three habitats and the decomposability of that carbon substrate. The species of grass (*Molinia*) used in this research is a perennial plant while heather and forest vegetation are slow growing, woody and relatively long lived plants. Fast growing perennial plants yield nutrient rich litter which is easily decomposed, while slow growing plants yield nutrient poor, recalcitrant litter, which takes longer to decompose (De Deyn et al., 2008). Therefore the grass litter would decompose more readily than the heather or forest litter. The degree of decomposition of soil carbon has been correlated with the amount of DOC released from the soil; less decomposed soils release DOC of higher concentration (van den Berg et al., 2012). Van den Berg et al. (2012) compared DOC concentrations of soil solutions collected beneath four typical UK habitats: grasslands; heathlands (lowlands dominated by shrub vegetation); moorlands (uplands dominated by shrub vegetation) and woodlands. In their study, Van den Berg et al. (2012) found that the concentration of DOC under the grasslands was lowest (average annual DOC 15.4 mg/L), highest under moorlands (average annual DOC 54.8 mg/L) and intermediate in heathlands (average annual DOC 29.45 mg/L) and woodlands (average annual DOC 28.87 mg/L). Van den Berg et al. (2012) also observed that the DOC concentration was correlated with the soil C/N ratio, with the DOC concentration increasing with increasing C/N ratio. The C/N ratio has been used as a measure of the decomposition of the soil with low C/N ratios indicating higher decomposition rates (van den Berg et al., 2012). Thus the work of van den Berg et al. (2012) shows that DOC concentration increased with decreasing decomposition of the soil. The work described in this chapter also supports the order of increasing DOC concentration follows the order of increasing C/N ratio, with the grassland DOC having the lowest DOC concentration and lowest C/N ratio (12.9 ± 0.1 %) and the heather the highest DOC concentration and highest C/N ratio (34.75 ± 0.1 %).

The results of this study also show compositional differences among the three DOC sources. SUVA was used as a proxy for aromaticity and the SUVA results indicated that the DOC produced from the organic horizons differed in their aromatic composition. The DOC extracted from O-horizon soil beneath heather had the highest SUVA (6.02 L m/mg), based on this it was inferred it was the most aromatic. The SUVA values of the forest DOC (5.39 L m/mg) and the grass DOC (4.39 L m/mg) were lower than the heather. Based on these SUVA values the grass DOC can be assumed to be the least aromatic since it had the lowest SUVA. The fractionation results supported the heather as the most aromatic of the three DOC sources but contradict the order of aromaticity between the grass and forest determined by SUVA. Of the three extracts the heather had the highest hydrophobic content (88%) and the forest the lowest (62 %). It has been found that the more aromatic the sample, the more hydrophobic it is and thus will have a higher SUVA (Parsons et al., 2007). Although, SUVA is not always reflective of the composition and reactivity of a sample (Weishaar et al., 2003), in this study the order of aromaticity implied by SUVA is more likely than the order of aromaticity implied by the fractionation results. This is due to the consideration of the lignin content of the three types of vegetation. Lignin is a high molecular weight macromolecule comprised of aromatic building units (Kögel-Knabner, 2002). Heather and forest both produce woody litter which has more lignin than non woody litter (Maser et al., 1988). Therefore it would be expected that DOC extracted from forest and heather soils would have more lignin and be more aromatic than DOC extracted from grassland soil; this was exhibited in the SUVA values obtained for the three DOC sources. It is possible that the fractionation result may have been an anomaly. Due to the volume of sample required for fractionation, replicates could not be undertaken. Without replicates it is not possible to determine the precision of the fractionation measurement.

3.4.2 DOC produced by organic horizons under different vegetation covers differ in their adsorption to mineral soil

The results from this study demonstrated differences in the adsorption to a common mineral soil of DOC from the three vegetation types. Sorption of the forest DOC was feasibly explained by all three isotherm models tested, however the Langmuir model with initial mass was the best fit for this DOC source. Both Langmuir isotherm models feasibly described sorption of the grass DOC but only after the removal of outliers within the data set. Sorption of the heather DOC was best explained by the linear mass isotherm.

The lack of an adequate fit of the grass DOC to the linear model may at first seem somewhat surprising. This is because the linear isotherm model has been shown to be adequate at describing DOC sorption at low initial concentrations of added DOC where saturation has not been reached (Kaiser et al., 1996; Pengerud et al., 2014; Ussiri and Johnson, 2004; Vance and David, 1992). The concentrations used in this study, including that of the grass DOC are all within the ranges used in the literature (Table 3.11) and saturation was not reached with any of the extracts tested here. Thus it might be expected that even if the linear mass isotherm is not the best fit of the three isotherm models it would at least be a feasible model for all DOC sources at low concentrations. The fact that this is not the case may be explained by the lignin composition of the three DOC sources. In the studies in which the linear model has been feasibly used, the DOC was sourced from beneath forest vegetation. As previously discussed in section 3.4.1, the forest DOC will have a higher lignin content than the grass DOC which may affect its sorptive beaviour. Jagadamma et al. (2012) tested the adsorption of five compounds (D-glucose, L-alanine, salicylic acid, sinapyl alcohol and oxalic acid) commonly found in soil organic carbon to soil from three soil orders (mollisols, ultisols, alfisols). It was observed that the lignin monomer sinapyl alcohol followed more of a linear sorption trend for all soils tested (Jagadamma et al., 2012). Thus the higher lignin content of the forest and heather would explain their feasible fits to the linear isotherm while the low lignin content of the grass could explain why this model was not an appropriate fit.

Table 3.11. Experimental parameters used by this study and other studies in the literature in sorption experiments where data was fitted to the initial mass isotherm.

Reference	DOC range	Ratio soil/solution	Vegetation cover on peat
(Vance and David, 1992)	0-67 mg/L	5g / 50ml	Hardwood forest
(Moore et al., 1992)	0-81 mg/L	5g/ 50ml	Yellow birch and Hemlock
(Kaiser et al., 1996)	0-72 mg/L	8g / 40ml	Forest
(Ussiri and Johnson, 2004)	0-120 mg/L	5g / 50ml	conifers
(Pengerud et al., 2014)	0-48 mg/L	3g / 30ml	Not given
Current study	4.5 to 31 mg/L	2g / 20ml	grass
	5 to 49 mg/L.	2g / 20ml	heather
	5 to 42 mg/L	2g / 20ml	forest

Within the range of concentrations tested for heather (5 -49 mg/L) and grass (4.5 – 31 mg/L) only desorption was seen. This can be explained by the fact that the range of concentrations used fell below the null points predicted for these two DOC sources by their best fit isotherms. For the heather DOC the linear isotherm predicted a null point (the point at which the switch from adsorption to desorption occurs) of 72.16 mg/L and for the grass DOC the predicted null points with the best fit Langmuir models (with and without the removal of outliers) ranged from 33.76 mg/L to 34.54 mg/L. The null point is a measure of the initial soil solution concentration for which there will be no net adsorption or net desorption of DOC (Kothawala et al., 2008; Vandenbruwane et al., 2007). Any values below the null point will result in net desorption while values above result in net adsorption (Vandenbruwane et al., 2007). Therefore since the predicted null points for DOC from both the heather and grass were above the range of concentrations tested only desorption was seen.

Within the experimental range (5 - 42 mg/L), adsorption was seen for the forest DOC at higher concentrations. For this DOC source, the predicted null points for all isotherm models (Linear = 25.00 mg/L; Langmuir X_i = 19.54 mg/L; Langmuir X_f = 19.42 mg/L) fell within the experimental range and so adsorption was observed for initial or final solution concentrations which exceeded the null point. The fact that some sorption is seen for forest DOC while the other two sources only show desorption also suggests there is a difference in the way DOC from these sources sorb. The results show that the mineral soil has a greater affinity for the forest DOC than for the DOC from the other two vegetation sources. It is not possible to compare the measures of binding affinity (linear mass m and k_d; Langmuir k) among the three isotherm models as they are derived differently. However, comparisons of the measures of binding affinity across vegetation types (Table 3.9) shows that the forest DOC has consistently higher values for all three isotherm models. This provides evidence for a greater binding affinity of forest DOC and possibly explains why some adsorption is seen for this source of DOC, but not for other sources. The mineral soil used in this study was sourced from beneath grass and as such it is unlikely to be saturated with DOC from either heather or forest. Additionally, the mineral soil was pre-treated to remove the native soil carbon which resulted in a 63% reduction in the native soil carbon. Consequently, the soil is unlikely to be saturated with grass DOC and the lack of sorption with this DOC source is as previously suggested most likely due to the experimental range falling below the null point for grass DOC. The results are therefore indicating specificity for forest DOC over DOC from grass and heather. The forest DOC is expected to bind better to the soil due to its high content of the aromatic compound lignin from woody litter. However the heather also produces woody litter and is known to contain more lignin than grass (Van Vuuren et al., 1993), but the DOC from this source shows no adsorption in the experimental range. Furthermore both the fractionation and the SUVA measurements suggested that the heather DOC was more aromatic than the forest DOC. It has been suggested that it is this highly humic/ aromatic DOC which is favoured for adsorption (Kaiser et al., 1996). However, the findings of this study contradict that. The results here are indicating the mineral soil is showing specificity for compounds within the forest DOC over those within heather DOC. This may be due to the differences in the composition of the lignin in these two plants. Lignin from gymnosperms such as the forest are predominantly comprised of monomers derived from coniferyl alcohol while the lignin from angiosperms such as the heather is comprised of almost equal parts of monomers derived from coniferyl alcohol and sinapyl alcohol (Kögel-Knabner, 2002). Therefore the mineral soil used in this study may be exhibiting a higher affinity for coniferyl alcohols. However, without knowledge of the specific chemical composition of each of the DOC sources used in this study and the specific chemical composition of the post adsorption DOC solutions, the possible high affinity of the soil for coniferyl alcohols cannot be confirmed. This study is indicating that the use of SUVA and possibly DOC fractionation into hydrophobic and hydrophilic fractions are not reliable for determining the sorption potential of DOC. However, as there were no replicates in the fractionation experiments it is not possible to draw firm conclusions on the reliability of using knowledge of the DOC fractions for predicting sorption.

The sorption behaviour identified here of DOC sourced from O-horizons beneath the three vegetation types has significant implications for the behaviour of DOC in upland catchments dominated by these vegetation covers. The concentrations tested in this experiment were similar to those recorded in the literature for soil solutions collected from O-horizons in the UK uplands (Buckingham et al., 2008; van den Berg et al., 2012). This could indicate that in uplands where vegetation is dominated by *Molinia* grass or the shrub *Calluna*, the percolation of soil solution from the O-horizon through the mineral horizon will result in net desorption of DOC at the concentrations typically seen in soil solution. In contrast, the percolation of soil solution from the O-horizon of forested catchments will result in DOC adsorption in the mineral soil.

3.4.3 DOC of high aromaticity is adsorbed to mineral soil and DOC of low aromaticity is released from mineral soil.

The changes observed in the SUVA values of the DOC solutions after sorption to the mineral soil further support there are differences in the sorptive interaction between the mineral soil and the three DOC sources. The heather and grass DOC show a decrease in SUVA following sorption. This indicates that the aromatics were preferentially adsorbed when the DOC interacted with the mineral soil. However for the forest DOC there was no significant change between the pre and post adsorption SUVA.

The adsorption isotherms for heather and grass show just desorption and from that it can be inferred that the soil's affinity for the DOC derived from these two substrates is low. However, this might not be true since the decrease in SUVA values for the heather and grass DOC indicates that an exchange of carbon with the mineral soil may have occurred, with aromatics being preferentially adsorbed. Thus the affinity might be greater than implied by concentrations of the post adsorption solutions but the effect was just lost because the isotherms consider changes in concentration and not compositional changes. At some point adsorption might be seen in the form of reducing DOC concentration once all of the carbon that can be displaced by the substrate has been displaced. However, this is an unlikely scenario since the concentrations required for this to occur would exceed those seen in the natural environment.

Unlike the heather and grass DOC which both showed decreasing SUVA values following adsorption to the mineral soil, the forest DOC did not show any significant change in SUVA after sorption to the mineral soil. This suggests that the aromatic fraction of forest DOC was not adsorbed by the mineral soil. This might be reflective of the limitations of SUVA which is a proxy measurement and may not always reflect the true composition and reactivity of DOC (Weishaar et al., 2003).

3.4.4 Implications for Upland land management

The work of this chapter is indicating that vegetation cover can be used as a means of managing the quantity and quality of DOC leached from catchments dominated by organo-mineral soils. The major source of DOC to a catchment is organic soil horizons (Dalva and Moore, 1991). As the soil solution percolates through the soil profile DOC may be adsorbed by mineral subsoils (Dalva and Moore, 1991). Sorption to mineral soil surfaces can greatly influence the quantity of DOC exported from soils (Tipping et al., 1999). The study by Tipping et al. (1999) observed higher concentrations of DOC in leachates collected from intact soil cores of a peaty gley than from soil cores of a brown earth and a micropodzol. The reduced DOC concentrations in the leachates of the brown earth and micro-podzol were attributed to their larger mineral horizons (Tipping et al., 1999). Considering that adsorption to mineral surfaces reduces the export of DOC, the observed differences in sorptive properties of the three DOC sources tested in this study suggests that vegetation cover could be used to manage the export of DOC in catchments dominated by organo-mineral soils. Further work is needed to test whether similar patterns of DOC sorption are detectable under field conditions.

DOC can be a problem for water companies due to the associated colour and potential to form disinfection by products with chlorine during the water treatment process. Parsons et al. (2005) in their study of the effects of natural organic matter character on the effectiveness of the water treatment process, observed that waters with a SUVA above 4 L m/mg were more reactive with chlorine to the formation of trihalomethanes (THM) but were easier to treat with the end result being a greater % removal of DOC .Conversely waters with a low SUVA (< 3) showed no relationship with the formation of THM but all resulted in THM levels less than the national standard of 100 µg/L (Parsons et al., 2005). The findings of this present study suggest that catchments where the major use is the extraction of water grass would be a favourable choice as the dominant vegetation. Although this DOC source resulted in net desorption of DOC there was an active exchange of DOC with the mineral soil which resulted in DOC with a lower SUVA value (range = 2.3 - 3.6 L m/mg), which is less likely to result in THM formation. Furthermore the value is above the minimum limit of 2 L m/mg at which treatment to remove DOC is not effective

(Weishaar et al., 2003). Therefore further removal of DOC in waters extracted from grass dominated catchments should still be effective to improve other features such as colour, odour and taste.

It should be noted that grasses such as the species used in this study (*M. caerulea*) have been shown to out compete other species of upland vegetation including forbs and shrubs (Chambers et al., 1999; Ross et al., 2012). This can lead to a decline in species richness which can compromise the ecosystem's ability to adapt to environmental change and could also lead to a loss of ecosystem function (Ross et al., 2012). In addition to being a major source for potable water within the UK, the uplands also provide other ecosystem services such as agricultural grazing, tourism and game shooting (Holden et al., 2007), and monospecific cultures of a single grass type may be less desirable for some stakeholders. Furthermore 75% of the world's heather moorland is located in the UK and these moorlands are considered to be rare habitats (Holden et al., 2007). Therefore, the planting of grass as a management tool for the control of DOC and improved water quality should be approached with caution and the importance of the other services provided by the uplands should be considered.

3.4.5 Experimental limitations

In this study pre-treatment of the mineral soil to remove native carbon resulted in only a 63% reduction in the native soil carbon. Based on past research by Jardine et al. (1989), it was thought the remaining soil carbon would limit the amount of DOC that can be adsorbed by the soil. However, the post-sorption decrease in SUVA for the heather and grass indicate an exchange in carbon between the soil solution and mineral soil. The ability of the soil to exchange DOC with the soil solution therefore indicates that the native soil carbon does not limit further DOC binding.

3.5 Conclusion

This study sought to determine the extent to which compositional differences in DOC sourced from organic soil beneath three vegetation types typically found in UK uplands affects the ability of the DOC to bind to mineral soil. From the findings of the study it was seen that DOC extracted from O horizons beneath heather, grass and forest differed in the quality and quantity of the DOC produced and the sorption to mineral soil. The DOC produced in O-horizon soil beneath heather and forest was more aromatic (as measured by SUVA) than DOC produced in O-horizon soil beneath grass. The compositional differences in DOC from these three sources influenced the way in which the DOC sorbed to mineral soil. Only DOC sourced from forest had the capacity for net adsorption to the mineral soil at the concentrations of DOC typically seen in upland catchments. Despite only net desorption occurring for grass and heather DOC, there was an exchange of DOC between the soil and soil solution. High molecular weight aromatic substances were adsorbed and lower molecular weight substances were released. The net desorption and greater export of low molecular weight DOC observed for DOC sourced from *Molinia* dominated grassland and heather moorlands implies that upland vegetation management could be an important tool in managing catchments for water quality.

4 The capacity of UK upland mineral soils to retain DOC and the factors controlling DOC sorption and desorption in mineral soils.

4.1 Introduction

The British uplands cover about one-third of the UK landmass and provide numerous ecosystem services including the supply of potable water (Reed et al., 2009). In recent decades there have been observed increases in the DOC in surface waters draining the UK uplands (Clutterbuck and Yallop, 2010; Evans et al., 2005; Monteith et al., 2007; Robson and Neal, 1996). The upland catchments are dominated by, organic soils including peats and organo-mineral soils such as stagnohumic gleys, stagnopodzols, humic-alluvial gleys and humic sandy gleys (Holden et al., 2006). Evans et al. (2005) noted a 91% increase in stream water DOC concentrations from 20 catchments draining thin ranker soils and organic rich soils such as peats, humic gleysols and humic podzols across the UK for the period 1988 to 2003. Research investigating the causes of DOC increases in water bodies has focussed on water quality within peatland catchments, including the relationship between amount of peat cover (as the DOC source) and DOC export (Hope et al., 1997) or the influence of management practices in these sensitive areas on the water quality (Clutterbuck and Yallop, 2010; Holden et al., 2012). Organo-mineral soils also play a significant role in the movement of DOC in the catchment by acting as sinks for the DOC; mineral horizons are able to retain some of the DOC thereby limiting its export to surface water (see section 2.5). It is therefore possible that the recent DOC increases in surface waters could be reflective of changes in the ability of organo-mineral soils to retain DOC. Examination of past studies using long term data shows trends in the concentration of soil solution DOC which both support and contradict this theory (Borken et al., 2011; Löfgren et al., 2011; Sawicka et al., 2016; Stutter et al., 2011; Vanguelova et al., 2010). Increasing DOC concentrations have been observed in soil solution collected in upper organic horizons of forest soils in the UK (Vanguelova et al., 2010) and Germany (Borken et al., 2011); while the deeper mineral horizons of the same catchments showed very little or no significant change. This suggests that the DOC increases observed in surface waters in these regions are due to export from organic soil horizons and that mineral horizons make no significant contribution to the DOC exported to surface waters. The lack of a significant contribution of mineral soils to DOC export seems to be further supported by studies which have shown decreasing DOC concentrations in soil solutions of mineral horizons (Löfgren et al., 2011; Löfgren and Zetterberg, 2011). Löfgren and Zetterberg (2011) in their study of long term data for 68 forested sites in Northern Sweden, observed a decreasing DOC trend in 46% of the sites, while 47% of the sites showed no significant change.

However, Sawicka et al. (2016) in their examination of long term (2002-2011) monitoring data observed increasing DOC in upper organic soil horizons of five UK forests: Grizedale, Alice Holt, Lady Bower, Llyn Brianne and Thetford. Sawicka et al. (2016) also observed increasing DOC trends in the B horizons of all the forests with the exception of Alice Holt which showed a decreasing DOC trend. The greatest increases in B horizon DOC were observed at two coniferous forest; Llyn Brianne, Wales and Lady Bower in the Upper Derwent Valley of Derbyshire, England (Sawicka et al., 2016). This could suggest a changing ability of the soils at these sites to retain DOC. Multi-site studies by Sawicka et al. (2016) and Stutter et al. (2011) suggest that the direction of trends may differ between soil types and horizons, and also vary between sites with different vegetation covers. Analysis of soil solution data collected between 1993 and 2010 for two UK grasslands, Glensaugh and Sourhope showed that for both sites soil water DOC is increasing in surficial organic horizons while in deeper horizons they show contrasting behaviour (Sawicka et al., 2016). The trend of increasing DOC concentration was upheld in the B horizon of the podzol at Glensaugh while the B horizon of the peaty gleyed podzol at the Sourhope showed a decreasing DOC trend with time (Sawicka et al., 2016). Similar observations were made by Stutter et al. (2011) in their study of long term data (1993-2007) for Glensaugh and Sourhope. The studies of Sawicka et al. (2016) and Stutter et al. (2011) could indicate that the capacity of the podzolic B horizon at Glensaugh to retain DOC is reduced with time and increasing inputs of DOC to the subsurface mineral horizon. The contrasting behaviour of the two deep soil horizons could be reflective of differences in the storage capacity of soils for DOC by soil type. The recent increases in DOC in surface waters might therefore reflect a reduced capacity of these soils to retain DOC. In order to understand and better predict the behaviour of DOC in these soils there needs to be a better understanding of the limits of these soils for the retention of DOC and the soil properties which control the retention and release of DOC in these organo-mineral soils.

Pre-existing soil organic carbon has been shown to limit any further sorption of DOC to mineral soils (Jardine et al., 1989; McDowell and Wood, 1984; Moore et al., 1992; Ussiri and Johnson, 2004). Jardine et al. (1989) found that the removal of organic carbon from a soil high in pre-existing organic carbon resulted in an almost four fold increase in adsorption of added DOC. Ussiri & Johnson (2004) found that soil horizons with the least amount of soil organic carbon strongly retained DOC while those with the most soil organic carbon showed little or no adsorption for DOC. This has led some authors to theorize that soil carbon potentially blocks active binding sites limiting the amount of DOC that can be absorbed (Kaiser and Guggenberger, 2000). This suggests that the capacity of mineral soils to adsorb DOC is finite and as such there will be a point at which all of these binding sites will become occupied and further adsorption would not occur. While there have been studies which used the Langmuir isotherm to quantify the maximum sorption capacities of soils in the USA (Jardine et al., 2006; Mayes et al., 2012; Moore and Turunen, 2004), Canada (Kothawala et al., 2009) and Belgium (Vandenbruwane et al., 2007), the potential sorption capacities of UK organo-mineral soils for DOC have not yet been estimated.

Several studies have shown correlations between DOC sorption and amorphous, organic and crystalline forms of aluminium (Al) and iron (Fe) (Kaiser et al., 1996; Kothawala et al., 2009; Mayes et al., 2012; Moore et al., 1992; Vandenbruwane et al., 2007). Kothawala et al. (2009) in their study of DOC sorption in 52 Canadian mineral soils found a positive relationship between the estimated maximum adsorption capacities of soils and the poorly crystalline or amorphous forms of Fe and Al oxides. Vandenbruwane et al. (2007) made a similar observation in their study of five horizons (E, Bh, Bs, BC, C) along the profile of a podzol sampled in Belgium, they also found a positive relationship between the estimated maximum adsorption capacities of soils and the amorphous forms of Fe and Al oxides (measured as oxalate extractable Fe and Al oxides). Furthermore, Jardine et al. (1989) found that treating soils with dithionite citrate bicarbonate to remove Fe oxides prior to sorption experiments resulted in a significant decrease in the adsorption of DOC when compared to untreated soils. A more recent study by Singh et al. (2016) also noted a decrease in DOC adsorption after the removal of Al and Fe oxides. Research therefore indicates that Fe and Al are significant binding sites for DOC.

Past studies have also shown clay content to be a major control on DOC sorption (Jardine et al., 1989; Kahle et al., 2004). Kothawala et al. (2009) observed that clay content was a secondary control on the maximum sorption capacity (Q_{max}) of soils for DOC. While other researchers have found clay content to be the dominant control on DOC sorption to mineral soils (Jardine et al., 2006; Mayes et al., 2012; Moore and Turunen, 2004). Jardine et al. (2006) using weathered Ultisols in the USA found that clay content was the best predictor of the soils' maximum adsorption capacity. Moore and Turunen (2004) using sandy mineral soils collected in Michigan USA also found clay content to be the dominant control on DOC adsorption. A study by Mayes et al. (2012) found that clay content and Fe oxide content accounted for most of the variability in the maximum adsorption capacity (Q_{max}) of the mineral soils they studied.

Clay content refers to soil particles which are less than 0.002 mm in size and can be comprised of clay minerals as well as sesquioxides and amorphous minerals (Rowell, 1994). Therefore it is possible that observed relationships with clay content could be due to the Fe and Al oxides in the clay sized fraction of soils. However, both Jardine et al. (2009) and Singh et al. (2016) found that although removal of the Fe and Al oxides from the mineral soil resulted in decreased adsorption, significant quantities of DOC were still adsorbed. These researchers attributed the adsorption in the absence of Fe and Al oxides to the remaining clay minerals in the soil. This therefore indicates that the aluminosilicate clays also have the capacity to adsorb DOC.

The literature clearly shows that the mineralogical make-up of the soil is of great importance in controlling the sorption of DOC. However, the mineralogical make-up of the soil can be highly variable by horizon and soil type, as such there may be variability in DOC sorption based on horizon sampled and soil order. Mayes et al. (2012) have found that the sorption capacities of different soil orders were related to the different properties of the soils. In Alfisols and Ultisols the Q_{max} values were most related to the clay content while in Mollisols the high concentration of existing soil carbon accounted for most of the variability in Q_{max}. Moore et al. (1992) found that the null point, which refers to the concentration of DOC entering the mineral layer at which adsorption and desorption are in equilibrium (Kerr and Eimers, 2012), varies by horizon. At concentrations lower than the null point desorption will be seen in the soil, while at concentrations higher than the null point adsorption will be seen in the soil (Barrow, 1987). Although not explicitly stated in the literature it would appear that when comparing soils, the higher the null point the greater the amount of DOC input that is required to promote adsorption and therefore desorption of DOC will be favoured in those soils with relatively high null points. Conversely, adsorption would be favoured in those soils with relatively low null points. In the study by Moore et al. (1992) the upper soil horizons such as Ae, Ahe, Bh, Bhf had relatively high null points , while the null points decreased in the other subsoil horizons (Bf, Bm, C and Ck). Therefore the upper soil horizons have the potential for greater desorption while the lower horizons have the potential for greater adsorption.

Adsorption to soil mineral surfaces is also influenced by other soil properties such as pH. The hydrous oxides of iron and aluminium have a pH dependent charge. At low pH these oxides are protonated and as such have an overall positive charge (vanLoon and Duffy, 2005), which favours the adsorption of the negatively charged organic ions of DOC. At higher pHs the mineral oxides have a negative charge (vanLoon and Duffy, 2005) which makes the sorption of the similarly charged DOC anions less favourable. Mayes et al. (2012) observed that soil pH explained 45 % of the variability in the soil sorption affinity for DOC among mineral soils ranging in pH from 3.3 to 8.2. In the study by Mayes et al. (2012) the sorption affinity decreased with increasing pH.

Historically (mid to late 1800's to 1970) many parts of Europe experienced widespread deposition of acid anions such as sulphur which would have led to the acidification of soils and waters (Monteith et al., 2007; Sawicka et al., 2016). During the lengthy acidification period, soil conditions would have been favourable for DOC adsorption to mineral soils (vanLoon and Duffy, 2005; Kennedy et al, 1996; see Section 2.7.2.5). This could have led to a great accumulation of DOC at mineral soil surfaces. Considering that pre-existing soil carbon limits the further binding of DOC then the accumulation of DOC under the acidified conditions could have led to soils becoming saturated with DOC. If as past research suggests mineral soils have a maximum sorption capacity, then it is possible that the increased DOC concentrations observed in upland surface waters are due to mineral soils being saturated. However no previous studies have sought to quantify the potential storage capacity of UK upland soils for DOC. Furthermore, previous studies have shown that the soil properties which control DOC sorption in mineral soils can vary by region, soil type and soil horizon. Therefore to predict the behaviour of DOC in these soils and manage the impacts of soils close to saturation there has to be an understanding of what soil properties are dominant in the control of sorption in UK upland soils.

This study was conducted to determine i) the soil properties which control the desorption of DOC in UK organo-mineral soils; ii) the total capacities of UK upland organo-mineral soils to adsorb DOC and iii) what properties influence the maximum adsorption capacity of these soils. The specific research questions were:

- What are the soil properties which influence the desorption of pre-existing soil carbon under experimental conditions?
- What are the maximum adsorption capacities (Q_{max}) of minerals soils typical of UK upland catchments as predicted by the modified Langmuir isotherm?
- What are the soil properties which influence the capacity of soils in the UK uplands to retain DOC?
- Are upland mineral soils currently carbon saturated, approaching carbon saturation or do they have the capacity to retain more DOC?

4.2 Methodology

The adsorption characteristics of 20 mineral soil samples from 11 UK upland soil profiles were determined using a batch experiment and the modified Langmuir equation. This enabled the maximum adsorption capacity (Q_{max}), the sorption affinity (k) and the null point (Np), where adsorption equals desorption, to be estimated. The DOC solution used for the batch experiment was derived from a single O-horizon. Soil properties were also characterised in order to determine which properties are significant in controlling DOC adsorption. The extent of saturation of the mineral soils was estimated using parameters derived from the Langmuir isotherm (amount of carbon that can be desorbed (b) and Q_{max}). Saturation was also measured using a saturation index derived from the soils' properties (pre-existing soil organic carbon and the sum of amorphous oxides of iron and aluminium).

4.2.1 Sites and sampling.

Twenty mineral soils consisting of four A, three E and thirteen B horizons representing eight humic gleysols and twelve humic podzols were collected from eleven sites in the UK (Table 4.1; 4.2, Figure 4.1). Samples were taken from the first mineral horizon beneath the O-horizon at all sites and the 2nd mineral horizon was taken at sites where it was accessible. The sites were dominated by a variety of vegetation covers including grasses, sedges, forest and shrubs which are typical of the UK uplands. At sites where there were areas dominated by different vegetation covers, samples were taken under each vegetation cover. The grasses and sedges were grouped together and identified as graminoids. Six soil samples were collected from forested sites, ten samples from graminoid sites and four samples from shrub dominated sites (Table 4.1). The annual precipitation for the 11 sites ranged from 751-2605 mm (Table 4.1). Soils were stored in zip locked plastic bags at 4°C until needed for analysis.

4.2.2 Soil preparation and characterisation

Mineral soils were dried in an oven at 40°C, gently crushed with a mortar and pestle and passed through a 2 mm sieve. All soils were then characterised based on pH, moisture content, organic matter content by the loss on ignition method and carbon and nitrogen content using a combustion analyser. The Fe and Al oxides in the mineral soils were extracted using acid ammonium oxalate, pyrophosphate and citrate dithionite to estimate non crystalline, organically bound and crystalline forms respectively. All soil analyses were done in triplicate. Method detection limits where stated were calculated as three times the standard deviation of the blanks (Van Reeuwijk, 1998). The blanks used for each method's limit of detection were the pooled blanks from all sections of this thesis. Unlike the mineral soil used in chapter three of this thesis, the mineral soils used in the experiment described here were not pre-treated to remove soil organic carbon. Soil organic carbon was not removed from the soils used in this experiment because it was one of the variables being tested to determine its influence on adsorption and desorption of DOC in mineral soils.

Using the method of Bascomb (1974), the pH of the dried mineral soil was measured first in water then in 0.01 M Calcium Chloride ($CaCl_2$) solution using a ratio of 1:2.5 w/v. The pH was measured using a Mettler Toledo MPH 225 glass electrode pH meter. The moisture content of the air-dried soils was determined by drying the soil at 105^oC and the organic matter content by the loss on ignition method of combusting the oven dried soils in a furnace at 500^oC overnight (Rowell, 1994). To determine soil carbon and nitrogen, soils were analysed using a Eurovector EA combustion analyser. The combustion analyser has a detection limit of 0.2 µg.

For the mineral soils, weakly crystalline and amorphous iron (Fe_o) and aluminium (Al_o) were extracted by shaking one gram of the < 2 mm fraction with 0.2 M acid ammonium oxalate (50 ml) in the dark for 4 hours (van Reeuwijk, 2002). Organically bound iron (Fe_p) and aluminium (Al_p) were extracted by shaking one gram of the < 2mm fraction with 0.1 M sodium pyrophosphate (100 ml) for 16 hours (van Reeuwijk, 2002). Both crystalline and non-crystalline iron (Fe_d) aluminium (Al_d) oxides were extracted using the Holmgren procedure which entailed shaking one gram of mineral soil in 60 ml of citrate dithionite reagent overnight for 16 hours (van Reeuwijk, 2002). The extracts were analysed using inductively coupled plasma-optical emission spectroscopy (ICP-OES). The method detection limits for the ammonium oxalate extractions were: Al_o = 0.06 mg/L and Fe_o = 0.03 mg/L. The detection limits for the pyrophosphate extractions were: Al_p = 0.03 mg/L and Fe_p = 0.05 mg/L. The detection limits for the dithionite extractions were: Al_d = 0.01 mg/L and Fe_d = 0.03 mg/L.

Table 4.1 Profiles of sites sampled for assessment of the degree of carbon saturation of UK soils.

Sampling point code	Site	Grid Location	Elevation (m)	Soil classification	Parent material	Annual rainfall (mm)	Dominant Vegetation
S1	Coal Burn	N 55°05’29.42 W 002°29’20.62	300	stagnohumic clay loam (Gill and McIntosh, 2001)	sandstones and shales (Gill and McIntosh, 2001)	1400 (Vanguelova et al., 2010)	*Molinia caerulea (Molinia)*
S2	Coal Burn	N 55°05’29.53 W 002°29’26.94	300	stagnohumic clay loam (Gill and McIntosh, 2001)	sandstones and shales (Gill and McIntosh, 2001)	1400 (Vanguelova et al., 2010)	*Picea sitchensis* (Sitka Spruce)
S3	Wye	N 52°27’45.84 W 003°44’23.04	470	peaty podzol (Monteith and Evans, 2005)	shale, gritstone (Monteith and Evans, 2005)	2665 (Hughes et al., 2012)	*Nardus strica, Festuca* sp. with *Eriphorum sp.*
S4	Hafren	N 52°28’32.64 W 003°42’09.92	390	peaty podzol (Monteith and Evans, 2005)	shale, gritstone (Monteith and Evans, 2005)	2545 (Hughes et al., 2012)	*Picea sitchensis* (Sitka Spruce)
S5	Marsden Moor	N 53^{o} 36’ 19.9 W 001^{o} 57’ 51.9	293	stagnohumic gley (Soil survey of England and Wales, 1976)	sandstone and shale (Blundell et al., 2013)	1234 (Blundell et al., 2013)	*Molinia caerulea (Molinia)*
S6	Carleton Moor	N 53^{o} 55.502’ W 002^{o} 03.693	340	Stagnopodzol (Soil survey of England and Wales, 1976)	millstone grit (British Geological Survey, 2016a)	1168 (nearest monitoring site Elslack reservoir; Yorkshire Water, personal communication, October 28th, 2013)	*Calluna vulgaris* (heather)
S7	Elslack	N 53^{o} 55. 772 W 002^{o} 05.049	291	Stagnopodzol (Soil survey of England and Wales, 1976)	Sandstone (British Geological Survey, 2016b)	1168 (Yorkshire Water, personal communication, October 28th, 2013)	*Pinus sylvestris* (Scots pine)

Table 4.1 (continued) Profiles of sites sampled for assessment of the degree of carbon saturation of UK soils.

Sampling point code	Site	Grid Location	Elevation (m)	Soil classification	Parent material	Annual rainfall (mm)	Dominant Vegetation
S8	Levisham	N 54^o 19.907’ W 000^o 42.972’	259	stagnopodzol (Soil survey of England and Wales, 1976)	sandstone (British Geological Survey, 2016c)	751.1 (nearest station High Mowthorpe) (Met-Office, 2016)	*Molinia caerulea*, young *Vaccinium sp.* (bilberry)
S9	Dalby forest	N 54^o 37.330 W 000^o 37.917	253	iron pan stagnopodzol (Ordinance Survey, 1976)	Sandstone (Wilson et al., 2001)	751.1 (nearest station High Mowthorpe) (Met-Office, 2016)	*Picea sitchensis (*Sitka Spruce)
S10	Nidderdale HS7	N 54^o 09.625 W 001^o 54.450	384	Cambic stagnohumic gley (Soil survey of England and Wales, 1976)	millstone grit (Chapman et al., 2010)	1393 (Chapman et al., 2010)	*Eriophrum sp., Vaccinium sp.*
S11	Nidderdale HS2	N 54^o 10.224 W 001^o 54.168	418	Cambic stagnohumic gley (Soil survey of England and Wales, 1976)	millstone grit (Chapman et al., 2010)	1393 (Chapman et al., 2010)	*Calluna vulgaris* (heather) with *Sphagnum* moss
S12	Nidderdale HS11	N 54^o 08.987 W 001^o 55.574	405	Cambic stagnohumic gley (Soil survey of England and Wales, 1976)	millstone grit (Chapman et al., 2010)	1393 (Chapman et al., 2010)	mainly *Eriophrum sp.*, some *Sphagnum sp.* (moss)
S13	Etherow	N 53^o 29.479 W 001^o 49.479	337	peaty podzols (Patrick et al., 1995)	millstone grit (Patrick et al., 1995)	1480 1190 (van den Berg et al., 2012)	*Molinia sp*, *Juncus sp.*, bracken
S14	Crowden	N 53^o 29.946 W 001^o 53.209	337	stagnopodzol (Soil survey of England and Wales, 1976)	sandstone and shale (Blundell et al., 2013)	958 (Blundell et al., 2013)	*Vaccinium sp., Molinia sp.*, *Sphagnum* mosses

Table 4.2. Description and depths of the soil horizons observed at the sites sampled within this study.

Site	Location	Soil Classification	Horizon	Horizon Depth (cm)
Coalburn (forest)	N 55°05′29.53 W 002°29′26.94	stagnohumic clay loam (Gill and McIntosh, 2001)	L+F	3
			H	17
			A	>7
Coalburn (graminoid)	N 55°05′29.42 W 002°29′20.62	stagnohumic clay loam (Gill and McIntosh, 2001)	O	40
			A	>8
Wye	N 52°27′45.84 W 003°44′23.04	peaty podzol (Monteith and Evans, 2005)	O	17
			E	4
			B	>10
Hafren	N 52°28′32.64 W 003°42′09.92	peaty podzol (Monteith and Evans, 2005)	O	24
			E	7
			B	25
Marsden	N 53^{o} 36’ 19.9 W 001^{o} 57’ 51.9	stagnohumic gley (Soil survey of England and Wales, 1976)	O	33
			E	4
			B	24
Carleton	N 53^{o} 55.502’ W 002^{o} 03.693	Stagnopodzol (Soil survey of England and Wales, 1976)	O	19
			Bg	19
			BCg	>40
Elslack	N 53^{o} 55. 772 W 002^{o} 05.049	Stagnopodzol (Soil survey of England and Wales, 1976)	L+F	10
			H	8
			A	15
			B	>33
Levisham	N 54^{o} 19.907’ W 000^{o} 42.972’	stagnopodzol (Soil survey of England and Wales, 1976)	O	13
			A	19
Dalby	N 54^{o} 37.330 W 000^{o} 37.917	iron pan stagnopodzol (Ordinance Survey, 1976)	O	17
			B	9
Nidderdale HS7	N 54^{o} 09.625 W 001^{o} 54.450	Cambic stagnohumic gley (Soil survey of England and Wales, 1976)	O	27
			B	>10
Nidderdale HS2	N 54^{o} 10.224 W 001^{o} 54.168	Cambic stagnohumic gley (Soil survey of England and Wales, 1976)	O	22
			B	>10
Nidderdale HS11	N 54^{o} 08.987 W 001^{o} 55.574	Cambic stagnohumic gley (Soil survey of England and Wales, 1976)	O	43
			Bg	25
			BCg	60
Etherow	N 53^{o} 29.479 W 001^{o} 49.479	peaty podzols (Patrick et al., 1995)	O	32
			B	>10
Crowden	N 53^{o} 29.946 W 001^{o} 53.209	stagnopodzol (Soil survey of England and Wales, 1976)	O	12
			B	>7

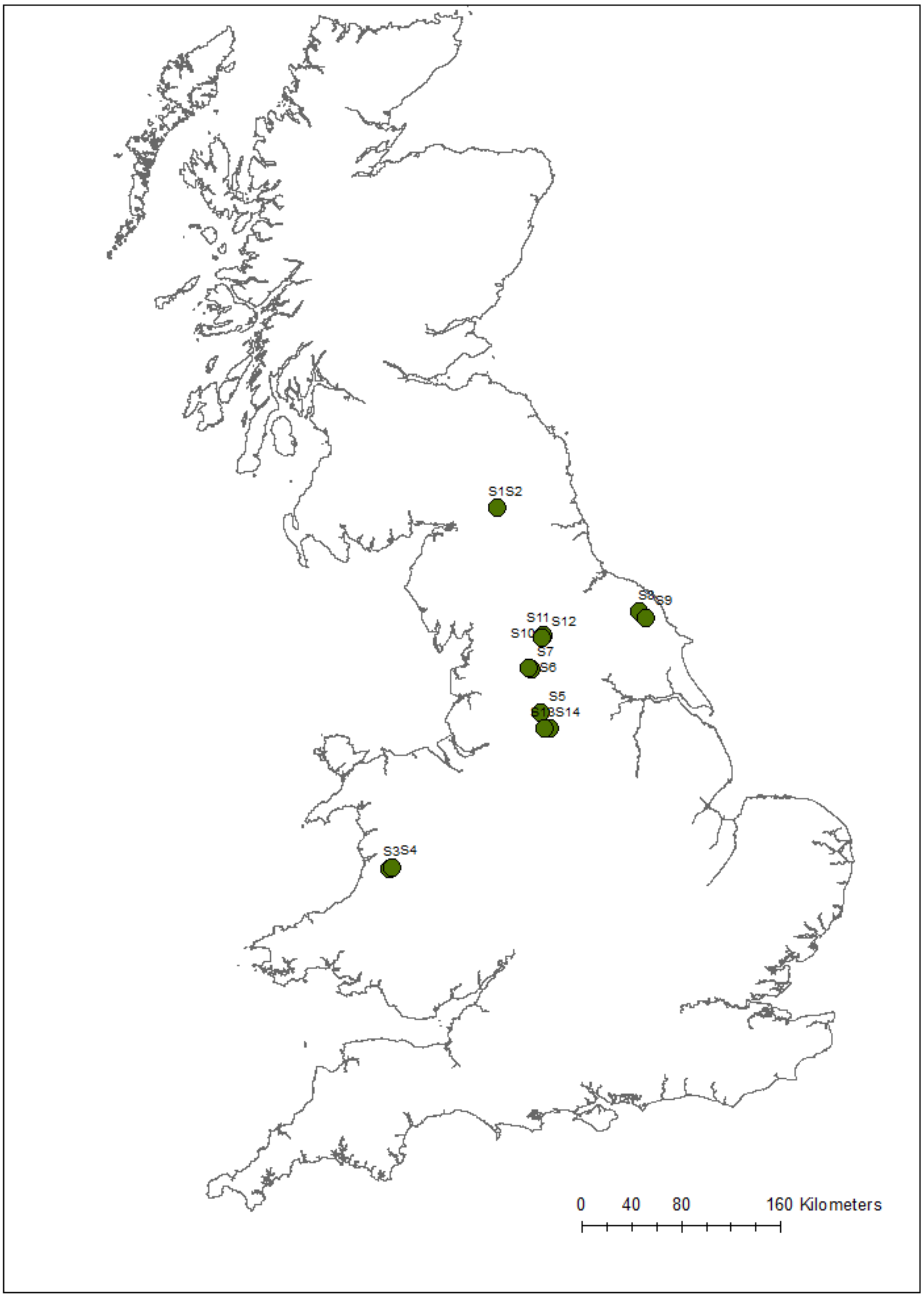


Figure 4.1. Location of the sampling sites. Site codes refer to the lists in table 4.1.

4.2.3 DOC Extraction.

Sorption experiments were conducted with DOC extracted from O-horizon soil dominated by heather. DOC concentrations higher than those typically seen in the field were required to fulfil the objective of determining the maximum adsorption capacity of soils. Heather dominated organic soil was used since this was shown to produce DOC of highest concentrations when compared to other types of vegetation typical of the upland UK habitats (see Table 3.5). Although DOC from heather dominated organic soil showed only desorption in the concentration range (5 - 49 mg/L) used in chapter 3, the data did exhibit an upward slope with increasing concentrations of added DOC (Figure 3.7) which would indicate the potential for adsorption at higher concentrations. The site sampled was situated at Marsden Moor, 53°37’06.73”N, 001°58’15.86”W. The intact O-horizon soil measuring 21 cm x 19 cm x 26 cm deep was returned to the laboratory where it was soaked in deionised water for 14 days then filtered. The leachate was separated from the soil by decanting into a glass bottle. The leachate was then filtered under suction, first using a glass fibre filter with nominal pore size 1.2 µm, followed by a 0.7 µm glass fibre filter and finally filtered using a 0.45 µm pre washed cellulose nitrate filter. The filtered leachate was analysed for DOC concentration.

The resulting stock solution was diluted with deionised water to give six solutions ranging in concentration from 16 mg/L to 112.9 mg/L, which represents the range of concentrations typically found in soil solutions draining O-horizons in UK uplands (van den Berg et al., 2012)

4.2.4 DOC Quantification

All DOC solutions were analysed for organic carbon content by thermal oxidation using an Analytik Jena Multi N/C 2100S analyser. This equipment uses a differential method to calculate total organic carbon (TOC) in a sample. The total dissolved carbon (TC) is determined by digestion of both organic and inorganic carbon and subsequent detection of the carbon dioxide released. The total inorganic carbon (TIC) from carbonates, hydro-carbonates and free carbon dioxide is measured in a separate TIC reactor. The TIC is subtracted from the TC to give the quantity of TOC in the sample. Since all solution samples analysed in this study were filtered to <0.45 µm, TOC was assumed to equate to DOC. Each batch of analyses included the use of a certified reference material (VKI WW4A) and a standard prepared with the commercially available TIC (1000 ± 10 mg/L, Fluka product 12003-250ML-F) and TOC (1000 ± 10 mg/L, Fluka product 76067-250ML-F) standard solutions. The method detection limit was determined to be 0.25 mg/L using the method of Van Reeuwijk (1998).

4.2.5 Batch Sorption Experiments

The method of Kothawala et al. (2009) was used for the sorption experiments. Thirty millilitres of DOC solution was added to three grams of soil in a 50 mL centrifuge tube. This was done in quadruplicate for each DOC solution. Tubes were placed on a horizontal shaker for 24 hours at 4°C. The supernatant was filtered through 0.45 µm nylon filters (Avonchem Ltd, Macclesfield, UK) and analysed for DOC as described in section 4.2.4. Desorption of pre-existing soil carbon was determined by adding 30 ml of deionised water to three grams of soil, this was done in quadruplicate for each soil. The adsorbed concentrations were corrected to account for any desorbed DOC

4.2.6 Sorption Isotherms

The adsorption of DOC to each mineral soil was modelled using the modified Langmuir isotherm which allows for the estimation of the maximum adsorption capacity (Kothawala et al., 2008; Vandenbruwane et al., 2007). The Langmuir isotherm (Eq 1) has also been used to model adsorption of solutes to soil, where RE (in mg/kg) is the amount of solute adsorbed to the surface, Q_{max} (in mg/kg)is the maximum adsorption capacity; k (kg soil/ mg DOC) is the binding affinity and X_f the final equilibrium concentration.

$$RE = \frac{Q_{max} \cdot k \cdot X_f}{1 + k \cdot X_f} \tag{1}$$

In its classic form Eq (1) does not have a desorption term to account for any pre-existing soil carbon with the potential to desorb into solution. Lilienfein et al. (2004) added a desorption parameter (b) to account for any pre-existing soil organic matter which may desorb at low added DOC concentrations, Eq (2). To account for the pre-existing soil carbon, adsorption was modelled using the modification of the traditional Langmuir equation described by Lilienfein et al. (2004.) The desorption term was determined experimentally using the solution blanks described in section 4.2.5.

$$RE = \frac{Q_{max} \cdot k \cdot X_f}{1 + k \cdot X_f} - b \tag{2}$$

The modified Langmuir isotherm could not be linearly transformed so these were solved iteratively using the Levenberg-Marquardt algorithm in the statistical software SPSS 22.0. The model efficiency (EF) was used to test the performance of the Langmuir isotherm. The

EF is a measure of the correspondence between the observed data and the modelled data with an EF = 1 indicating a perfect fit of the model (Kothawala et al., 2008; Vandenbruwane et al., 2007).

4.2.7 Estimation of carbon saturation of soils

The extent to which the mineral soils are saturated with carbon was estimated using the method of Vandenbruwane et al. (2007). This entailed calculating the percentage saturation using the ratio of the DOC desorbed (b) to the maximum capacity of the soils to retain carbon (Q_{max}). This is described in Equation 3 where S_{BQ} refers to the estimate of carbon saturation.

$$\mathrm{S_{BQ}} = \frac{b}{Q_{max}}\, x\, 100 \tag{3}$$

The extent to which the soils are saturated was also calculated using the saturation index SOC/(Fe_o+Al_o) (henceforth referred to as SI_{SOC}), which assumes that weakly crystalline and amorphous Fe and Al are the main sites of adsorption (Kindler et al., 2011; Pengerud et al., 2014).

The two measures of saturation differ in their assumptions; S_{BQ} makes no assumptions about the nature of binding sites but is based on modelled parameters, while SI_{SOC} uses experimentally derived measures.

4.2.8 Statistical Analysis

The statistical significance of any differences in soil and sorption properties between soil types, among horizons and among dominant vegetation covers was analysed by one-way ANOVA in cases of normally distributed data or by Kruskal Wallis in cases where normality did not exist or was not achieved by data transformation. With the exceptions of pH, Q_{max}, clay content and exchangeable cations all soil properties and sorption characteristics were log transformed to normalise the data. The log transformation did not normalise the parameter for sorption affinity (k), instead k was transformed by using the power function of -0.5. The measured sorption term RE_{112} was normalised by squaring the variable. Linear regression was performed between sorption characteristics derived from the iteratively solved Langmuir isotherm and soil properties. Regression models were developed for sorption characteristics using stepwise multiple regression with forward selection using the statistical software SPSS version 22. Variables were allowed into the model equation if the p-value was > 0.05 and retained if the p-value was < 0.1.

4.3 Results

4.3.1 Comparison of Soil Properties between soil classification groups, horizons and vegetation covers.

Soil organic carbon (SOC) content of the mineral horizons ranged from 9.1 g/kg to 81.6 g/kg (Table 4.3 and Figure 4.2). There were significant differences (H (2) = 28.96, $p < 0.01$) in soil carbon content among horizons (Figure 4.2). The carbon content of the A horizons (median = 63.5 g/kg) was higher than that of the B horizons (median = 20.6 g/kg, U = 0, $p < 0.001$) and E horizons (median = 36.6 g/kg, U = 10, p =0.001). No statistically significant differences in soil carbon were observed among vegetation covers (H (2) = 3.286, p = 0.193) or between soil classification groups (U = 318.5, p = 0.087).

Soil clay content ranged from 3.0 ± 0.5% to 32.3 ± 0.9 % (Table 4.3 and Figure 4.3). Figure 4.3 shows the distribution of the soil clay contents by horizons for the two soil groups (podzols and gleysols), and the three vegetation covers (forests, graminoids, shrubs). Although the clay content was highest in the E horizons (median = 23.2), followed by the B horizons (median = 12.6) then the A horizons (median = 9.3), the differences in clay content between horizons were not statistically significant (H (2) = 5.71, p = 0.058). There were also no significant differences in soil clay contents when data were compared among vegetation covers (H (2) = 2.829, p = 0.243) or between soil types (U = 411, p= 0.751).

Soil pH in $CaCl_2$ ranged from 2.8 to 4.0 (Table 4.3 and Figure 4.4). There were also no significant differences in pH when data were compared between soil types (U = 418, p = 0.833; Figures 4.4 A and 4.4 B), among horizons (H (2) = 1.484, p = 0.476; Figure 4.4) or vegetation covers (H (2) = 1.837, p = 0.399; Figures 4.4 C, 4.4 D and 4.4 E).

Table 4.3 Soil Properties including soil organic carbon (SOC), soil organic nitrogen (SON), pyrophosphate , oxalate and dithionite extractable iron (Fe_p, Fe_o, Fe_d), pyrophosphate, oxalate and dithionite extractable Aluminium (Al_p, Al_o, Al_d), Cation exchange Capacity (ECEC). Standard error of the mean is given in brackets, n = 3

Site	**Horizon**	**pH ($CaCl_2$)**	**Sand %**	**Silt %**	**Clay %**	**SOC g/kg**	**SON g/kg**	**C/N**	**Fe_p g/kg**	**Fe_o g/kg**	**Fe_d g/kg**	**Al_p g/kg**	**Al_o g/kg**	**Al_d g/kg**	**ECEC $cmol_c kg^{-1}$**
Coal Burn forest	Ah	3.96 (0.01)	63.2 (0.5)	24.0 (0.6)	12.9 (1.0)	46.0 (1.0)	3.51 (0.0)	13.3 (0.1)	4.49 (0.02)	7.54 (0.05)	8.23 (0.18)	1.48 (0.02)	1.87 (0.01)	0.79 (0.01)	6.18 (0.04)
Coal Burn grassland	Ah	3.61 (0.01)	59.3 (0.5)	26.3 (1.2)	14.5 (1.2)	82.0 (1.4)	3.41 (0.0)	24.5 (0.08)	1.10 (0.01)	1.13 (0.02)	9.42 (0.22)	1.64 (0.04)	1.87 (0.05)	1.93 (0.02)	2.69 (0.19)
Wye	Bs	3.88 (0.00)	27.8 (3.5)	48.5 (2.0)	23.7 (1.7)	36.7 (0.1)	2.54 (0.01)	14.45 (0.14)	20.08 (0.14)	36.32 (0.44)	47.46 (0.27)	1.74 (0.07)	3.25 (0.01)	1.50 (0.03)	8.40 (0.02)
	E	3.69 (0.00)	29.1 (0.4)	48.5 (1.1)	22.4 (0.9)	19.0 (0.0)	1.53 (0.02)	12.45 (0.21)	1.05 (0.02)	1.32 (0.00)	2.30 (0.03)	3.29 (0.05)	1.99 (0.02)	3.79 (0.08)	10.30 (0.19)
Hafren	Bs	3.86 (0.01)	33.3 (1.3)	47.2 (0.8)	19.4 (1.0)	19.9 (0.1)	1.37 (0.02)	14.49 (0.29)	17.03 (0.33)	29.95 (0.76)	52.79 (0.50)	3.44 (0.11)	3.49 (0.05)	4.81 (0.05)	7.84 (0.02)
	Eag	3.53 (0.01)	4.0 (0.2)	63.7 (0.9)	32.3 (0.9)	12.5 (0.0)	1.01 (0.01)	12.41 (0.23)	0.39 (0.02)	0.54 (0.02)	0.81 (0.01)	1.69 (0.02)	1.94 (0.03)	1.23 (0.01)	11.67 (0.22)
Marsden Moor	E	3.07 (0.02)	65.4 (0.8)	29.1 (1.4)	5.5 (1.2)	19.9 (0.2)	0.69 (0.02)	29.00 (0.97)	10.27 (0.13)	13.57 (0.06)	19.43 (0.40)	1.38 (0.01)	1.60 (0.01)	1.75 (0.03)	9.78 (0.04)
	Bg	2.79 (0.02)	65.6 (0.7)	27.7 (0.7)	6.8 (1.3)	45.0 (0.4)	1.47 (0.01)	30.60 (0.46)	0.80 (0.02)	0.77 (0.01)	1.02 (0.02)	1.21 (0.06)	0.90 (0.01)	1.00 (0.03)	7.45 (0.02)

Table 4.3 (continued) Soil Properties including soil organic carbon (SOC), soil organic nitrogen (SON), pyrophosphate , oxalate and dithionite extractable iron (Fe_p, Fe_o, Fe_d), pyrophosphate, oxalate and dithionite extractable Aluminium (Al_p, Al_o, Al_d), Cation exchange Capacity (ECEC). Standard error of the mean is given in brackets, n = 3.

Site	Horizon	pH ($CaCl_2$)	Sand %	Silt %	Clay %	SOC g/kg	SON g/kg	C/N	Fe_p g/kg	Fe_o g/kg	Fe_d g/kg	Al_p g/kg	Al_o g/kg	Al_d g/kg	ECEC $cmol_c kg^{-1}$
Carleton Moor	Bg	3.23 (0.01)	59.4 (0.2)	27.7 (0.1)	12.9 (0.2)	22.3 (0.4)	0.91 (0.02)	24.38 (0.24)	0.32 (0.01)	0.33 (0.01)	0.41 (0.01)	1.53 (0.01)	1.65 (0.02)	1.34 (0.00)	11.54 (0.36)
	BCg	3.88 (0.04)	55.0 (0.2)	25.6 (1.2)	19.4 (1.2)	9.1 (0.1)	0.57 (0.02)	16.11 (0.72)	3.50 (0.11)	5.76 (0.04)	11.89 (0.36)	1.65 (0.02)	2.08 (0.00)	1.81 (0.07)	8.81 (0.10)
Elslack	A	2.99 (0.02)	68.8 (0.7)	25.7 (1.0)	5.6 (0.7)	40.5 (0.2)	1.48 (0.02)	27.46 (0.45)	0.45 (0.01)	0.49 (0.01)	0.57 (0.02)	1.07 (0.03)	1.05 (0.02)	1.20 (0.01)	7.24 (0.05)
	B	3.71 (0.02)	62.6 (0.9)	30.5 (0.7)	6.9 (0.6)	10.9 (0.1)	0.45 (0.02)	24.61 (1.30)	8.57 (0.16)	12.85 (0.25)	20.46 (0.31)	1.99 (0.02)	2.64 (0.01)	2.38 (0.12)	8.13 (0.03)
Levisham	Ah	3.37 (0.01)	71.7 (0.7)	25.4 (0.9)	3.0 (0.5)	81.6 (0.3)	3.05 (0.01)	26.74 (0.14)	2.43 (0.04)	2.35 (0.03)	3.54 (0.02)	1.08 (0.03)	0.85 (0.01)	0.90 (0.01)	7.90 (0.03)
Dalby forest	B	3.14 (0.03)	36.7 (0.9)	54.3 (0.3)	9.0 (0.9)	37.6 (0.4)	1.49 (0.02)	25.23 (0.61)	0.35 (0.02)	0.32 (0.04)	0.54 (0.07)	1.51 (0.03)	1.05 (0.01)	1.26 (0.02)	6.35 (0.04)
Nidderdale HS7	Bg	3.56 (0.02)	58.5 (0.8)	28.3 (1.7)	13.3 (1.4)	20.7 (0.2)	1.25 (0.01)	16.48 (0.10)	4.35 (0.15)	13.74 (0.63)	24.09 (1.64)	1.63 (0.03)	2.15 (0.02)	1.87 (0.06)	10.41 (0.10)

Table 4.3 (continued) Soil Properties including soil organic carbon (SOC), soil organic nitrogen (SON), pyrophosphate , oxalate and dithionite extractable iron (Fe_p, Fe_o, Fe_d), pyrophosphate, oxalate and dithionite extractable Aluminium (Al_p, Al_o, Al_d), Cation exchange Capacity (ECEC). Standard error of the mean is given in brackets, n = 3.

Site	Horizon	pH ($CaCl_2$)	Sand %	Silt %	Clay %	SOC g/kg	SON g/kg	C/N	Fe_p g/kg	Fe_o g/kg	Fe_d g/kg	Al_p g/kg	Al_o g/kg	Al_d g/kg	ECEC $cmol_c kg^{-1}$
Nidderdale HS2	Bg	3.00 (0.01)	79.3 (0.4)	16.1 (0.4)	4.6 (0.0)	31.6 (0.3)	0.96 (0.01)	32.82 (0.76)	0.42 (0.01)	0.42 (0.00)	0.45 (0.01)	0.92 (0.02)	0.73 (0.01)	0.67 (0.01)	5.68 (0.02)
Nidderdale HS11	Bg	3.66 (0.01)	39.2 (0.5)	34.6 (1.0)	26.1 (0.9)	27.7 (0.4)	1.20 (0.01)	23.16 (0.17)	1.20 (0.02)	1.87 (0.02)	1.60 (0.01)	2.69 (0.13)	2.70 (0.02)	1.82 (0.04)	14.48 (0.11)
	BCg	4.01 (0.01)	34.6 (0.5)	40.6 (1.0)	24.8 (0.9)	20.1 (0.2)	1.03 (0.01)	19.44 (0.19)	1.73 (0.01)	8.75 (0.08)	8.23 (0.40)	1.88 (0.05)	2.66 (0.02)	1.62 (0.11)	10.71 (0.04)
Etherow	Bs	3.44 (0.02)	55.1 (0.4)	39.3 (1.0)	5.6 (0.9)	34.1 (0.6)	1.16 (0.02)	29.31 (0.55)	0.16 (0.01)	0.15 (0.00)	0.16 (0.00)	2.41 (0.05)	2.10 (0.01)	2.06 (0.04)	9.07 (0.08)
Crowden	Bs	3.42 (0.02)	81.0 (0.5)	15.2 (0.8)	3.8 (0.3)	30.4 (0.9)	1.70 (0.04)	17.89 (0.20)	4.31 (0.05)	4.59 (0.09)	7.07 (0.14)	1.50 (0.03)	1.35 (0.05)	1.33 (0.02)	7.87 (0.16)

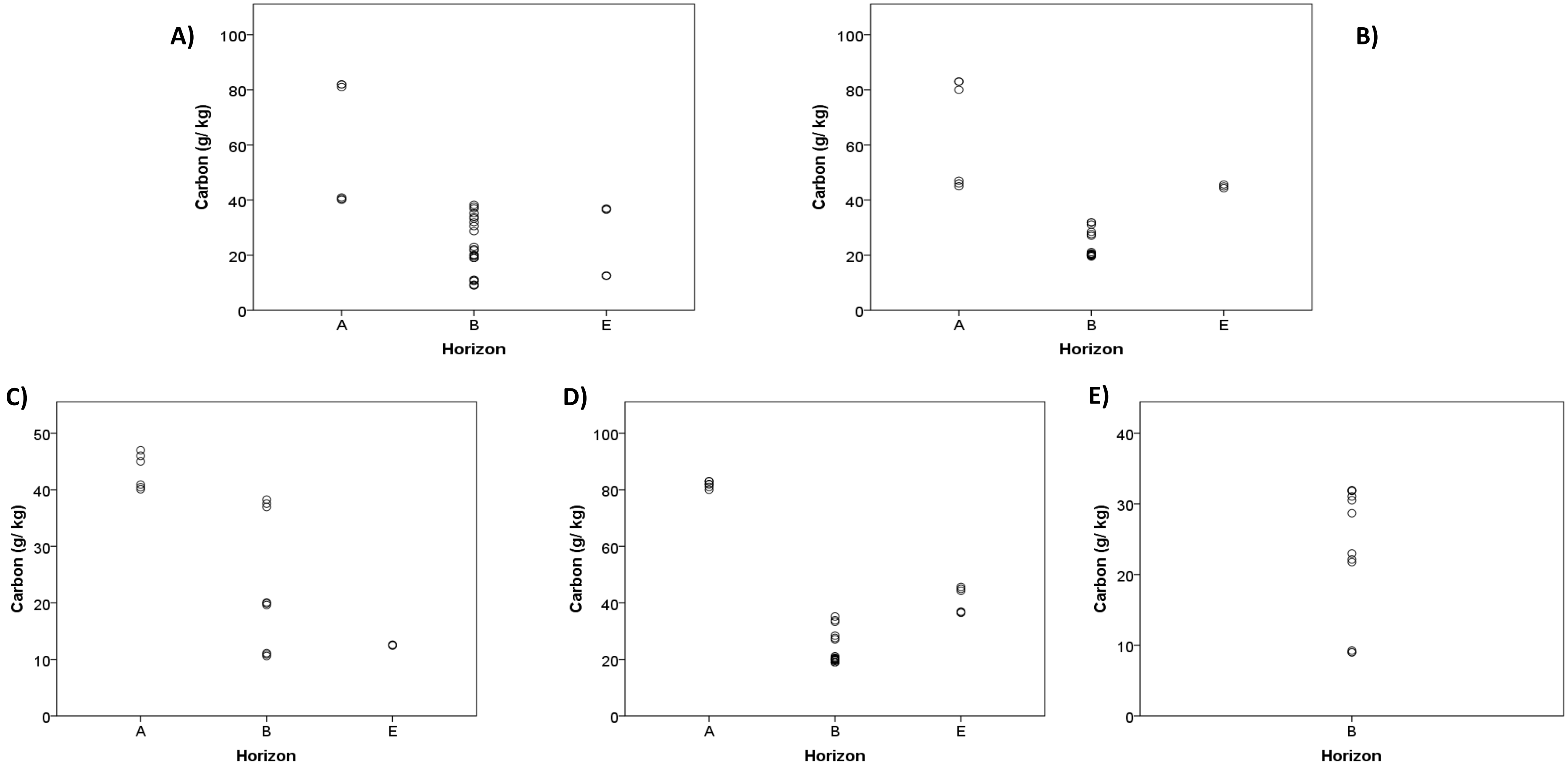


Figure 4.2 Comparison of soil carbon content by horizons for: A) podzols (A = 6, B = 24, E = 6) ; B) gleysols (A = 6, B = 15, E = 3) ; C) forests (A = 6, B = 9, E = 3); D) graminoids (A = 6, B = 18, E = 6); E) shrubs (B =12). Dot plots are showing pooled results of replicate samples.

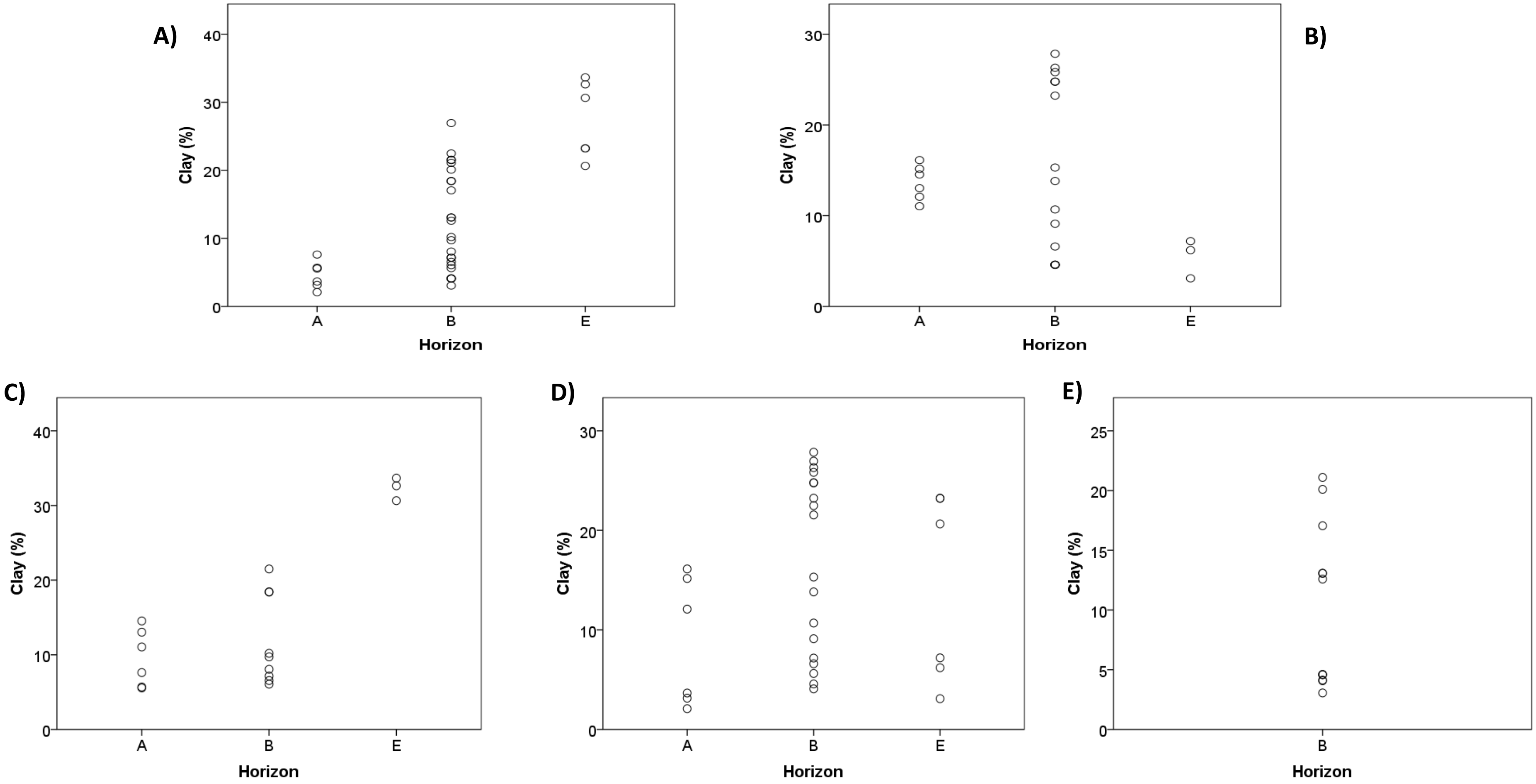


Figure 4.3 Comparison of percentage clay content by horizons for: A) podzols (A = 6, B = 24, E = 6) ; B) gleysols (A = 6, B = 15, E = 3) ; C) forests (A = 6, B = 9, E = 3); D) graminoids (A = 6, B = 18, E = 6); E) shrubs (B =12). Dot plots are showing pooled results of replicate samples.

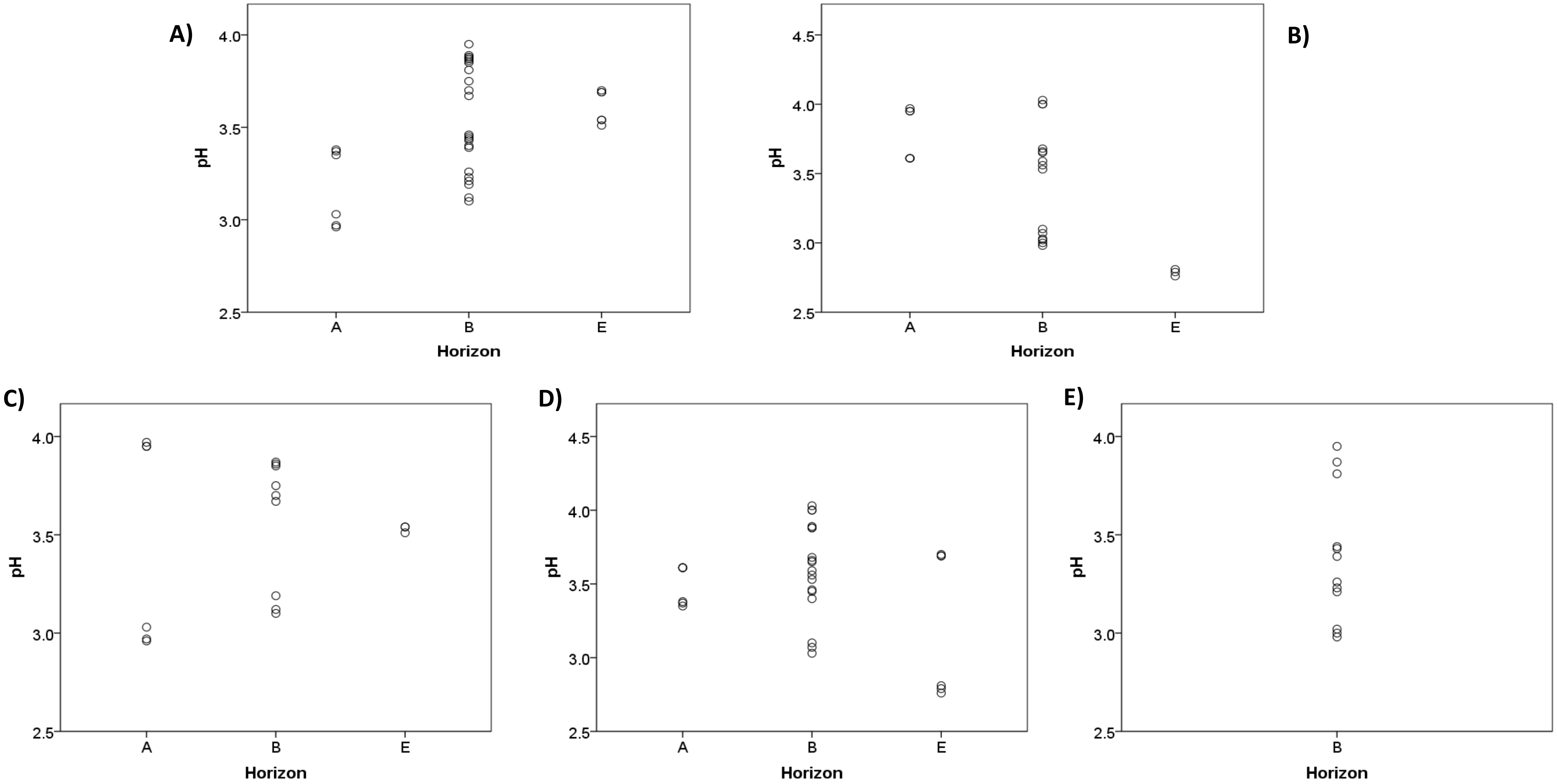


Figure 4.4 Comparison of soil pH by horizons for: A) podzols (A = 6, B = 24, E = 6) ; B) gleysols (A = 6, B = 15, E = 3) ; C) forests (A = 6, B = 9, E = 3); D) graminoids (A = 6, B = 18, E = 6); E) shrubs (B =12). Dot plots are showing pooled results of replicate samples.

The podzols had higher amounts of all forms of extractable Al and Fe than the gleysols (Figure 4.5). However, the difference in extractable Al and Fe between the podzols and gleysols was not statistically significant: Al_d (U = 344.5, p = 0.187); Al_o (U = 395, p = 0.577); Al_p (U = 326, p= 0.110); Fe_d (U = 367, p = 0.327); Fe_o (U = 354, p = 0.239); Fe_p (U = 375, p= 0.390)

The extractable Al among the three horizons (Figure 4.6) differed significantly, Al_d (H(2) = 14.802, p = 0.001); Al_o (H(2) = 10.016, p = 0.007); Al_p (H(2) = 10.351, p= 0.006). The Al_d content of the B horizons (median = 1.80 g/kg) was significantly higher than that of the A horizons (median = 1.06 g/kg, U = 103.5, p = 0.004) and the E horizons (median = 1.23 g/kg, U = 58.0, p = 0.001). The Al_p content of the A horizons (median = 1.28 g/kg) was significantly lower than that of the E horizons (median = 1.65 g/kg, U = 24, p = 0.034) and the B horizons (median = 1.67 g/kg, U = 98.5, p = 0.003). The Al_o content of the B horizons (median = 2.10 g/kg) was significantly greater than that of the E horizons (median = 1.91 g/kg, U = 99, p = 0.043) and the A horizons (median = 1.43 g/kg, U = 113.5, p = 0.007). The dithionite, oxalate and pyrophosphate extractable Fe all followed the order B > A > E (Figure 4.6 D, E and F), however, the differences in extractable Fe among the horizons were not significant: Fe_d (H (2) = 3.437, p = 0.179); Fe_o (H (2) = 4.281, p = 0.118); Fe_p (H (2) = 5.491, p= 0.064).

The amounts of extractable Al and Fe in the mineral soils did not differ significantly among the three categories of vegetation covers studied (Figure 4.7) : Al_d (H (2)= 5.014, p = 0.082); Al_o (H (2) = 5.523, p = 0.063); Al_p (H (2) = 5.580, p= 0.061); Fe_d (H (2)= 3.331, p = 0.189); Fe_o (H (2) = 3.445, p = 0.179); Fe_p (H (2) = 1.643, p= 0.440).

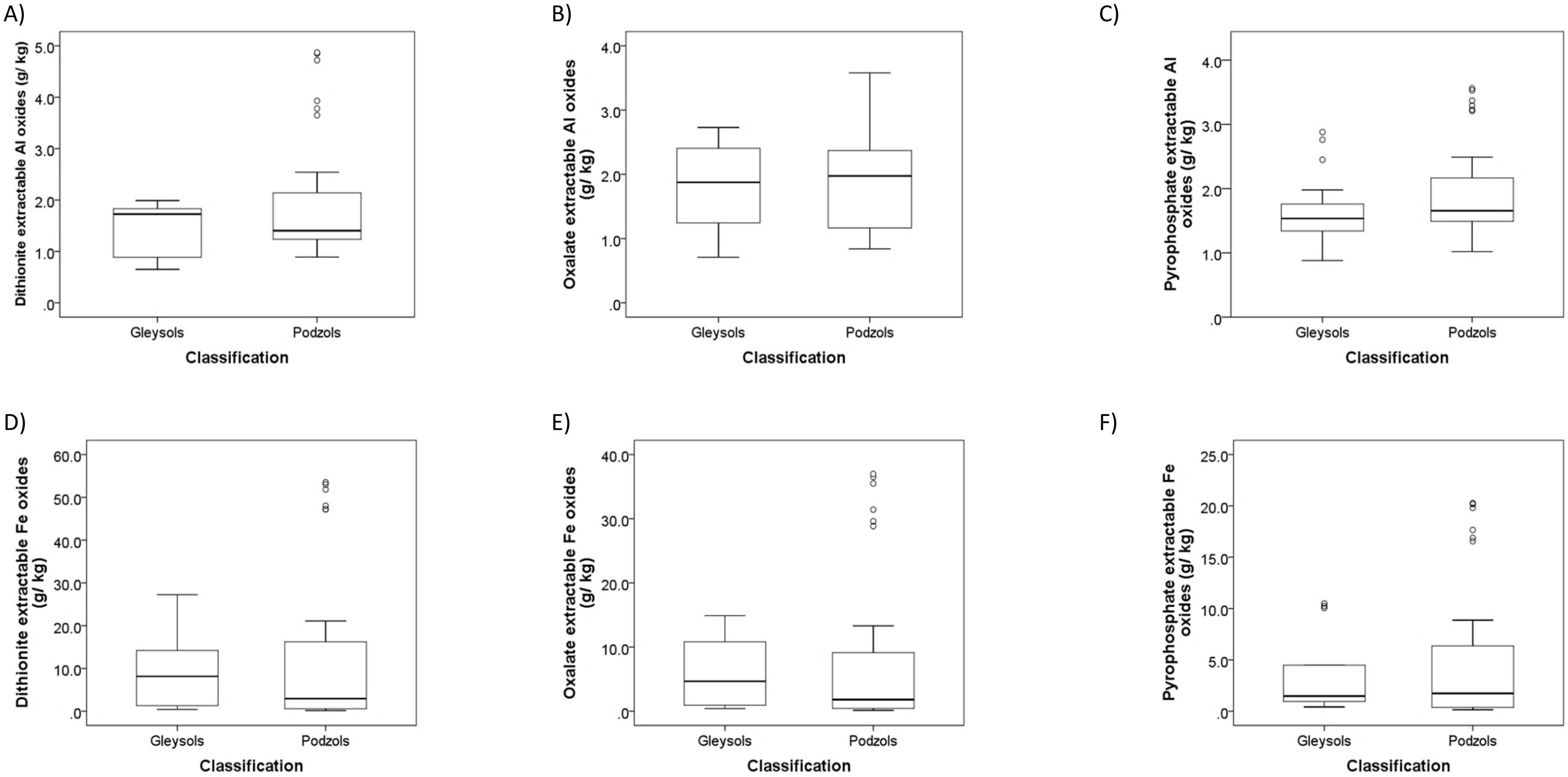


Figure 4.5 Distribution of extractable aluminium and iron between gleysols (n =24) and podzols (n =36). Boxplots show pooled results of replicate samples. The line in the middle of the box represents the median value, the top of the box represents 75% of the distribution and the bottom of the box represents 25% of the distribution. The lower and upper whiskers represent 10% and 90% of the distribution respectively. Points represent outliers which are below or above 1.5 x the interquartile range.

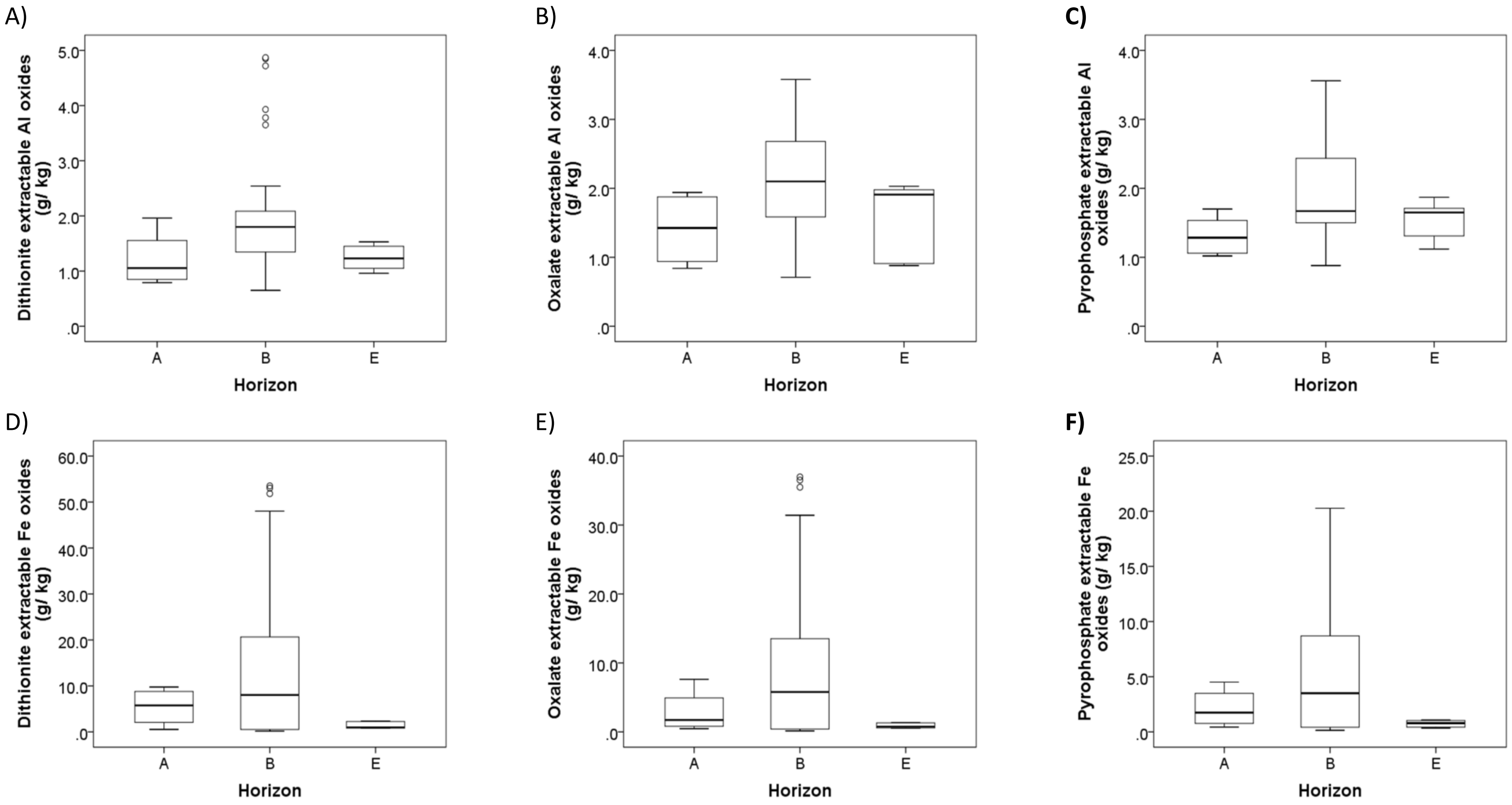


Figure 4.6 Distribution of extractable aluminium and iron among A (n = 12), B (n = 39) and E (n =9) soil horizons. Boxplots show pooled results of replicate samples. The line in the middle of the box represents the median value, the top of the box represents 75% of the distribution and the bottom of the box represents 25% of the distribution. The lower and upper whiskers represent 10% and 90% of the distribution respectively. Points represent outliers which are below or above 1.5 x the interquartile range.

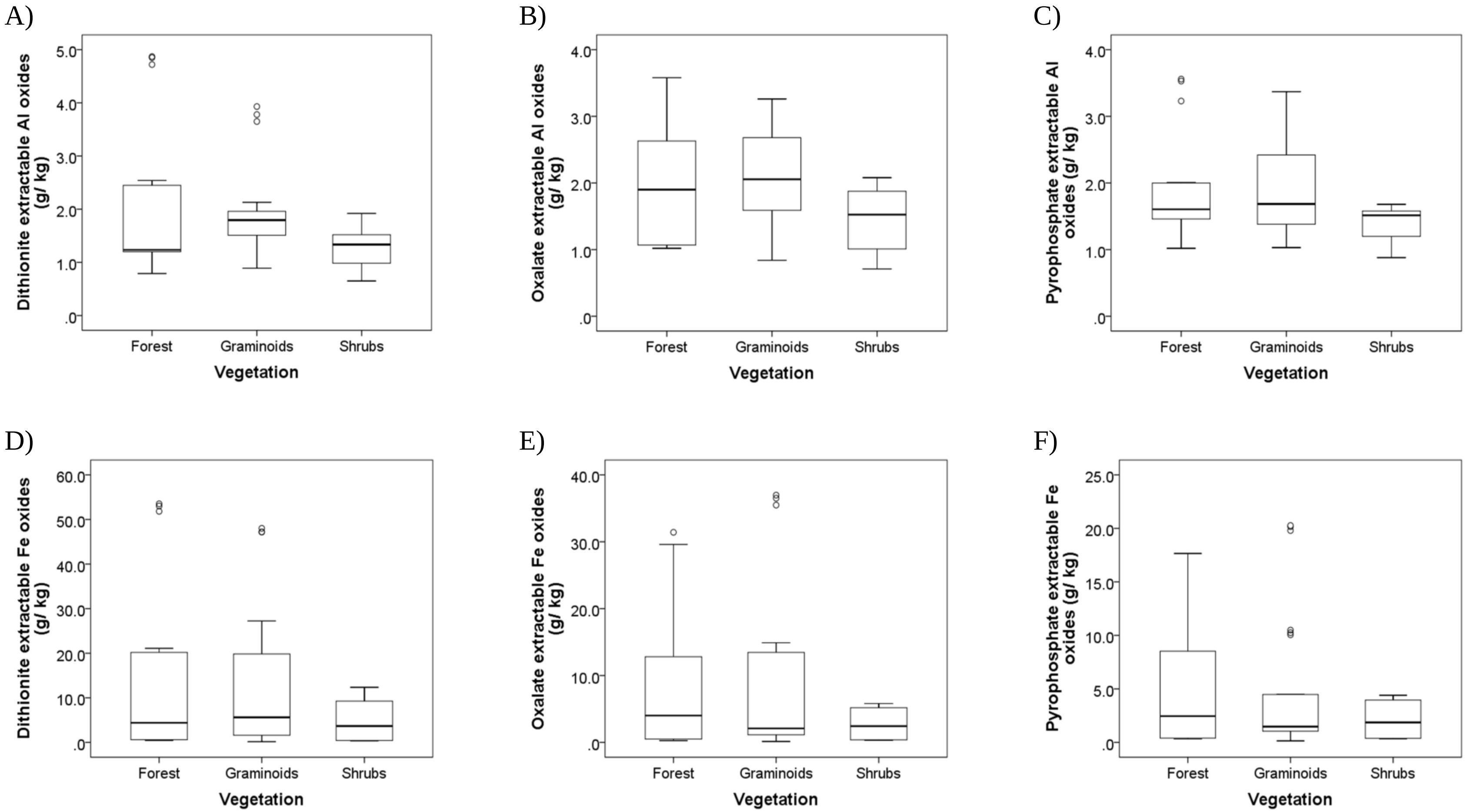


Figure 4.7 Distribution of extractable aluminium and iron in mineral soils collected beneath forest (n = 18), graminods (n= 30) and shrubs (n = 12). Boxplots show pooled results of replicate samples. The line in the middle of the box represents the median value, the top of the box represents 75% of the distribution and the bottom of the box represents 25% of the distribution. The lower and upper whiskers represent 10% and 90% of the distribution respectively. Points represent outliers which are below or above 1.5 x the interquartile range.

4.3.2 Measured sorption parameters

4.3.2.1 *Desorption with no added DOC*

Desorption of DOC ranged from 79.74 mg/kg to 640.36 mg/kg (Table 4.4) with an average of 237.7 ± 29.4 mg/kg. Although mean desorption was greater in the podzols (274.8 ± 44.6 mg/kg) than that of the gleysols (182.0 ± 20.6 mg/kg) (Figure 4.8 A), this was also not significant ($U = 31$, $p = 0.208$). Greater mean desorption was observed in the A horizons (321.1 ± 114.4 mg/kg) than the B horizons (223.1 ± 28.3 mg/kg) and E horizons (189.7 ± 37.1 mg/kg) (Figure 4.8 B). The higher desorption in the A horizons was reflective of their higher carbon content (Figure 4.1 B). However, these differences in desorption among the horizons were not significant ($H (2) = 0.660$, $p = 0.719$). Analysis of desorption based on vegetation cover (Figure 4.8 C) showed that desorption from soils was similar for all three vegetation types ($H (2) = 0.571$, $p = 0.751$). The mean desorption for the soils beneath graminoids was 231.5 ± 48.3 mg/kg, for forests was 243.3 ± 52.3 mg/kg and shrubs 244.9 ± 53.7 mg/kg.

4.3.2.2 *Sorption at the highest concentration of added DOC (RE_{112})*

For all soils analysed the adsorption (RE_{112}) at the maximum mass of DOC added (1126.7 ± 0.1 mg/kg expressed on a dry soil basis) ranged from 448.3 mg/kg to 964.8 mg/kg (Table 4.4) with a mean of 723.4 ± 38.6 mg/kg. Mean adsorption for the gleysols (730.0 ± 64.8 mg/kg) was similar to that of the podzols (719.0 ± 50.1 mg/kg) (Figure 4.9A). Among the horizons, mean adsorption decreased in the order: B horizons (767.2 ± 47.9 mg/kg) > E (678.2 ± 94.5 mg/kg) horizons > A (615.0 ± 80.6 mg/kg) horizons (Figure 4.9 B) however these differences were not statistically significant ($H (2) = 2.819$, $p = 0.244$). Among the vegetation covers, mean adsorption decreased in the order graminoid soils (767.6 ± 53.8 mg/kg) > forests soils (700.6 ± 74.9 mg/kg) > heather moorland soils (647.1 ± 87.5 mg/kg) (Figure 4.9 C), these differences were also not significant ($H (2) = 2.293$, $p = 0.318$).

Table 4.4. Measured sorption parameters for 20 UK upland mineral soils: including desorption (b) and sorption at the maximum concentration of added DOC (RE_{112}).

Soil Classification	**Site**	**Horizon**	**b** mg/kg	**RE_{112}** mg/kg
Humic gleysol	Coal Burn forest	Ah	195.2	783.9
	Coal Burn grassland	Ah	123.1	720.5
	Marsden	Bg	166.1	693.5
	Marsden	E	205.5	490.9
	Nidderdale HS7	Bg	210.8	850.1
	Nidderdale HS2	Bg	267.0	448.3
	Nidderdale HS 11	Bg	208.8	887.7
	Nidderdale HS 11	BCg	79.7	964.8
Humic podzols	Wye	Bs	201.1	904.5
	Wye	E	262.5	749.8
	Hafren	Bs	168.8	860.5
	Hafren	E	140.6	793.9
	Elslack	A	325.8	460.7
	Elslack	B	162.0	832.4
	Carleton	Bg	219.6	599.5
	Carleton	BCg	116.9	869.6
	Levisham	Ah	640.4	495.0
	Dalby	B	467.3	472.2
	Etherow	Bs	216.6	919.4
	Crowden	Bs	376.1	671.0

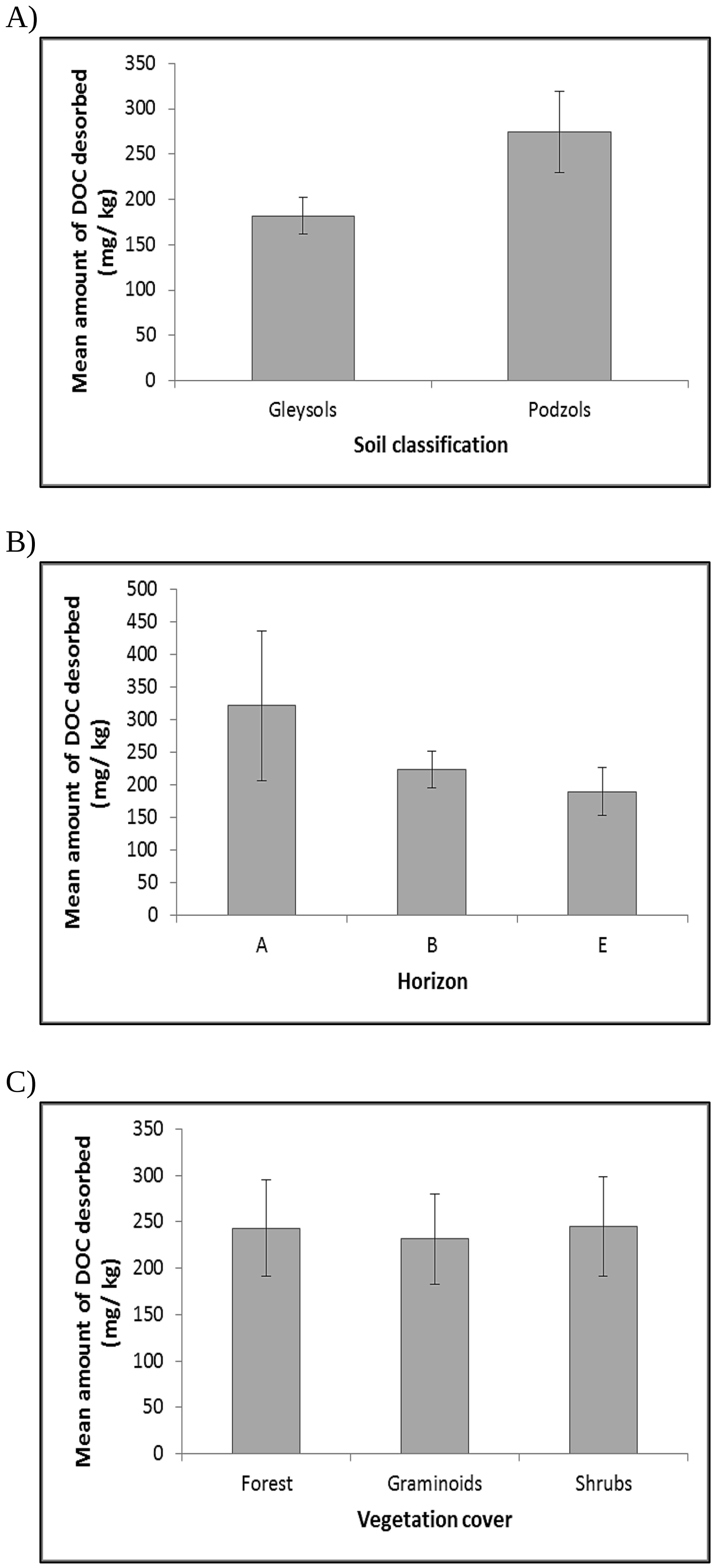


Figure 4.8. Comparison of mean DOC desorbed by mineral soils when DOC free solutions are added: A) between gleysols (n=8) and podzols (n =12), B) among soil horizons A (n=4), B (n=13), E (n=3) and C) among vegetation covers forest (n= 6), graminoids (n=10), shrubs (n=4). Error bars represent standard error of the mean.

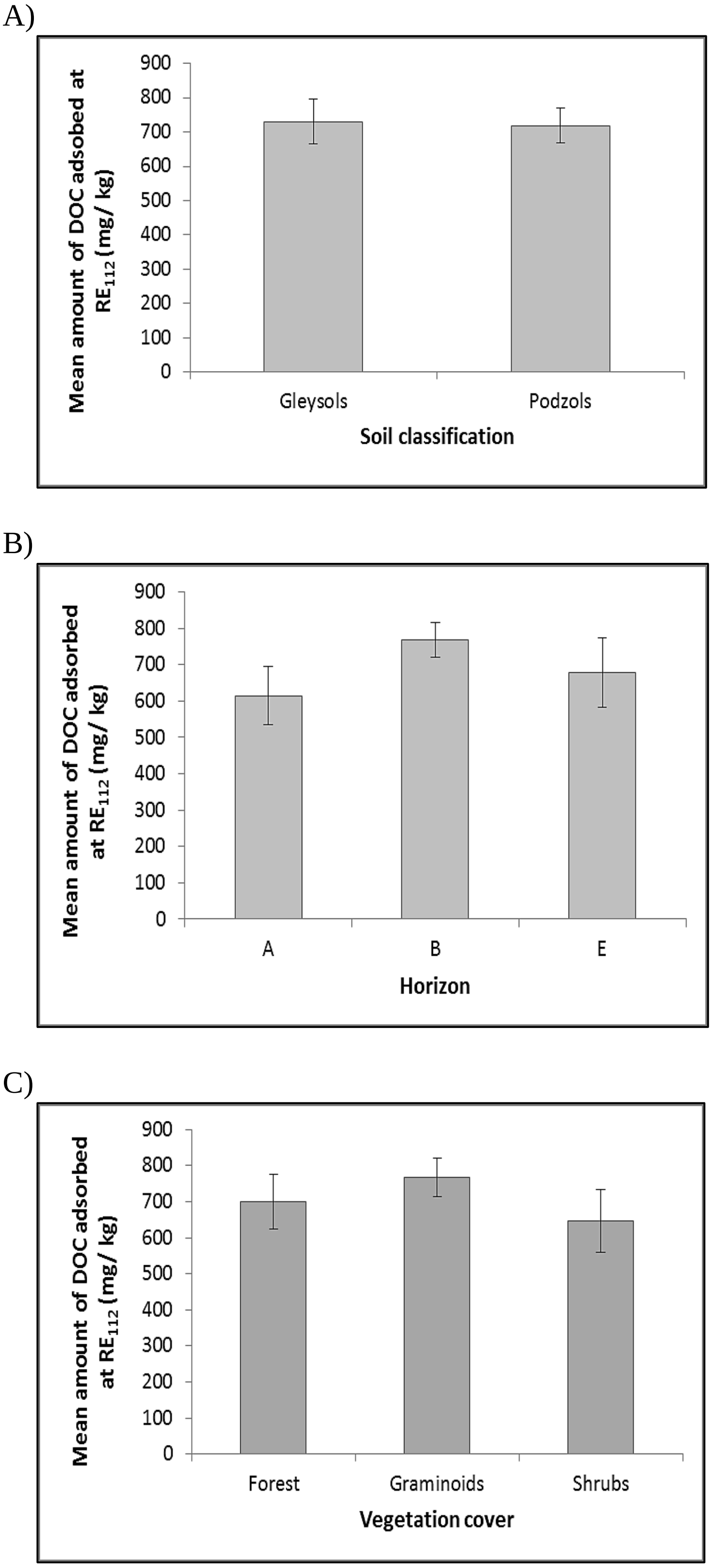


Figure 4.9. Comparison of average DOC adsorbed by mineral soils for 1126.7 mg/ kg of added carbon (the maximum of added carbon): A) between gleysols (n=8) and podzols (n =12), B) among soil horizons A (n=4), B (n=13), E (n=3) and C) among vegetation covers forest (n= 6), graminoids (n=10), shrubs (n=4). Error bars represent standard error of the mean.

4.3.3 Modelled sorption parameters

4.3.3.1 *Qmax*

A wide range of Q_{max} estimates was obtained, the lowest Q_{max} value was 835 mg/kg and this was for the B horizon soil sampled from Nidderdale HS2, while the highest Q_{max} estimate of 6003 mg/kg was measured for the E horizon soil sampled at Wye (Table 4.5). Mean Q_{max} values were higher for soils beneath graminoids (3947 ± 573 mg/kg) than for soils beneath forest (2421 ± 430 mg/kg) or shrubs (1868 ± 402 mg/kg). ANOVA showed that the differences among vegetation covers was statistically significant (F= 7.218, df= 2, p= 0.016), a Tukey's post hoc test revealed that the soils beneath graminoids had significantly (p = 0.046) higher Q_{max} estimates than soils beneath shrubs, while all other differences were not significant. Although the B horizons had higher Q_{max} values (mean = 3359 ± 465 mg/kg) than the E (mean = 3129 ± 1461 mg/kg) and A (mean = 2103 ± 376 mg/kg) horizons, the differences were not statistically significant (F= 3.179, df= 2, p= 0.096). Similarly the differences between the gleysols (mean = 3236 ± 628 mg/kg) and podzols (mean = 2965 ± 481 mg/kg) were not significant (F= 2.022, df= 1, p= 0.193).

Figures 4.10 to 4.13 show the sorption isotherms with fitted modified Langmuir curves for all soils. The predicted Langmuir curves (solid lines) fit well with the experimental data (diamond shaped points), EF values ranged from 0.69-0.96 (Table 4.5). The graphs also show the predicted Q_{max} values (dashed lines).

4.3.3.2 *Sorption Affinity (k)*

The sorption affinity (k) of the soils ranged between 0.001 kg/mg to 0.014 kg/mg with a mean k of 0.003 ± 0.00 kg/mg and a median k of 0.0025 kg/mg. There were no significant differences in the estimated k values when horizons (H (2) = 0.555, p = 0.758), vegetation covers (H (2) = 1.619, p = 0.445) or soil types (U = 33, p = 0.270) were compared using either the Mann Whitney test or the Kruskal Wallis test.

4.3.3.3 *Null point (Np)*

The null point ranged from 2 mg/kg to 782 mg/kg with a mean null point of 111.3 ± 40 mg/kg and a median of 39.5 mg/kg. There were no significant differences in the null point when horizons (H (2) = 2.029, p = 0.363), vegetation covers (H (2) = 0.480, p = 0.786) or soil types were compared (U = 43, p = 0.734).

Table 4.5. Sorption parameters derived from the modified Langmuir isotherm including the maximum adsorption capacity (Q_{max}), the sorption affinity (k), the null point (Np) and the model efficiency (EF).

Soil Classification	Site	Horizon	Q_{max} mg/kg	k kg/mg	Np mg/kg	EF
Humic gleysol	Coal Burn forest	Ah	2702	0.003	26.0	0.93
	Coal Burn grassland	Ah	2805	0.001	46.0	0.96
	Marsden	Bg	2848	0.001	61.9	0.91
	Marsden	E	1227	0.001	201.1	0.83
	Nidderdale HS7	Bg	5558	0.001	39.0	0.88
	Nidderdale HS2	Bg	835	0.003	157.0	0.80
	Nidderdale HS 11	Bg	5372	0.001	40.0	0.92
	Nidderdale HS 11	BCg	4543	0.010	2.0	0.91
Humic podzols	Wye	Bs	3791	0.006	9.0	0.88
	Wye	E	6003	0.002	22.9	0.84
	Hafren	Bs	3242	0.005	11.0	0.87
	Hafren	E	2159	0.004	17.0	0.88
	Elslack	A	1505	0.001	276.0	0.85
	Elslack	B	3853	0.014	3.0	0.93
	Carlton	Bg	1699	0.001	148.4	0.84
	Carlton	BCg	2718	0.003	15.0	0.90
	Levisham	Ah	1403	0.003	279.9	0.74
	Dalby	B	1065	0.001	782.0	0.69
	Etherow	Bs	5922	0.001	38.0	0.77
	Crowden	Bs	2220	0.004	51.0	0.91

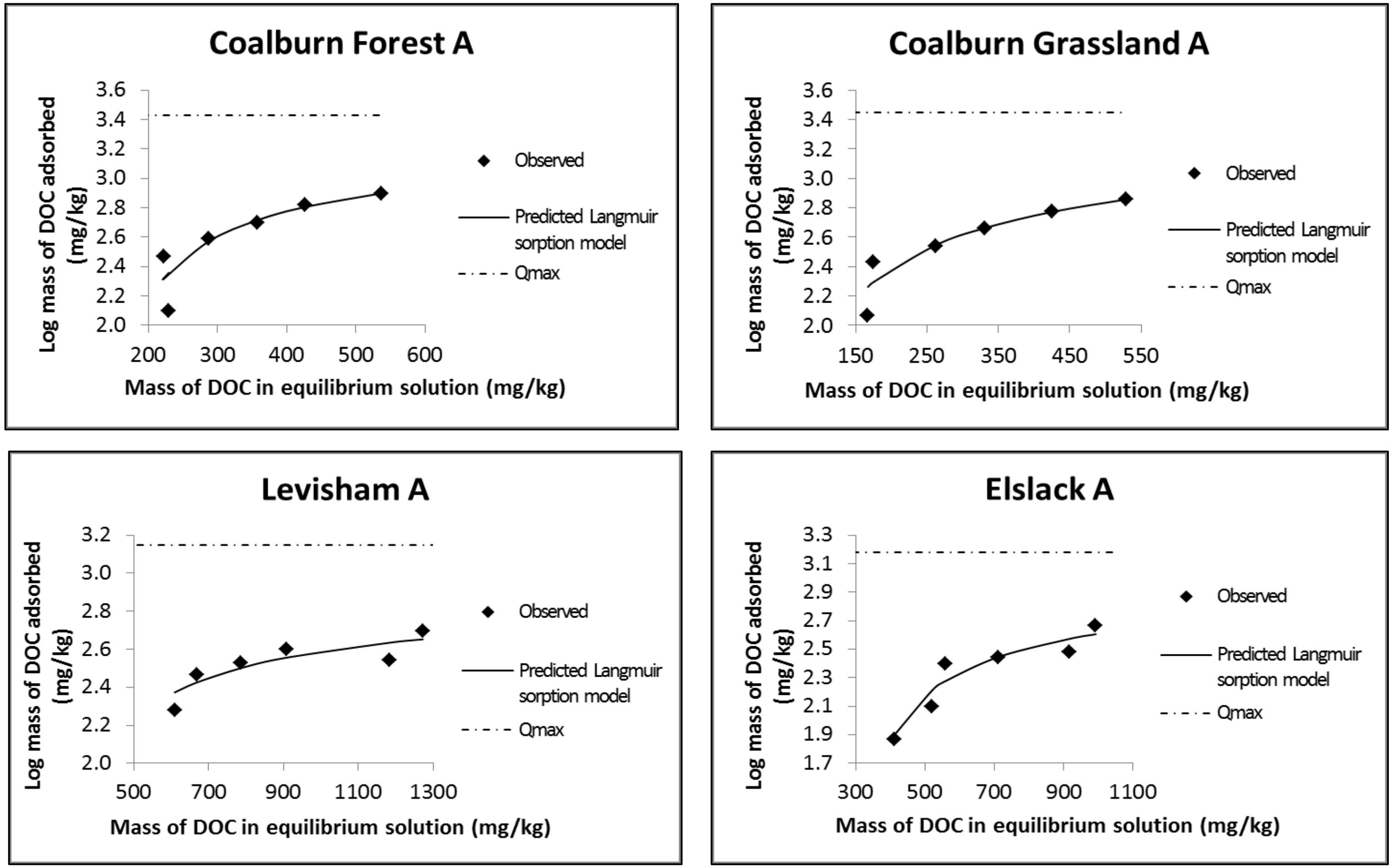
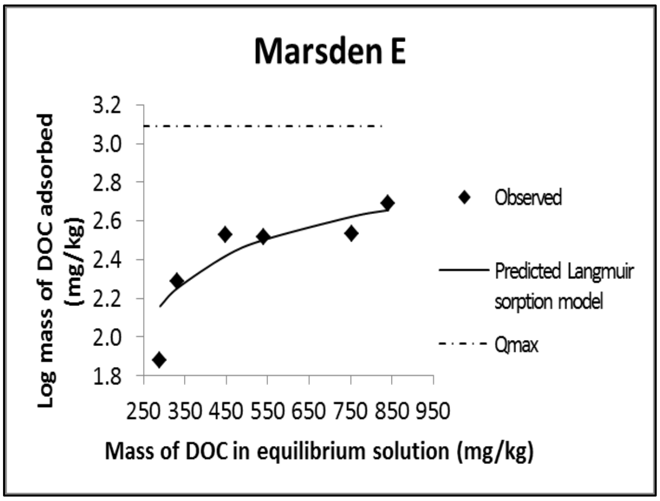
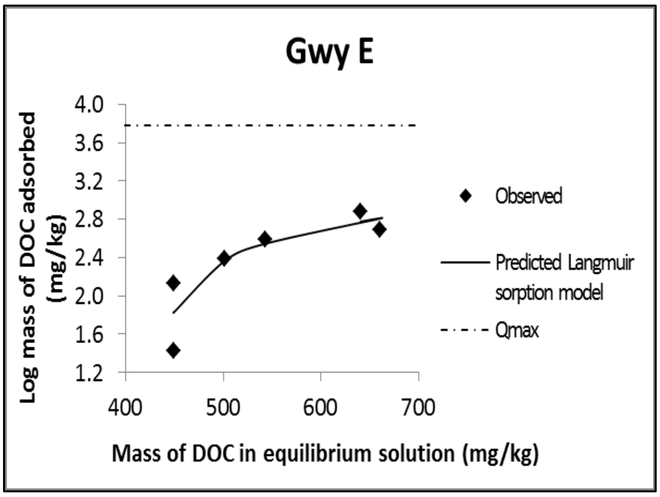


Figure 4.10 Langmuir sorption isotherms of dissolved organic carbon on A horizon soils





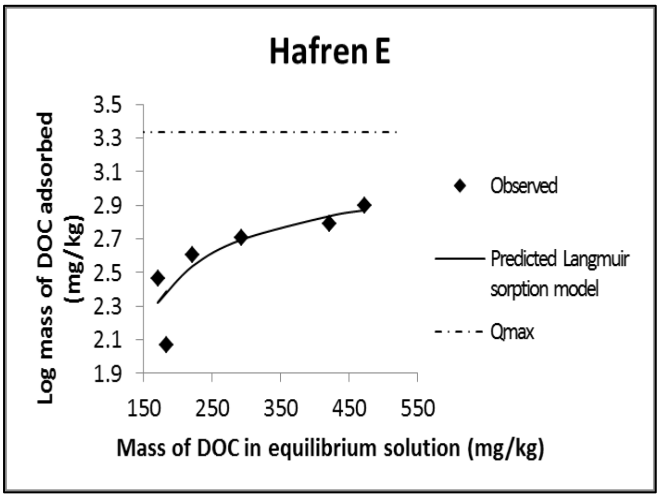


Figure 4.11 Langmuir sorption isotherms of dissolved organic carbon on E horizons mineral soils

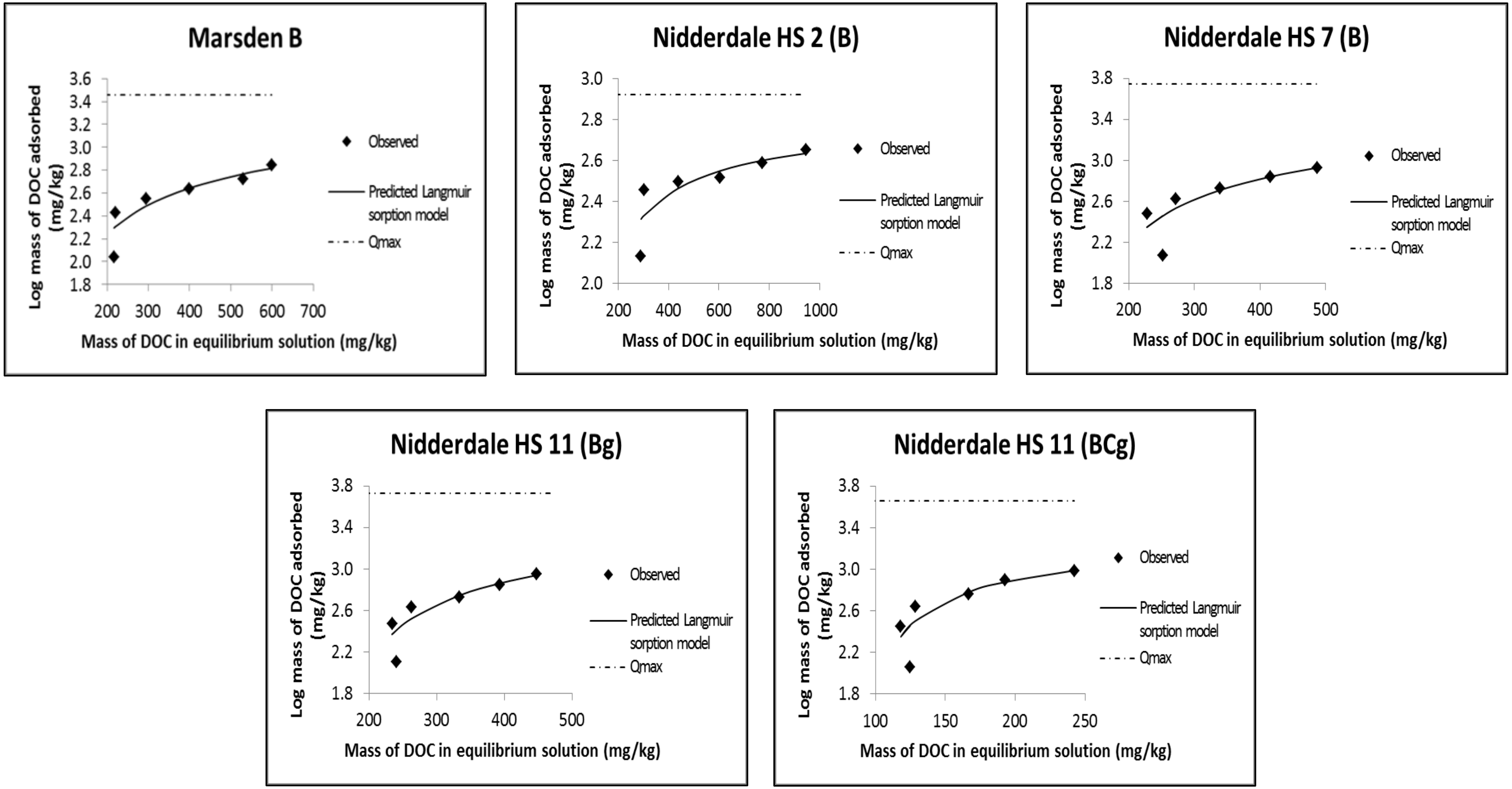


Figure 4.12. Langmuir sorption isotherms of dissolved organic carbon on B horizons of humic gleysols

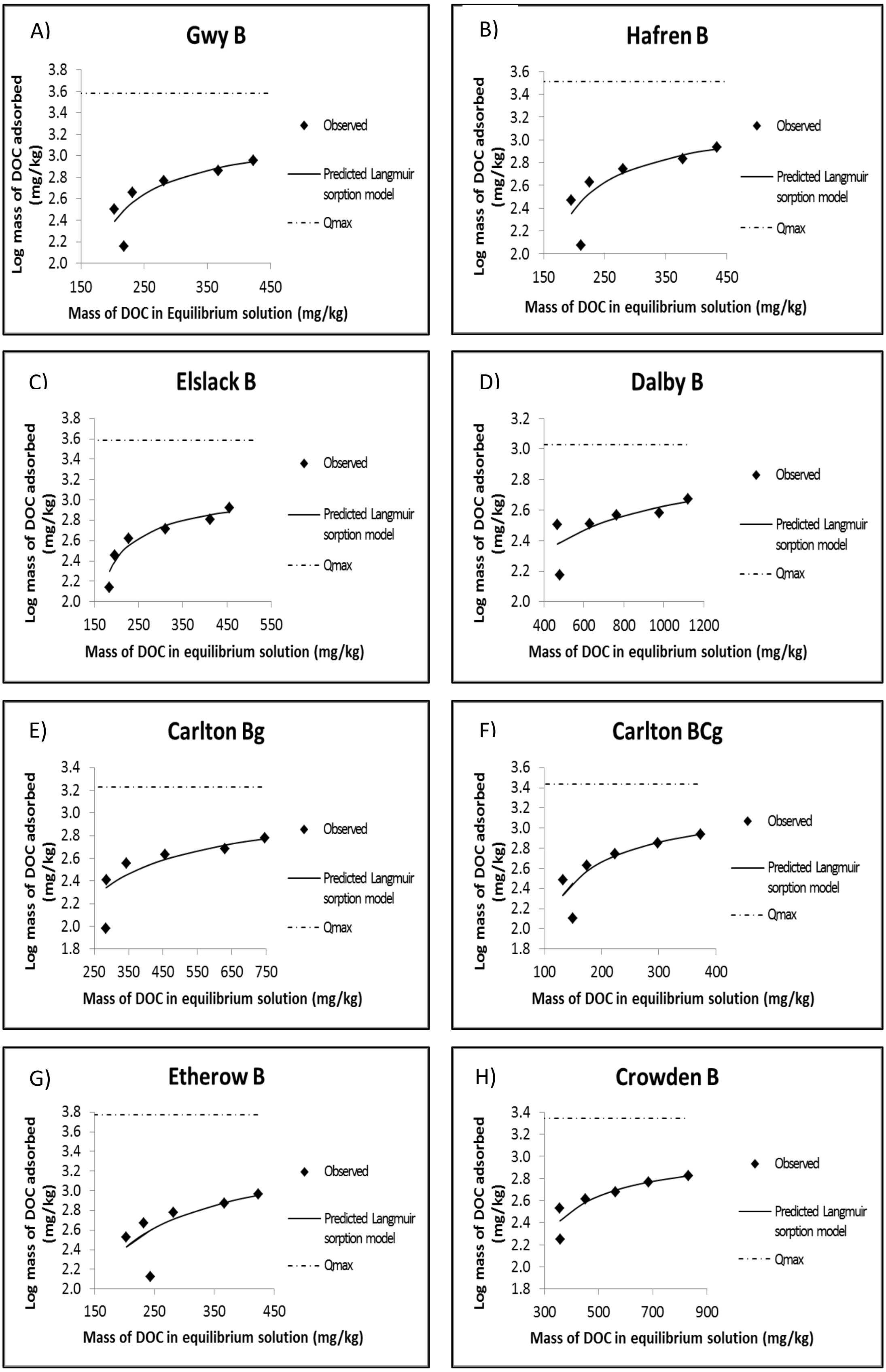


Figure 4.13 Langmuir sorption isotherms of dissolved organic carbon on B horizons of humic podzols.

4.3.4 Degree of carbon saturation of soils

The two measures of saturation, S_{BQ} and SI_{SOC}, showed differences between soils and between saturation measures in the degree of saturation of the 20 soils tested (Table 4.6). Based on the saturation estimates derived from the relationship b/Q_{max} (S_{BQ}) the least saturated soil was the BCg horizon of the gleysol sampled at the Nidderdale HS11, this had an S_{BQ} value of 1.76% (Table 4.6). The most saturated soil was the Ah horizon of the podzol sampled at Levisham, this had an S_{BQ} value of 45.6%. The mean S_{BQ} for all soils was 12.5 ± 3 %. Among the vegetation covers mean S_{BQ} values for the soils decreased in the order shrubs (16.4 ± 8 %) > forest (14.8 ± 6 %) > graminoids (10.2 ± 4 %), the differences among vegetation covers were not significant (H (2) = 3.522, p = 0.172). The A horizons had higher S_{BQ} values (mean = 19.7 ± 9) than the B horizons (mean = 11.1 ± 4 %) and the E horizons (mean = 9.2 ± 4 %) however the differences were not significant (H (2) = 1.519, p = 0.468). Similarly the difference between the gleysols (mean = 9.4 ± 4 %) and the podzols (mean = 14.5 ± 4 %) was not significant (U = 37, p = 0.427).

Based on the saturation index SI_{SOC} derived from the relationship $SOC/(Fe_o+Al_o)$, the least saturated soil was the Bs horizon sampled from the podzol at the Hafren, this had a SI_{SOC} of 0.56. Conversely the most saturated soils were the Bg horizon sampled at Nidderdale HS2 which had a SI_{SOC} of 27.48 and the B horizon at Dalby which had a SI_{SOC} of 27.45. Among the vegetation covers mean SI_{SOC} values for the soils decreased in the order shrubs (13.3 ± 7.7) > forest (10.8 ± 5.1) > graminoids (10.7 ± 3.3), the differences among vegetation covers were not significant (H (2) = 0.669, p = 0.716). The A horizons had higher SI_{SOC} values (mean = 21.0 ± 5.4) than the B horizons (mean = 9.7 ± 3) and the E (mean = 4.0 ± 1.4) however the differences were not significant (H (2) = 1.990, p = 0.370). Similarly the difference in SI_{SOC} between the gleysols (mean = 12.1 ± 4.5) and podzols (mean = 10.4± 3) was not significant (U = 39, p = 0.521).

While the two measures of saturation agreed that among vegetation covers the order of decreasing saturation is heather> forest > graminoids and among horizons the order is A > B >E, they differed in the degree of saturation between the two soil types. Using S_{BQ} the podzols were more saturated, while SI_{SOC} has shown the gleysols were more saturated.

Table 4.6. Comparison of the degree of saturation of upland mineral soils using the saturation estimates: i) S_{BQ} (the amount of DOC desorbed (b) as a percentage of the maximum amount of DOC that can be retained by the soils (Q_{max}) and ii) SI_{SOC} (the ratio of soil organic carbon to the total sum of the amorphous Fe and Al oxides of the soil).

Soil Classification	Site	Horizon	S_{BQ} (%)	SI_{SOC}
Humic gleysol	Coal Burn forest	Ah	7.22	4.89
	Coal Burn grassland	Ah	4.39	27.33
	Marsden	Bg	5.83	26.95
	Marsden	E	16.74	1.31
	Nidderdale HS7	Bg	3.79	1.30
	Nidderdale HS2	Bg	31.96	27.48
	Nidderdale HS 11	Bg	3.89	6.06
	Nidderdale HS 11	BCg	1.76	1.76
Humic podzols	Afon Gwy	Bs	5.31	0.93
	Afon Gwy	E	4.37	5.74
	Hafren	Bs	5.21	0.56
	Hafren	E	6.52	5.04
	Elslack	A	21.65	26.30
	Elslack	B	4.21	0.70
	Carlton	Bg	12.92	11.26
	Carlton	BCg	4.30	1.16
	Levisham	Ah	45.64	25.5
	Dalby	B	43.90	27.45
	Etherow	Bs	3.66	15.16
	Crowden	Bs	16.94	5.12

4.3.5 Controls on measured and modelled sorption parameters.

4.3.5.1 *Desorption*

The logarithm of the amount of DOC desorbed (log b) was negatively correlated to Al_o (r= -0.557, p= 0.012; Figure 4.14 A; Table 4.7) and clay content (r = -0.478, p= 0.033, Figure 4.14 B; Table 4.7). There was also a weak positive correlation between SI_{SOC} and log b (r = 0.461, p = 0.041; Figure 4.14C; Table 4.7). A stepwise linear regression showed that Al_o was the strongest predictor variable for desorption and that none of the other measured variables successfully improved the regression model.

4.3.6 Adsorption at RE_{112}

The transformed variable RE^2_{112} was most strongly correlated to Al_o (r= 0.862, p <0.001; Figure 4.15A; Table 4.7) and soil pH (r =0.801 p<0.001; Figure 4.15B; Table 4.7). This measured variable also showed moderate correlation with log Al_p (r= 0.771, p<0.001; Figure 4.15C), SI_{SOC} (r = -0.704, p=0.001; Figure 4.15D; Table 4.7), clay content (r = 0.573, p=0.008; Figure 4.15E; Table 4.7) and log Fe_o (r = 0.527, p = 0.017; Figure 4.15F; Table 4.7) and weak correlation with log Fe_d (r=0.480, p=0.032; Figure 4.15 G; Table 4.7). A stepwise linear regression showed that Al_o was the strongest predictor variable for RE^2_{112}, explaining 73% of the variation in RE^2_{112}, and that none of the other measured variables successfully improved the regression model (Table 4.8).

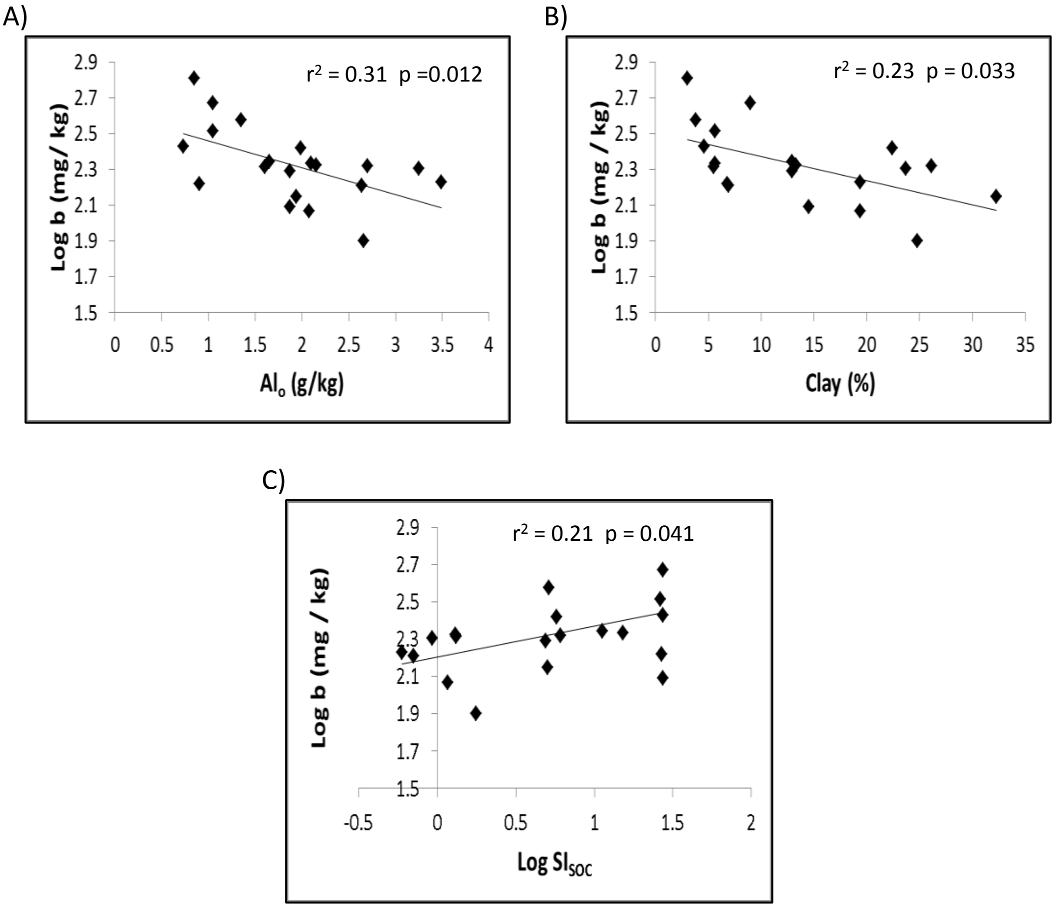


Figure 4.14. Relationships between the logarithm of the desorption term (b) and the most significant soil properties A) the amorphous aluminium oxides and hydroxides B) percentage clay content and C) log of the saturation index SI_{SOC}

Table 4.7 Correlation coefficients (r) between sorption characteristics and soil properties, * indicates the value is significant at the 0.05 level, ** indicates the value is significant at the 0.01 level. Variables include: pH; Al_o (oxalate extractable aluminium); ECEC (effective cation exchange capacity) ; SOC (soil organic carbon); Fe_o, Fe_p and Fe_d, acid oxalate, pyrophosphate, and citrate dithionite extractable oxides of iron; Al_p, and Al_d pyrophosphate and citrate dithionite extractable oxides of aluminium; b (desorption of pre-existing soil carbon), Q_{max} (maximum adsorption capacity); np (null point); RE^2_{112} (adsorption at the highest concentration of added DOC):; SI_{SOC} (saturation index); S_{BQ} (saturation estimate); and clay content.

	pH	Al_o	ECEC	Log SOC	Log Fe_o	Log Fe_p	Log Fe_d	Log Al_p	Log Al_d	Log b	Q_{max}	Log NP	RE^2_{112}	$k^{-0.5}$	Log SI_{SOC}	Log S_{BQ}	Clay
pH	1																
Al_o	0.796**	1															
ECEC	0.173	0.349	1														
Log SOC	-0.308	-0.421	-0.540*	1													
Log Fe_o	0.597**	0.627**	0.062	-0.271	1												
Log Fe_p	0.499*	0.546*	-0.041	-0.193	0.972**	1											
Log Fe_d	0.596**	0.597**	-0.092	-0.204	0.964**	0.955**	1										
Log Al_p	0.663**	0.928**	0.339	-0.280	0.440	0.401	0.415	1									
Log Al_d	0.503*	0.856**	0.161	-0.321	0.550*	0.539*	0.582**	0.872**	1								
Log b	-0.438	-0.551*	-0.060	0.404	-0.316	-0.192	-0.338	-0.350	-0.373	1							
Q_{max}	0.584**	0.625**	0.482*	-0.303	0.266	0.155	0.237	0.604**	0.492*	-0.328	1						
Log NP	-0.825**	-0.759**	-0.245	0.557*	-0.604**	-0.486*	-0.579**	-0.570**	-0.529*	0.726**	-0.591**	1					
RE^2_{112}	0.801**	0.864**	0.367	-0.424	0.527*	0.404	0.480*	0.771**	0.659**	-0.646**	0.791**	-0.861**	1				
$k^{-0.5}$	-0.619**	-0.365	0.012	0.373	-0.506*	-0.464*	-0.454*	-0.214	-0.156	0.233	-0.012	0.678**	-0.364	1			
Log SI_{SOC}	-0.651**	-0.784**	-0.348	0.685**	-0.856**	-0.793**	-0.794**	-0.609**	-0.686**	0.461*	-0.445*	0.756**	-0.704**	0.513*	1		
Log S_{BQ}	-0.656**	-0.737**	-0.330	0.396	-0.344	-0.209	-.348	-.629**	-.526*	0.798**	-0.742**	0.783**	-0.832**	0.187	0.527*	1	
Clay	0.630**	0.645**	0.509*	-0.412	0.219	0.095	0.209	0.576**	0.370	-0.478*	0.456*	-0.624**	0.573**	-0.362	-0.406	-0.604**	1

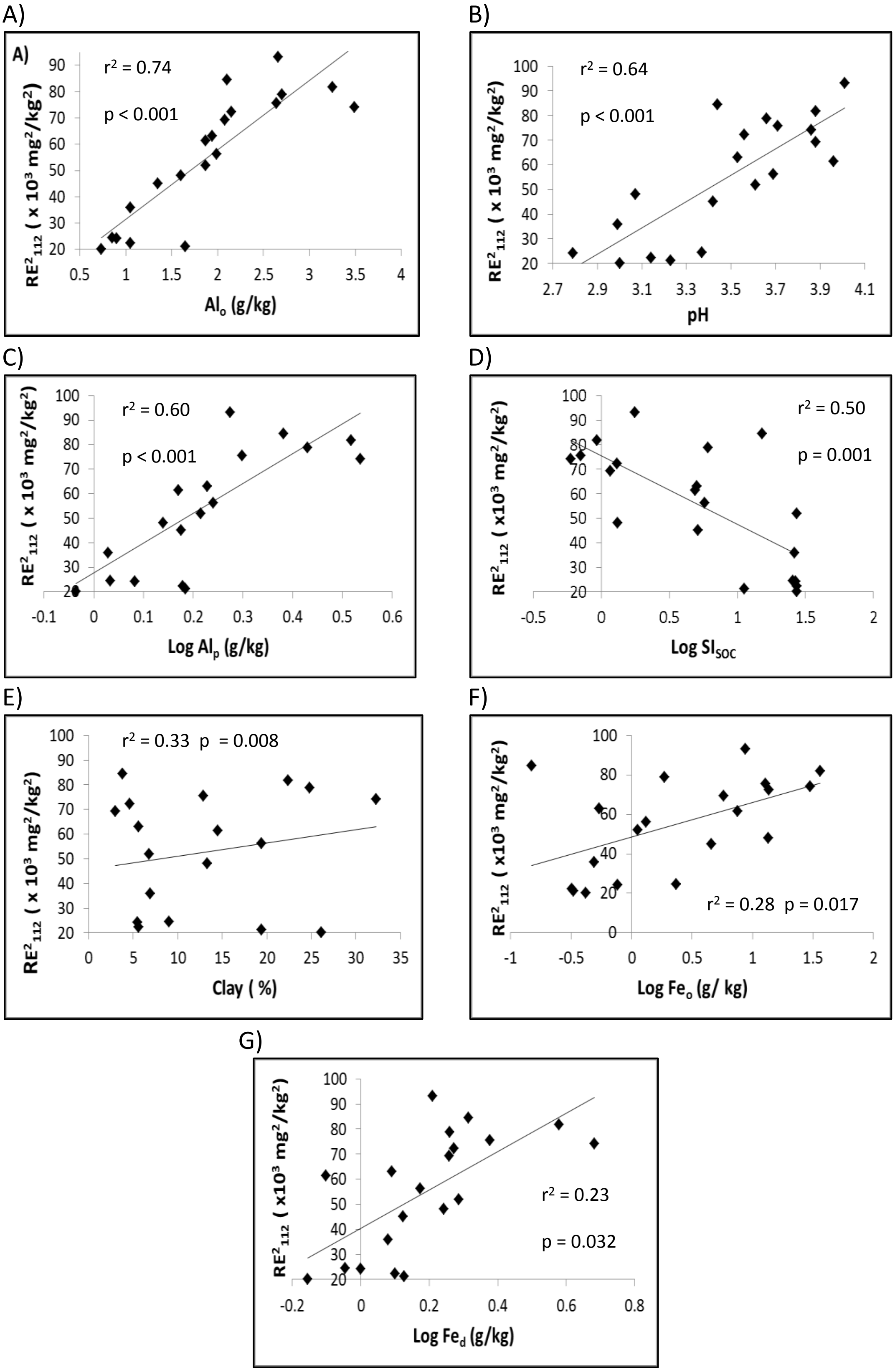


Figure 4.15 Relationship between sorption at the highest applied concentration RE_{112} and the most significant soil properties A) the amorphous aluminium oxides and hydroxides (Al_o) B) pH, C) organically bound Al (Al_p), D)Log of the saturation index SI_{SOC}, and E) percentage clay, F) amorophous iron oxides and hydroxides (Fe_o), G) crystalline and non-crystalline iron (Fe_d)

Table 4.8. Regression models showing key relationships between the sorption parameters: RE^2_{112}, desorption (log b) and soil properties as derived from stepwise multiple regression. Model 1: predictor variables entered were Al_o, carbon, pH, clay, ECEC and log Fe_o. Model 2: predictor variables entered were Al_o, % clay, pH, Fe_o, and soil carbon.

Model	Regression Equation	R^2	R^2_{adj}	F	p	Degrees of Freedom	
1	Log b = 2.605 – 0.148 Al_o	0.304	0.265	7.846	0.012	regression residual total	1 18 19
2	RE^2_{112} = 51926 + 263567 Al_o	0.746	0.732	32.137	<0.001	regression residual total	1 18 19

4.3.6.1 *Q_{max}*

Q_{max} was positively correlated to all forms of extractable aluminium (Table 4.7): Al_o (r = 0.625, p = 0.003; Figure 4.16A), log Al_p (r = 0.604, p = 0.005; Figure 4.16 B), log Al_d (r = 0.492, p = 0.027; Figure 4.16C). There was also a positive relationship between Q_{max} and clay content (r = 0.456, p = 0.044; Figure 4.16D), effective exchangeable cation capacity (ECEC) (r = 0.482, 0.031; Figure 4.16E) and pH (r = 0.584, p = 0.007; Figure 4.16F). Although the strongest single predictor variable was Al_o which accounted for 39 % of the variability in Q_{max}, stepwise multiple regression revealed that together pH and ECEC resulted in a regression model which accounted for a greater amount (49 %) of the variability in Q_{max} (Table 4.9). There was no significant correlation between Q_{max} and any of the extracted forms of Fe.

4.3.6.2 *Sorption affinity (k)*

The transformed variable for sorption affinity ($k^{-0.5}$) was most strongly correlated to soil pH with which it showed a negative relationship (r = -0.619, p = 0.004; Figure 4.17A; Table 4.7). This meant the sorption affinity k was positively related to pH since the value of $k^{-0.5}$ decreases when k increases. There were also moderate to weak negative correlations between $k^{-0.5}$ and the logarithm of the extractable forms of Fe: log Fe_o (r = -0.506, p=

0.023; Figure 4.17B; Table 4.7), log Fe_p (r = -0.464, p = 0.039; Table 4.7), log Fe_d (r=-0. 454, p = 0.044; Table 4.7). Therefore there was a positive relationship between k and the Fe content of the mineral soils.

4.3.6.3 ***Null point***

The null point was correlated to all measured soil properties with the exception of the ECEC (Table 4.7). There were strong negative correlations between the null point and pH (r = -0.825, p < 0.001; Figure 4.18A), and Al_o (r = -0.759, p = < 0.001; Figure 4.18B). It showed moderate negative correlations with clay content (r = - 0.624, p =0.003; Figure 4.18C), log Al_p (r = -0.570, p = 0.009; Figure 4.18D), log Al_d (r = -0.529, p = 0.016), log Fe_o (r = -0.604, p = 0.0005; Figure 4.18E), log Fe_p (r = -0.486, p = 0.030), log Fe_d (r = -0.579, p= 0.007; Figure 4.18F) and a positive relationship with SOC (r= 0.557, p =0.011).

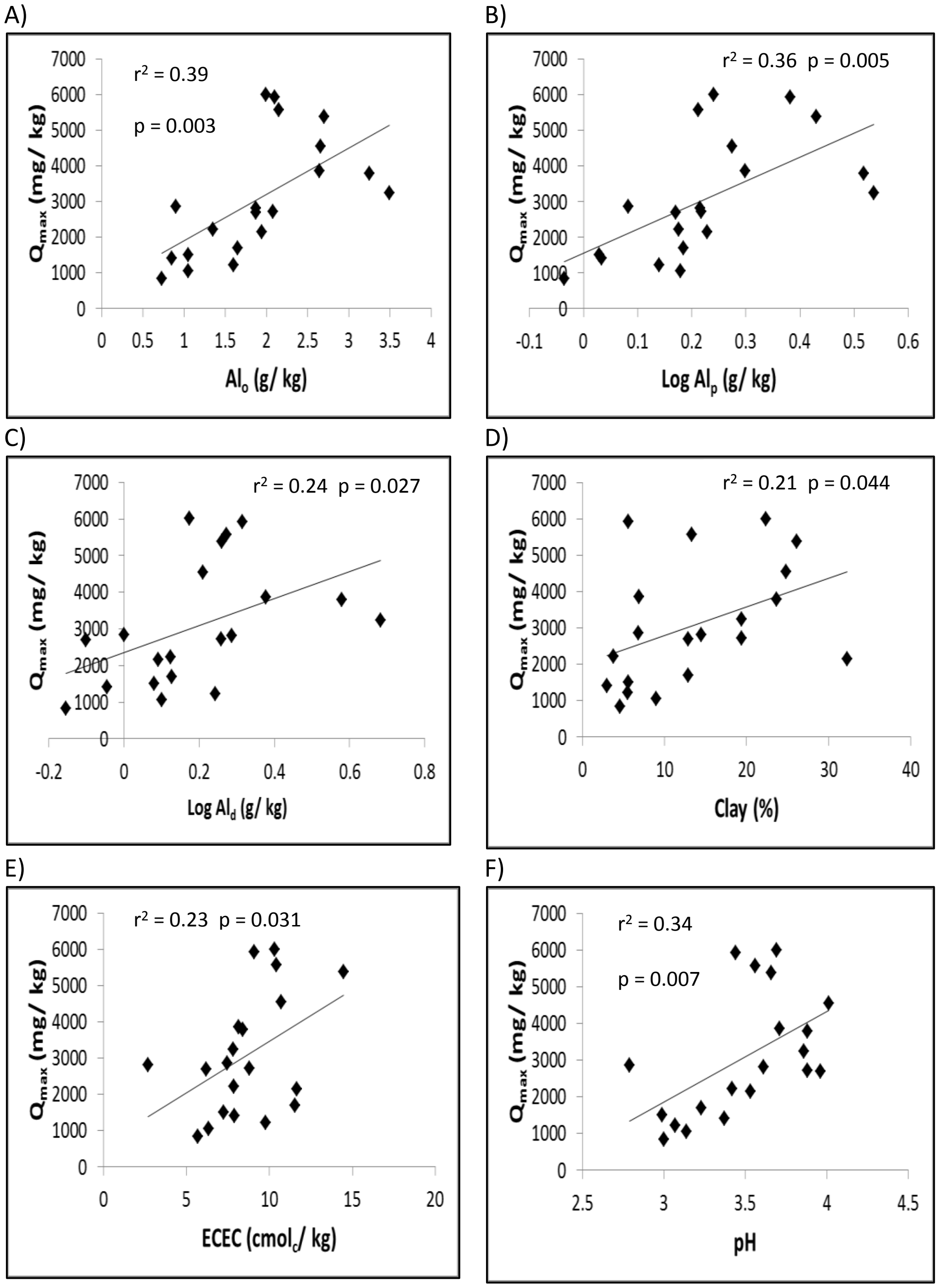
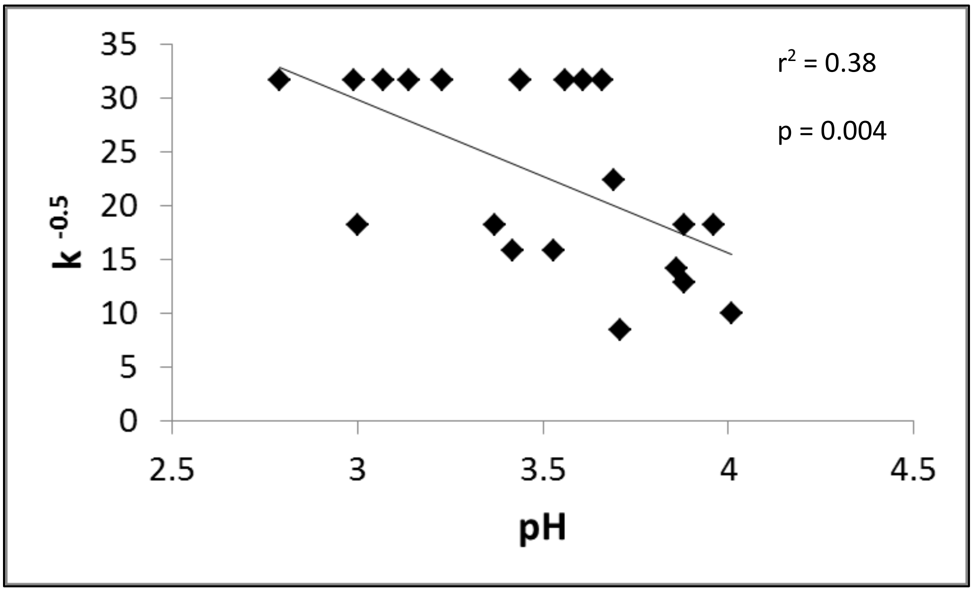


Figure 4.16. Relationships between the maximum adsorption capacity (Q_{max}) and the most significant soil properties A) the amorphous aluminium oxides and hydroxides (Al_o), B) the organically bound aluminium oxides and hydroxides (log Al_p), C) the amorphous and crystalline forms of aluminium oxides and hydroxides (log Al_d) D) percentage clay content E) effective cation exchange capacity (ECEC), F) pH

Table 4.9. Regression models showing key relationships between the modelled sorption parameters: maximum adsorption capacity (Q_{max}), sorption affinity ($k^{-0.5}$), null point (Np) and soil properties as derived from stepwise multiple regression.

Model	**Regression Equation**	**R^2**	**R^2_{adj}**	F	p	Degrees of Freedom	
1	$Q_{max} = 542.41 + 1335\ Al_o$	0.391	0.357	11.561	0.003	regression	1
						residual	18
						total	19
2	$Q_{max} = 2404.8\ pH + 256.5\ ECEC - 7531.4$	0.490	0.431	8.183	0.003	regression	2
						residual	17
						total	19
3	$k^{-0.5} = 75.076 - 14.963\ pH$	0.384	0.349	11.202	0.004	regression	1
						residual	18
						total	19
4	$\log Np = 6.965 - 1.532\ pH$	0.681	0.664	38.502	< 0.001	regression	1
						residual	18
						total	19
5	$\log Np = 5.042 - 1.341\ pH + 0.873\ \log\ SOC$	0.783	0.757	30.656	< 0.001	regression	2
						residual	17
						total	19

A)



B)

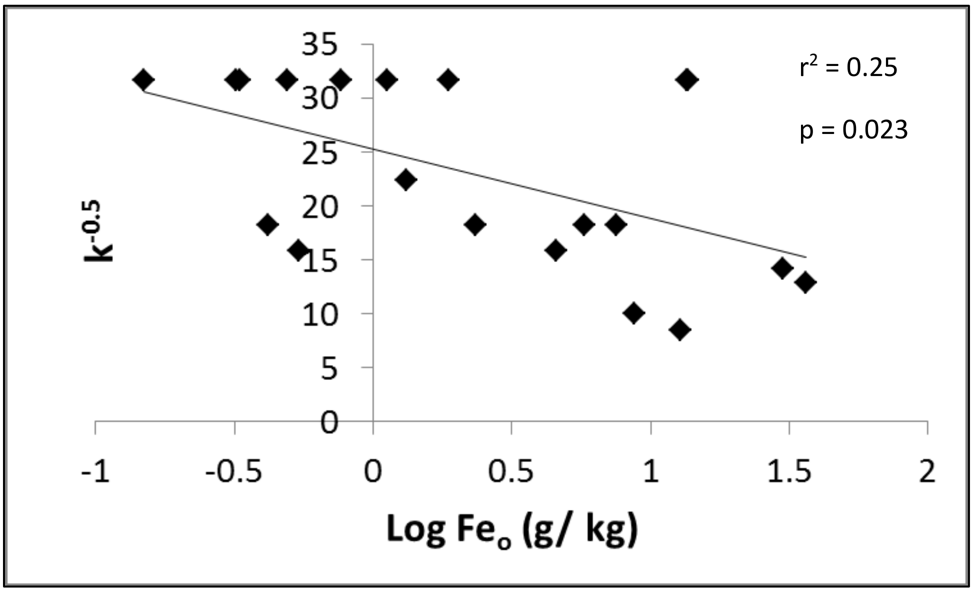


Figure 4.17. Relationships between the sorption affinity ($k^{-0.5}$) and the most significant soil properties A) pH and B) the amorphous iron oxides and hydroxides (Fe_o)

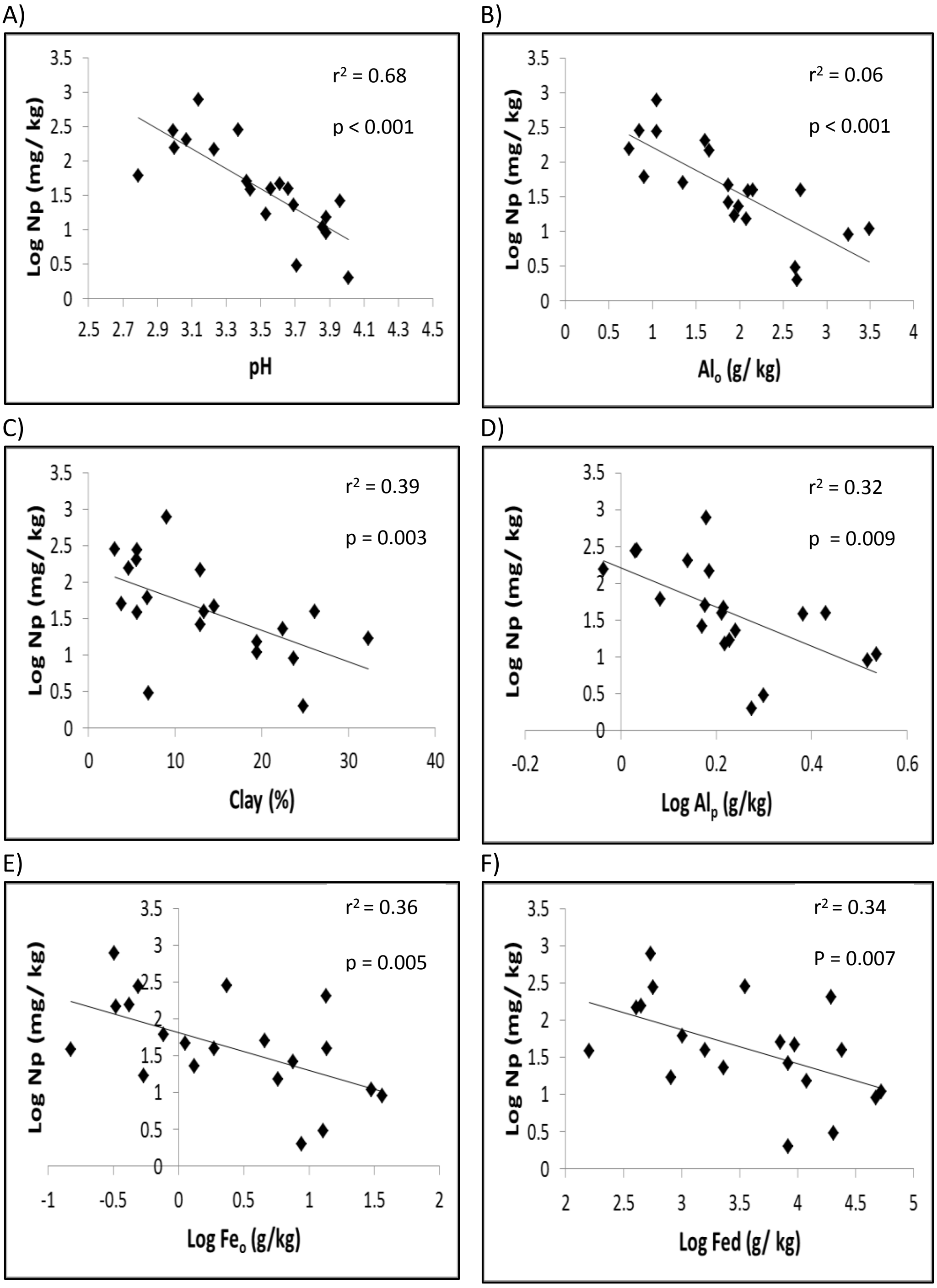


Figure 4.18. Relationships between the null point (Np) and the most significant soil properties A) pH, B)the amorphous aluminium oxides and hydroxides (Al_o), C) clay content D) the organically bound aluminium oxides and hydroxides (log Al_p), E) the amorphous iron oxides (Log Fe_o), F) the amorphous and crystalline forms of iron oxides and hydroxides (log Fe_d)

4.4 Discussion

The work described in this chapter shows that the UK upland mineral soils are not currently saturated and therefore do have capacity to retain more DOC. It was found that desorption in these soils was not controlled by the amount of existing total SOC but instead by the amorphous forms of Al and the extent to which these mineral sites are saturated with carbon as measured by SI_{SOC}. The dominant controls on the capacity to sorb DOC in these soils were the amount of amorphous Al_o and pH. These main findings and their implications for DOC dynamics within upland catchments will be discussed further in this section.

4.4.1 Desorption of DOC from UK upland mineral soils

An interesting and surprising finding of this study was the lack of a significant relationship between the amounts of soil organic carbon and desorption of carbon from the mineral soils. This is surprising because most previous studies show a significant positive relationship between the amount of soil organic carbon and DOC desorption from the mineral soil (Kaiser et al., 1996; Kothawala et al., 2009; Moore et al., 1992). Kaiser et al. (1996) and Moore et al., (1992) tested the correlations between DOC desorption and soil carbon using DOC desorption parameters derived from the linear initial mass isotherm while Kothawala et al., (2009) used desorption terms derived from the modified Langmuir isotherm. Kaiser et al. (1996) and Kothawala et al. (2009) both used solutions with no added DOC in their experiments, as in this study. However, rather than using the measured desorption of DOC, these researchers used desorption terms estimated from their isotherm models. The degree of agreement between the estimated desorption terms and the measured desorption was not given in the studies by (Kaiser et al., 1996; Kothawala et al., 2009). Therefore it is not possible to determine to what extent the relationships between the estimated desorption term and soil carbon is likely to represent what will occur with the actual mineral soil. However, the work described in this chapter used an experimentally observed desorption term to determine statistical relationships with soil properties as it was thought that this is more likely to be representative of what will occur with these soils. Conversely, the use of a DOC free solution in the desorption studies could also have led to the observed lack of a relationship between soil organic carbon and desorption which might not be seen in the field. The findings of chapter three of this thesis showed that there is an active exchange of DOC between the mineral soil and the soil solution. At low concentrations of added DOC, desorption of DOC from the mineral soil was seen for all three DOC sources (forest, heather, grass) (see section 3.4.2). Additionally, the SUVA of the DOC sourced from beneath heather and grass decreased following contact with the mineral soil indicating that the adsorption of DOC of high aromatic character led to the release of DOC of low aromaticity (see section 3.4.3). It is possible that by using a DOC free solution in the experiment described in this chapter, desorption of DOC from the soil may have been limited by the absence of DOC in solution to stimulate the active exchange with the mineral soil. Additionally, had different DOC sources been used in this experiment the relationship with soil carbon may have been different. In chapter three it was observed that DOC extracted from the organic horizons beneath forest, heather and grass differed in their null point values (see section 3.4.2). Considering that the null point is the point at which there is a switch from desorption to adsorption (Kerr and Eimers, 2012), the findings of chapter three suggest that the amount of desorption could vary by DOC source. Therefore, if desorption differs by DOC source then the relationship between desorption and soil carbon could also differ by DOC source.

While the amount of soil carbon was not significantly related to the desorption (log b), there was a significant correlation between (log SI_{SOC} and log b ($r = 0.461$, $p = 0.041$). Therefore the correlation between log b and log SI_{SOC} indicates that it is the amount of carbon bonded to mineral surfaces that determines DOC desorption rather than the total amount of soil carbon. Within the literature similar observations were made; Kindler et al. (2011) found that as SI_{SOC} (referred to as SOC/(Fe+Al_o) in the literature) increased the release of DOC increased. Penegrud et al. (2014) had similar findings using sorption parameters derived from the initial mass isotherm; they found that the desorption potential which they inferred from the null point increased as SI_{SOC} increased in the range 0.5-2.1. A high SI_{SOC} means that there is a lot of C present that may not be bound to Fe_o and Al_o; it could be bound to other sites within the soils or it could be particulate organic carbon. Kaiser and Zech (1999) in a study of the desorption of DOC from goethite, $Al(OH)_3$ and a B horizon soil found that most of the DOC bound to mineral surfaces was irreversibly bound. Therefore it could be inferred that carbon which is not in stable associations with mineral surfaces could potentially be desorbed, this could explain the positive relationship between SI_{SOC} and desorption.

Desorption of soil carbon was negatively related to Al_o ($r = -0.551$, $p = 0.012$) and to clay content ($r = -0.478$, $p = 0.033$). The finding of a negative relationship between these soil properties and desorption suggests that Al_o and clay are significant sites of adsorption and that SOC bound to these are not readily desorbed into DIW. This supports the prevailing theory within the literature that clays and the metal oxides and hydroxides are important in the retention of DOC to mineral soil surfaces (Gu et al., 1994; Guggenberger and Zech, 1992; Kahle et al., 2003; Kahle et al., 2004; Kaiser et al., 2002; Kaiser and Guggenberger, 2000; Kothawala et al., 2009; Mayes et al., 2012). However, the strong negative relationship between desorption and Al_o is also indicating that in these UK upland mineral soils the amorphous oxides of Al have the most stabilizing effect out of all the possible sorptive surfaces for DOC. This is in contrast to findings by Mikutta et al. (2006) who demonstrated that the Fe oxides and hydroxides were better at carbon protection after examining twelve acid subsoils collected in neo-tropical and temperate forest.

4.4.2 Adsorption of DOC to mineral soils

4.4.2.1 *The maximum sorption capacity of Upland soils*

This study has shown that the maximum sorption capacity of these soils varies significantly (p= 0.016) with the vegetation cover with soil collected from beneath graminoids having a greater potential to sorb carbon than soils beneath shrubs and forest. This finding could be due to preferential sorption for the DOC substrate used in these experiments. In this study the DOC was extracted from peat beneath heather. The litter of heather is known to be comprised in part of syringyl lignin (Hetherington and Anderson, 1998), the monomeric precursors of this syringyl lignin include sinapyl alcohol and sinapic acid (Gleason and Chollet, 2012). A study by Jagadamma et al. (2012) which looked at the sorption of five model DOC constituents (glucose, L-alanine, salicylic acid, sinapyl alcohol and oxalic acid) to three USA soil orders (Mollisols, Ultisols and Alfisols) found that Mollisols which are grassland soils showed a higher sorption of sinapyl alcohol and oxalic acid than the other soil orders tested. Lehmann and Cheng (1988) also observed greater sorption of sinapic acid in grassland soils when compared to forest soils. Therefore, the greater Q_{max} seen for soils sampled beneath graminoids may be due to the preferential sorption of the syringyl lignin monomers of heather. The exact mechanism for this preferential sorption is unknown and does not appear to be represented by the soil properties that were measured in this study as indicated by a lack of a significant effect of vegetation type on parameters thought to be indicative of sorption sites. Furthermore, the finding in chapter three in which the mineral soil sampled beneath grassland at Coalburn in Kielder forest showed only desorption in the experimental range 5-49 mg/L of added heather DOC, seems contradictory to the theory that graminoid soils are showing a preference for the syringyl lignin monomers of heather. However, mineral soil sourced from beneath grassland at Coalburn in Kielder forest was also used in the experiment described in this chapter and net adsorption was seen across the experimental range (16-112.9 mg/L). The difference in sorption behaviour of the Coalburn grassland mineral soil between the two studies could be reflective of the pre-treatment process that was used in the experiment described in chapter three. The pre-treatment of the mineral soil used in chapter three with sodium hypochlorite might have altered some of the sorption sites on the mineral soil.

Interestingly there were no statistically significant differences in Q_{max} estimates across soil types or soil horizons. It was surprising to find that there were no significant differences in Q_{max} values across the three horizons tested. Especially since the strongest predictor of Q_{max} was Al_o and it was observed that the Al_o content of the B horizons was significantly higher than that of the E horizons ($p = 0.043$) and the A horizons ($p = 0.007$). It might be expected that the B horizons as a group would be able to retain higher amounts of DOC and therefore have higher Q_{max} values. The lack of a difference in Q_{max} values by horizon type might be due to the effects of sorption to other surfaces within the mineral soil. For example, clay content was found to have a significant linear relationship with Q_{max} ($r = 0.456$, $p = 0.044$) and although it could not successfully be incorporated into a regression model with Al_o or any of the other parameters, in a regression model on its own it accounted for 20.8% of the variability in Q_{max}. This suggests that crystalline clay minerals could also be contributing to sorption, as was suggested by Kaiser and Zech (1999) for goethite. However in these experiments no relationship was observed between Q_{max} and the crystalline forms of Fe (included in the dithionite extractable Fe). It is therefore not clear why clay content may be a useful predictor of Q_{max}. Among the three horizons tested, clay content was higher in the E horizons (median = 23.2), followed by the B horizons (median = 12.6) then the A horizons (median = 9.3). It is possible sorption to clay surfaces other than Al_o counterbalances the effects of the reduced sorption to Al_o in these horizons. Alternatively, the lack of a significant difference in Q_{max} by horizon could be due to the effects of pH on Q_{max}. There was a strong positive relationship between pH and Q_{max} ($r = 0.584$, $p = 0.007$, Figure 4.16F). The soil horizons used in this study showed no significant differences in pH. Therefore it is likely that although the soil horizons differ in their Al_o content, the similarities in pH counterbalance the potential effect of Al_o on Q_{max}.

The finding that Al_o is the strongest predictor of Q_{max} is both consistent and contradictory with previous studies. Several studies show a correlation between aluminium oxides and oxyhydroxides and the ability of soils to adsorb DOC (Kothawala et al., 2009; Moore et al., 1992; Vandenbruwane et al., 2007), however in addition to Al they often also show a strong relationship with Fe oxides and oxyhydroxides. The Fe_o contents of the soils studied here (0.42 – 36.2 g/kg) were much larger than the Fe_o contents of the soils studied by Kothawala et al. (2009) (0.0002 – 0.0263 g/kg; Table 4.10) and Vandenbruwane et al. (2007)

(0.111– 2.32 g/kg; Table 4.10). The differences in the Fe_o contents could explain why a relationship was seen in the studies by (Kothawala, 2009) and (Vandenbruwane et al., 2007) but not in this current study. The DOC concentrations used in this study (Table 4.11) were similar to those in the studies by (Kothawala, 2009) and (Vandenbruwane et al., 2007) however the lower Fe_o content of their soils may have been a limiting factor in the sorption of DOC in their soils. Therefore a significant relationship was observed between Fe_o and Qmax as Fe_o increased. However in this study with the large Fe_o content of the soils and at the DOC concentrations used, Fe_o may not have been a limiting factor and so sorption to the soils would not have changed proportionally to the Fe_o content. Thus no relationship was observed between Fe and Q_{max}.

Conversely, the lack of a relationship with Fe could be due to most of the Fe sorption sites in these soils being already saturated with carbon, and therefore further sorption to these sites would be limited. Q_{max} is a term derived based on data obtained in the batch sorption experiments. In these experiments sorption to the soil will occur where there are available sorption sites, if the iron oxide sites are mostly saturated prior to conducting the sorption experiments then sorption at these sites will be limited. Therefore a significant relationship between maximum sorption capacity and Fe may not be observed.

Table 4.10. Comparison of soil properties of the mineral soils used in this study with studies in the literature which used the Langmuir isotherm to model adsorption. Properties listed include soil pH, soil organic carbon (SOC), percentage clay, oxalate extractable iron (Fe_o), pyrophosphate extractable iron (Fe_p), dithionite extractable iron (Fe_d), oxalate extractable aluminium (Al_o), pyrophosphate extractable aluminium (Al_p), dithionite extractable aluminium (Al_d). ND = No Data.

Reference	pH	SOC (g/kg)	Clay %	Fe_o (g/kg)	Fe_p (g/kg)	Fe_d (g/kg)	Al_o (g/kg)	Al_p (g/kg)	Al_d (g/kg)
(Kothawala et al., 2009)	3.4 - 7.6	2.9 ± 8.8 – 70.4 ± 6.2	4.25 -38.4	0.0002 – 0.0263	0.0001 – 0.0189	0.0004 – 0.0335	0.0002 – 0.0379	0.0001 – 0.0164	ND
(Mayes et al., 2012)	3.3 - 8.2	0.212 -20.1	0.9 – 67.4	ND	ND	1 -51	ND	ND	ND
(Vandenbruwane et al., 2007)	ND	0.46 ± 0.02 – 13.9 ± 0.1	0.1 – 1.3	0.111 ± 0.001 – 2.32 ± 0.14	ND	ND	0.0958 ± 0.0091 – 4.58 ± 0.08	ND	ND
This study	2.8 - 4	9.1-82	3 – 32.3	0.42 – 36.2	0.42-20.8	0.45 – 47.46	0.73 – 3.49	0.92 – 3.44	0.7 – 4.81

Table 4.11. Comparison of sorption parameters of the mineral soils used in this study with those in the literature which used the Langmuir isotherm to model adsorption. Sorption parameters include the maximum adsorption capacity (Q_{max}), the sorption affinity (k), the desorption term (b) and the null point (Np). ND = No data.

Reference	Concentration of DOC used (mg/kg)	Q_{max} (mg/kg)	k	b (mg/kg)	Np (mg/kg)
(Kothawala et al., 2009)	0 – 1200	60 - 5500	0.03 ± 0.01 – 0.43 ± 0.29	4 - 256	12 - 875
(Mayes et al., 2012)	0-6000	111 ± 33 – 6554 ± 2288	0. 004 ± 0.003 - 0.307 ± 0.119	ND	ND
(Vandenbruwane et al., 2007)	0 - 1000	374.94 – 2600.92	0.32 x 10^{-3} – 57.88 x 10^{-3}	41.77 - 623.12	2.28 – 156.61
This study	0- 1129	835 - 6002	0.001 – 0.014	79.74 – 640.36	0-782

4.4.2.2 *The null point*

In this study the best single predictor of the null point was soil pH which accounted for 68% of the variability in the null point. The incorporation of the log soil carbon into a multiple regression with the pH could explain a greater amount (78%) of variability in the null point. The findings here differ from the literature; most studies which looked at the soil properties that control null points of mineral soils report linear regressions where the null point was best predicted by the positive effects of poorly crystalline oxides of Al and Fe and the negative effects of the soil carbon (Kothawala et al., 2009; Moore et al., 1992). Considering that the null point is a measure of the soil solution DOC concentration at which adsorption and soil desorption are in equilibrium (Kerr and Eimers, 2012; Kothawala et al., 2009), then it makes sense that the null point should be controlled by the oxides of Fe and Al (which are the potential binding sites) and the soil carbon (which is the potential source of DOC for desorption). While this study does show negative correlation between log Np and Al_o ($r = -0.759$, $p < 0.001$), and log Fe_o ($r = -0.604$, $p = 0.005$), pH was more strongly correlated to log Np ($r = -0.825$, $p = < 0.001$). The finding that pH is the most significant predictor variable could be due to sorption of DOC to mineral surfaces being a pH dependent process (Kennedy et al., 1996). In several studies recent increases in DOC export to surface waters have been attributed to an increased solubility of DOC due to pH increases in catchment soils (Ekström et al., 2011; Evans et al., 2012; Monteith et al., 2007; Sawicka et al., 2016). At lower pHs the mineral surface is protonated and has a positive charge which favours the attraction and sorption of the negatively charged organic ions of DOC to the mineral surface. As the pH increases however the mineral surfaces become deprotonated resulting in a net negative charge and the repulsion of the organic anions of DOC (Jardine et al., 1989). However, the soils in this study were all acidic and did not support the theory of increasing DOC desorption/less adsorption with increasing pH. Instead it was observed that adsorption increased with increasing soil pH towards a maximum of pH 4. It is likely that the pH control on sorption within these soils centres around a pH optimum (4-4.5) as observed by Jardine et al. (1989) and Kennedy et al. (1996). As pHs move away from the optimum less adsorption is seen (Jardine et al., 1989; Kennedy et al., 1996). Considering that the null point is a measure of equilibrium between adsorption and desorption if adsorption is controlled by pH then the null point equilibrium would be sensitive to pH changes.

A wide range of null points was observed, 2 mg/kg to 782 mg/kg however no significant differences were found when horizons, vegetation cover or soil types were compared. This is consistent with findings of Kothawala et al. (2009) who studied DOC sorption in 52

Canadian mineral soils and found no relationship between the null point and soil horizon. However it contradicts the findings by Moore et al. (1992) who found a significant relationship between the null point and soil horizon for the 48 Canadian mineral soils they studied. The differences in the three studies are most likely due to the method of derivation of the null point. In the study described in this chapter as well as the work of Kothawala et al. (2009) the modified Langmuir isotherm was used to estimate the null points; however Moore et al. (1992) used the linear initial mass isotherm to estimate their soils' null points.

4.4.2.3 *Sorption Affinity (k)*

The sorption affinity was positively correlated to the soil pH. This was contradictory to the findings of Mayes et al. (2012) who in a similar study using American soils, found a negative relationship between pH and k. However, the positive relationship observed here is likely due to the fact that the pHs of the soils tested were below 4 (range was 2.8 -4.0). Research has shown an optimum DOC sorption pH of 4- 4.5, above and below which sorption decreases (Jardine et al., 1989; Kennedy et al., 1996). Therefore, since the soils tested here had a pH of 4 or below, the sorption affinity increased as the pH increased towards the optimum. Conversely, in studies which incorporated soils with pHs above the optimum such as the work of Mayes et al. (2012), the sorption affinity decreased with increasing pH.

4.4.3 Are UK Upland soils saturated?

The observation of adsorption across the experimental range of concentrations for all soils tested indicates that these soils still have the capacity to adsorb DOC and therefore are not currently saturated. However, using the measures of saturation described in the literature it is not possible to feasibly determine how close these soils are to becoming saturated.

In this study two measures of carbon saturation were used and they gave differing results on the degree of saturation of these upland soils. Using S_{BQ} (range was 1.76 % to 45.64%), it was found that these mineral soils are currently not saturated and that they still have the capacity to retain large amounts of DOC. S_{BQ} is derived from the ratio b/Q_{max} which uses the desorption term derived from the modified Langmuir model as a measure of the amount of initially adsorbed DOC (Vandenbruwane et al., 2007). However, as shown by Kaiser and Zech (1999) much of the DOC sorbed to mineral surfaces may be irreversibly bound. Kaiser and Zech (1999) studied the adsorption and desorption of DOC on goethite, amorphous Al $(OH)_3$ and a B horizon subsoil by first conducting adsorption experiments with varying concentrations of DOC extracted from O-horizon soil beneath a forest. This was followed by desorption experiments using solutions of differing pHs and ionic strengths, where they found that very little DOC was desorbed especially under solution conditions similar to those used in the sorption experiments (Kaiser and Zech, 1999). Therefore, the desorption term only accounts for the DOC which is readily desorbed and so to use it as a measure of the initially adsorbed DOC in determining the extent to which soils are saturated may result in the underestimation of saturation.

Using SI_{SOC} which ranged from 0.56 to 27.48, some of these soils appear to be over saturated with organic carbon. SI_{SOC} uses the ratio of $SOC/(Fe_o+Al_o)$ as an indicator of the saturation of the available adsorption sites in the soils (Kindler et al., 2011; Pengerud et al., 2014). However, SOC not only includes DOC sorbed to Al and Fe oxides but also includes carbon bound to other soil components and particulate organic matter; this therefore leads to an overestimation of saturation of the Al_o binding sites. Although this term overestimates the saturation of the DOC binding sites it is still very useful as an indicator of saturation for making comparisons of adsorption and desorption potential among different soils. Kindler et al. (2011) found that as the ratio of $SOC/(Fe_o+Al_o)$ increased as the experimental adsorption of DOC to subsoil decreased and the release of DOC increased. Pengerud et al. (2014) had a similar finding using sorption parameters derived from the initial mass isotherm, they found that the sorption affinity of the soil for DOC decreased with increasing $SOC/(Fe_o+Al_o)$ while the desorption potential which they inferred from the null point increased with increasing $SOC/(Fe_o+Al_o)$. In this study SI_{SOC} was also correlated with desorption (b) ($r = 0.461$, $p = 0.041$; see section 4.4.1) and Q_{max} ($r = -0.445$, $p < 0.05$)

4.4.4 Experimental limitations

One limitation of this study is that soils typically do not meet the criteria for using the Langmuir isotherm for describing adsorption. Langmuir assumes that the sorbent has a fixed number of identical sites where adsorption can occur, that adsorption is reversible and that there is no interaction between adsorbate molecules (Sparks, 2003). However, soil is a heterogeneous surface with multiple differing sites for adsorption of DOC and as shown by Kaiser and Zech (1999) some of the DOC adsorbed is irreversibly bound. The Langmuir isotherm was used in this study and in other studies (Jardine et al., 2006; Lilienfein et al., 2004; Mayes et al., 2012; Vandenbruwane et al., 2007) due to its ability to estimate the maximum sorption capacity of sorbents. Comparison of the measured sorption term RE_{112} and the Langmuir estimated Q_{max} shows the impact not meeting the underlying assumptions of the isotherm can have. Although RE_{112} and Q_{max} both indicate that amorphous oxides of Al and soil pH are the dominant controls on DOC sorption within these soils, they differ on the significance of the role of Fe in DOC sorption to these soils. The results of this chapter indicated there was no correlation between Q_{max} and the amount of Fe in these soils. However, the measured parameter RE_{112} shows a moderate positive correlation to the amorphous forms of Fe, this indicates that Fe does exert a control on the sorption of DOC in these soils. Therefore the maximum adsorption capacity derived from the Langmuir isotherm may not always reflect the true capacity of soils to retain DOC. The differences between the estimated sorption parameters and the measured sorption parameters stresses that the interpretation of the sorption parameters derived from the Langmuir isotherm should be approached with some caution. Although the Langmuir isotherm does not allow for accurate quantification of the soils' maximum sorption capacities, it does still allow for comparison of the sorption behaviour between soils (Figure 4.19).

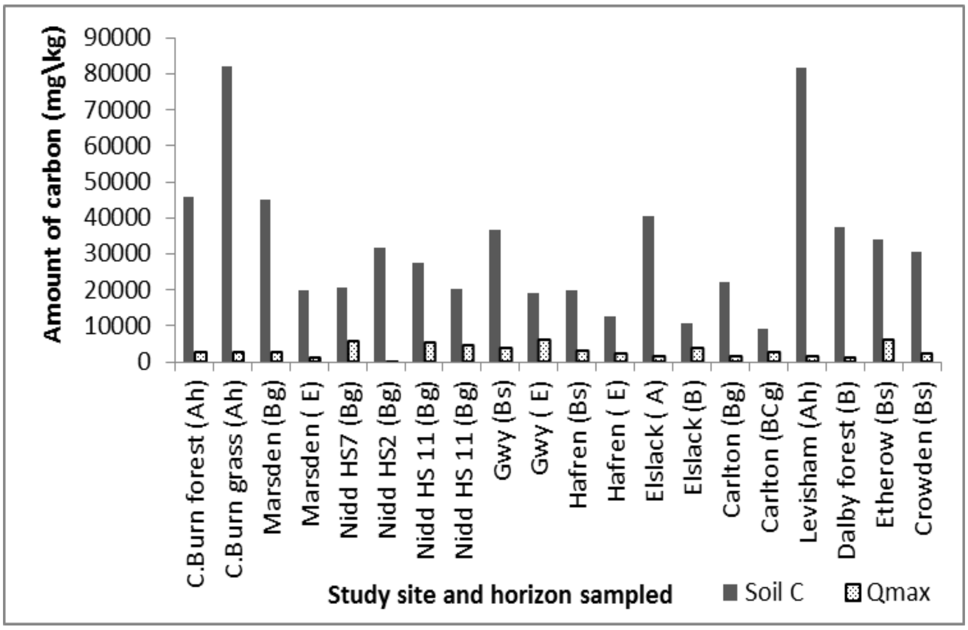


Figure 4.19. Comparison of soil organic carbon (Soil C) and estimated maximum adsorption capacity (Q_{max}) for 20 UK upland mineral soils.

4.4.5 Implications for DOC sorption in UK Upland soils

The findings of this study show that the UK upland soils studied here have the capacity to retain large amounts of carbon and that their DOC binding sites are currently not saturated. This suggests that increases in surface water DOC are not attributable to a declining capacity of mineral soil to retain DOC. This study has shown that while the adsorption capacity of these soils is predominantly controlled by their mineralogical make-up it is the pH which determines the affinity of the soil for the substrate and in so doing determines whether or not sorption of DOC occurs. This suggests that although these upland soils have the capacity to retain more carbon, the pH of soils within the catchments could be resulting in conditions which do not favour the adsorption of DOC leading to the observed increased DOC export from these soils. Several studies within the literature have suggested that the increased DOC export is the result of catchments showing recovery from acidification (increasing pH) as a result of reduced acid deposition (Clark et al., 2010; Clark et al., 2011; Evans et al., 2006; Evans et al., 2012; Monteith et al., 2007; Sawicka et al., 2016). The decreasing acidity (increasing pH) results in greater solubilisation and export of DOC from soils (Monteith et al., 2007). However, the soils analysed in this chapter were all acidic (pH <4) and adsorption increased with increasing pH. While recovery from acidification could be driving pH increases in the catchments leading to the increased solubilisation of DOC in organic horizons, it is unlikely to be currently driving increased DOC export from these mineral soils since these soils are still very acidic. Instead it is likely that these soils which have pHs less than the optimum for DOC adsorption are exhibiting a lower affinity for DOC. Increases in DOC concentrations in organic horizons have been observed for several UK catchments (Buckingham et al., 2008; Sawicka et al., 2016; Stutter et al., 2011; Vanguelova et al., 2010). This would suggest higher inputs of DOC from the organic horizon to the mineral horizon will occur. It could be that although the mineral soils are able to retain DOC, they are not able to retain amounts that would compensate for the increased input from the organic horizons due to their low affinity for DOC.

While the DOC binding sites currently are not saturated they do have the potential to become saturated (under favourable pH conditions) and leach increased amounts of DOC. This is indicated by the association of Q_{max} and Al_o and the relationship between desorption and SI_{SOC}. From these observed associations it can be gathered that the Al_o are the DOC binding sites and as these become occupied by DOC SI_{SOC} increases resulting in greater potential for desorption. Therefore in light of the finite capacity of these soils to retain DOC in stable associations with soil minerals, there has to be a greater consideration of ways in which DOC inputs within the catchment can be reduced. The observation of a positive relationship between Q_{max} and the soils vegetated with graminoids suggests that choice of vegetation is one way of controlling DOC inputs and exports in these soils. Further work is needed to determine if the relationship between graminoid soils and Q_{max} is upheld with other vegetation sources of DOC.

4.5 Conclusion

This study sought to determine the total capacities of UK upland soils to adsorb DOC and what properties influence the maximum adsorption capacity of these soils. This study has shown that these soils have the capacity to retain more DOC. However, the commonly used Langmuir isotherm may not accurately model the maximum sorption capacity and so its use to quantify the sorption capacity of soils should be approached with some caution. The measures of carbon saturation typically used within the literature (b/Q_{max}) and $SOC/(Fe_o+Al_o)$ do not provide feasible estimates of the extent of saturation of these soils and as such should be used qualitatively to make comparisons between soils rather than quantitatively. Despite not being able to quantify the maximum sorption capacities and the degree of saturation of these soils, this study has still shown that UK upland soils are currently not saturated as suggested by the observation of net adsorption in all soils across the experimental range of added DOC concentrations. Therefore, the increased export of DOC from these soils to surface waters is possibly being driven by other controls such as pH change rather than by the lack of available sorption sites. Within this study pH differences among the mineral soils was the most important factor in explaining variation in the sorption parameters. The soil pH was the most important predictor of the Null point (Np) and the sorption affinity (k); pH was also significantly correlated with Q_{max} ($r = 0.584$; $p = 0.007$). Therefore the increased DOC export from these catchments is more likely being controlled by the pH of the soils within the catchments. One current prevailing theory within the literature suggests that pH changes as a result of recovery from acidification are the cause of increased DOC export from soils (Clark et al., 2010; Clark et al., 2011; Evans et al., 2006; Evans et al., 2012; Monteith et al., 2007; Sawicka et al., 2016). While the findings here do suggest that pH changes could be the cause, they are also suggesting that the decreasing acidity favours adsorption in these mineral soils. It could be that increasing soil pH up to the threshold for optimum adsorption (pH 4.5) is likely to lead to greater adsorption of DOC within these mineral soils. However, the increased production and solubilisation of DOC in the organic horizons (Evans et al., 2012) outweighs the pH effect on the adsorption of DOC in the mineral layer. Additionally this study has shown that the predominant mode of DOC sorption in these soils is through bonding with amorphous forms of Al and that the Fe oxides seem not to be an important control on sorption within these soils.

5 The influence of retention time on the adsorption of dissolved organic carbon to mineral soil.

5.1 Introduction

This chapter investigates whether retention time within the mineral soil has an impact on the amount of DOC adsorbed or released.

In recent years, weather patterns have changed such that the UK has been experiencing wetter winters and drier summers. For example, Osborn et al. (2000) noted an increasing trend in average winter precipitation upon examining the records of 110 UK weather stations for the period 1961 to 1995. The greatest increases were seen in the western and upland regions (Osborn et al., 2000). The winter precipitation increases were the result of an increase in the number of wet days; an increase in the daily amount of precipitation on those wet days also contributed to the observed increases seen in the west (Osborn et al., 2000). Precipitation records for summer showed a decrease in the number of wet days over the 34 year period for 90 of the 110 sites studied, this resulted in a weak decreasing trend in the summer precipitation (Osborn et al., 2000). The research of Fowler and Kilsby (2003) also highlighted changing weather patterns in the UK by showing increasing trends in annual precipitation especially in the west and north of the UK. It is expected that the UK will continue to experience increasing temperatures and changes in hydrological patterns (Jenkins et al., 2009). According to Jenkins et al. (2009), by the 2080's under a medium emissions scenario (50% probability threshold) minimum daily temperatures are expected to rise between 2.7 ^{O}C to 4.1 ^{O}C in the summer and 2.1 ^{O}C to 3.5 ^{O}C in winter. Additionally, by the 2080's under a medium emissions scenario (50% probability threshold) average maximum temperatures are expected to rise between 2.8 ^{O}C to 5.4 ^{O}C in the summer and between 1.5 ^{O}C to 2.5 ^{O}C in the winter (Jenkins et al., 2009). Jenkins et al. (2009) have also predicted that by the 2080's the UK will see decreased precipitation in the summer (down by about -40 %), increased precipitation in the winter (up by about +33 %) and an increase in the frequency and severity of storm events (medium emissions scenario; 50% probability threshold). Climate predictions made by Jenkins et al. (2009) were relative to a 1961-1990 baseline. A greater understanding of how changes in precipitation are likely to influence DOC production, retention and export in soils is needed to prevent or manage impacts to surface water bodies.

Increasing temperature and hydrological changes (due to changes in precipitation) are likely to lead to changes in DOC production, composition and export from soil to water. Increases in temperature will result in increased production of DOC as shown by Moore and Dalva (2001) and Freeman et al. (2001a). Moore and Dalva (2001) found that the rate of DOC release from soils and plant tissues at 22 ^{O}C was an average of 2.4 times greater than at 4 ^{O}C. Peat soil warming experiments in the range 2-20 ^{O}C conducted by Freeman et al. (2001a) also confirmed a positive relationship between temperature and DOC production. Increasing temperature could also lead to enhanced evaporation and possibly cause an increase in DOC due to a concentration effect. Increased rainfall could result in increased export of DOC from the soil to the surface waters depending on catchment soil types and the direction of flow of catchment runoff (Chapman and Palmer, 2016). Catchments where poorly draining soils such as peat and gleysols dominate have high rainfall-runoff ratios while catchments where freely draining soils such as podzols dominate are likely to have a low rainfall-runoff ratio with a long water residence time; therefore high DOC concentrations are only seen during high flow events with increase being exhibited as flow increases (Chapman and Palmer, 2016; Dawson et al., 2008). Increased precipitation and rainfall events could lead to greater export of DOC if surface runoff dominates or it could lead to greater transport of DOC to mineral horizons where a prolonged retention time could possibly influence DOC sorption. Therefore the influence of prolonged retention time on the sorption of DOC requires further investigation to determine and manage the possible impacts of the predicted precipitation increase.

DOC in catchment waters show seasonal variability with concentration maxima occurring in the autumn and minima in the spring (Halliday et al., 2012). Halliday et al. (2012) analysed the hydro-chemical properties of stream samples taken in the Upper Hafren catchment, Plynlimon, Wales, using both high frequency sampling data (samples taken every 7 hours 2007-2009) and low frequency sampling data (samples taken weekly for the period 1990-2010). In the research of Halliday et al. (2012) it was observed that DOC concentration peaks occurred in the autumn and minima occurred in spring. The increased concentrations in autumn were attributed to the wetting-up of the soils after the period of highest biological activity in the summer (Halliday et al., 2012; Neal et al., 2005).

Research has shown that organo-mineral soils play a significant role in the retention and release of DOC within a catchment and that the DOC at sites dominated by such soils also shows variability with the seasons and during extreme weather events (Kaiser and Guggenberger, 2005; Tipping et al., 1999). At several of the upland areas of the UK where surface water DOC increases have been observed, organo-mineral soils are present. The UK acid waters monitoring network (AWMN) is made up of 22 surface water bodies in catchments across the most acid sensitive regions of the UK. Fifty percent of the AWMN catchments contain organo-mineral soils (summarised from (Monteith and Evans, 2000). After 10 years (1988-1998), surface waters at 17 of the AWMN sites showed significant increasing DOC trends (Monteith and Evans, 2000), after 15 years (1988-2003) all 22 sites were showing increasing trends in DOC (Monteith, 2005) and after 20 years (1988-2008) these rising trends were maintained at 21 of the 22 sites (Kernan et al., 2010). In England and Wales, 11.3% of the landmass is comprised of organo-mineral soils including gleys, stagnohumic gleys, humic podzols and stagnohumic podzols (Holden et al., 2006). Of these organo-mineral soils, stagnohumic gleys are one of the most abundant organic soil types and cover 3.9% of England and Wales (Holden et al., 2006). Like all gley soils, stagnohumic gleys are susceptible to seasonal saturation caused by high rainfall or water table changes (Avery, 1980). With the predicted changes in temperature and precipitation it is likely that these gley soils will experience longer periods of saturation which in turn could mean a longer contact time of percolating soil solutions with soil minerals.

Many studies have shown that mineral soil removes DOC from soil solution as it percolates through the soil profile (Kaiser and Guggenberger, 2000; Kothawala et al., 2009; Moore et al., 1992). The adsorption of DOC to mineral soil surfaces is thought to be influenced by chemical reactions between the soil solution and the soil surface as well as by microbial processes (Kalbitz et al., 2000; McDowell and Likens, 1988). Jardine et al. (1989) showed that when DOC was fractionated it was the hydrophobic fraction which was preferentially adsorbed to mineral surfaces and Kaiser et al. (1997) showed that aromatic carbon was more strongly adsorbed to mineral surfaces than alkyl carbon. Therefore, it appears that the chemical composition of DOC has a major impact on its adsorption to the mineral soil. Differences in the ability of mineral soil to retain DOC based on differences in the source of DOC was also highlighted by the research in Chapter 3 of this thesis which highlighted that mineral soil retained more DOC that was leached from forest vegetation compared to heather and grass vegetation.

Some studies suggest that reduced DOC retention time as a result of storm flow events may lead to diminished adsorption of DOC to forest mineral soils (Hongve et al., 2004; Kaiser and Guggenberger, 2005). Storm flow events can lead to a shift from vertical flow through the mineral horizon to greater near surface flow through surface organic horizons (Hongve et al., 2004). There is also the possibility of rapid vertical movement of the DOC through the mineral horizons leading to a reduced contact time with mineral surfaces and possible greater export of DOC (Kaiser and Guggenberger, 2005). Based on this it might be assumed that the reverse is also true, and an increased retention time leads to an increased adsorption of DOC but no studies exist to support this. However it has not been widely researched how increases in retention time of soil solution will affect the retention and release of DOC from mineral soils, such as stagnogleys.

The export of DOC to surface waters within a catchment is controlled by the ability of vegetation, microbial and soil processes to produce and remove DOC as well as the hydrological pathways within the catchment (Tranvik and Jansson, 2002). In the UK, DOC concentrations have increased in the upland waters (Evans et al., 2005; Monteith et al., 2014; Monteith et al., 2007). The UK uplands are sites dominated by a mixture of natural and semi natural vegetation, including grasses, dwarf shrubs and forest species. The uplands also experience moderate to high rainfall and are dominated by carbon rich soils which are either perennially wet (some peats) or prone to seasonal waterlogging (organo-mineral soils). It is well known that the most carbon rich soils in the catchment are a major source of DOC in streams (Hope et al., 1997; Palmer et al., 2005; Worrall et al., 2002). With climate models predicting increases in winter rainfall (Jenkins et al., 2009), it may be assumed that there will be an increase in the period of water saturation of these soils or in the case of extreme rainfall events there will be an increase flushing of DOC from these soils. While there is a great amount of research looking at the effects hydrological changes can have on peat soils, there is limited information which looks at the effect of prolonged saturation on the retention and release of DOC in mineral soils.

This study sought to understand the influence of soil solution retention time on DOC adsorption to mineral soil by answering the following questions.

- Does the retention time of soil solution influence the amount of DOC adsorbed to mineral soil?
- Does the influence of vegetation type on the DOC quality (as shown in Chapter 3) affect the retention time required for sorption equilibrium to be reached between the soil and soil solution?
- Does the concentration of DOC entering the mineral horizon affect the time required for sorption equilibrium to be reached between the soil and soil solution?

5.2 Methods

This study investigated the influence of soil solution retention time on DOC adsorption to mineral soil using DOC leached from organic horizons beneath the grass species *Molinia caerulea* henceforth referred to as GDOC, and the shrub *Calluna vulgaris* henceforth referred to as HDOC. DOC was obtained by soaking each organic horizon in deionised water. The DOC obtained from each source was then characterised based on chemical properties such as pH and specific ultra violet absorbance at 254 nm (SUVA). Sorption experiments were conducted with each DOC source and a single common mineral soil. The mineral soil used was chosen from the least disturbed site to be representative of the site's natural state prior to changes in vegetation under new land management regimes. Leachates were characterised for SUVA and pH. The leachate DOC concentrations were used to construct isotherms to describe and compare the sorption behaviour of each DOC source.

5.2.1 Field site and soil sampling

Soils for this experiment were collected on September 26th, 2014 from Marsden moor, Huddersfield, Yorkshire located at 53° 36' 10.40''N 1° 57' 45.59''W. Soils at this site are comprised of blanket peat of the Winter Hill association on the moor tops , seasonally waterlogged cambic stagnohumic gley soils of the Wilcocks 1 association on gentle to moderate slopes and iron pan stagnopodzols of the Belmont association on the lower slopes (Jarvis et al., 1984). Most of the catchment soils are developed on sandstone and shales (Blundell et al., 2013). Vegetation at Marsden has been identified as a mixture of grasses (*Molinia sp.*), sedges (*Eriophorium sp.*) and scattered dwarf shrub (*Calluna vulgaris*).

For this study intact organic horizons were taken from beneath *C. vulgaris* (heather) and *M.caerulea* (grass). DOC extracted from organic horizons beneath grass and heather showed the least adsorption to mineral soil in the work described in chapter three of this thesis. However, the predominant vegetation types in the UK uplands are shrubs and acid grassland (Averis et al., 2004) and so are likely to be the major vegetation sources of DOC in the UK uplands. Therefore organic soils beneath heather and grass were chosen as the DOC sources to investigate whether sorption increased with increasing retention time. The mineral soil used was B horizon soil from a cambic stagnohumic gley located beneath grassland. A stagnohumic gley was selected since these soils are prone to seasonal waterlogging (Avery, 1980), and therefore lengthier times of water retention. Similar to the work in chapter three, the stagnogley used in this study was selected from beneath a grassland. The mineral soil was also sourced from beneath a grassland because the findings in chapter four seem to suggest that soils beneath graminoids (which includes grasses) have the ability for greater retention of DOC.

5.2.2 Experimental approach.

5.2.2.1 *Soil preparation and characterisation*

The mineral soil was oven dried at 40°C, gently crushed and passed through a 2 mm sieve. For the organic soils any obvious live vegetation and roots were handpicked from the soil. All soils were then analysed for pH, moisture content, organic matter content by the loss on ignition method (LOI) and carbon and nitrogen content using a combustion analyser. Mineral soils were also analysed for amorphous Al and Fe and organically bound Al and Fe using acid ammonium oxalate and pyrophosphate extractions respectively. All soil analyses were done in triplicate. Method detection limits where stated were calculated as three times the standard deviation of the blanks (Van Reeuwijk, 1998). The blanks used for each method's limit of detection were the pooled blanks from all sections of this thesis. The soils used in this chapter were not pre-treated to remove soil organic carbon since it was found that the removal of soil organic carbon from the mineral soil used in the experiment described in chapter three, did not enhance adsorption of DOC sourced from organic soils beneath heather and grass (see Chapter 3). Additionally, soil organic carbon was not removed from the soils used in the experiment described in chapter four of this thesis and its presence did not prevent further adsorption of DOC sourced from organic soils beneath heather.

Using the method of Bascomb (1974), the pH of the dried mineral soil was measured first in water then in 0.01 M Calcium Chloride ($CaCl_2$) solution using a ratio of 1:2.5 w/v. The pH was measured using a Mettler Toledo MPH 225 glass electrode pH meter. For organic soils the pH in water and 0.01 M $CaCl_2$ were measured using the method of Robertson et al. (1999), which entailed the use of field moist soil samples in a ratio of 1:2 w/v. The moisture content of the soils was determined by drying the soil at 105°C and the organic matter content by the loss on ignition method of combusting the oven dried soils in a furnace at 500°C overnight (Rowell, 1994). To determine soil carbon and nitrogen, soils were analysed using a Eurovector EA combustion analyser. The combustion analyser has a detection limit of 0.2 µg.

Amorphous Fe and Al contents of mineral soils were extracted by shaking one gram of the < 2 mm fraction with 0.2 M acid ammonium oxalate (50 ml) in the dark for 4 hours. The organically bound Fe and Al were extracted by shaking one gram of the < 2mm fraction with 0.1 M sodium pyrophosphate (100 ml) for 16 hours (van Reeuwijk, 2002). The extracts were analysed using inductively coupled plasma-optical emission spectroscopy (ICP-OES). The method detection limits for the ammonium oxalate extractions were: Al = 0.06 mg/L and Fe = 0.03 mg/L. The detection limits for the pyrophosphate extractions were: Al = 0.03 mg/L and Fe = 0.05 mg/L.

5.2.2.2 *Preparation of DOC solutions*

The DOC was obtained using a modification of the method presented in Kothawala et al. (2009). Intact LFH horizon measuring approximately 50 cm x 50 cm x 20 cm was soaked in deionised water for two weeks in a plastic storage box. The leachate was collected in glass bottles and filtered under suction, first using a glass fibre filter with nominal pore size 1.2 µm, followed by a 0.7 µm glass fibre filter and finally filtered using a 0.45 µm pre washed cellulose nitrate filter. The HDOC was diluted with deionised water to give four DOC solutions ranging in concentration from 2 mg/L to 101.8 mg/L. The GDOC was diluted to give four DOC solutions ranging from 2 mg/L to 95.85 mg/L. The concentrations and chemical properties of the solutions used are given in Table 5.1.

Table 5.1 Properties of DOC solutions used

Vegetation cover	**Stock and target concentrations**	**Actual DOC concentration (mg/L)**	**pH**	**Conductivity (µS)**	**SUVA ($\text{Lmg}^{-1}\text{m}^{-1}$)**
GDOC	Stock	204	3.92	153	
	100	95.9	4.07	85	4.74
	60	57.7	4.22	56	4.70
	20	20.1	4.54	23	4.90
	2	2.0	5.20	4	4.42
HDOC	Stock	136.3	3.52	183	
	100	101.8	3.65	136	5.11
	60	60.8	3.86	88	5.15
	20	20.8	4.25	35	5.05
	2	2.0	5.06	5	4.90

5.2.2.3 *Soil column construction and assembly*

Soil columns were constructed using BD Plastipak 100 ml syringes (Figures 5.1a and 5.1b). The syringes were modified by cutting the plunger away from the plunger tip, a hole was drilled in the plunger tip and a tap tool used to make 0.476 cm threads in the drilled hole. A hose barb was then inserted to be used as a handle for removing the cap. A stopcock was attached to the tip of each syringe to control the movement of leachate out of the columns. The modified columns are shown in Figures 5.2a and 5.2b.

The columns were assembled by packing 1.5 g of glass wool into the base of each column. Sixty grams of dried mineral soil was gradually weighed into each column with gentle tapping on the column between each soil addition. The columns were packed to a total height of approximately 70 mm with the initial 20 mm being comprised of the glass wool and the remaining 50 mm comprised of mineral soil. The density of soil in each column was approximately 1.2 g/cm^3. Four replicates were packed for each DOC solution (concentrations 2 – 100 mg/L). A packed soil column is shown in figure 5.2a.

Figure 5.1. 100 ml syringe before modification for use as soil columns, a) assembled syringe and b) disassembled syringe.

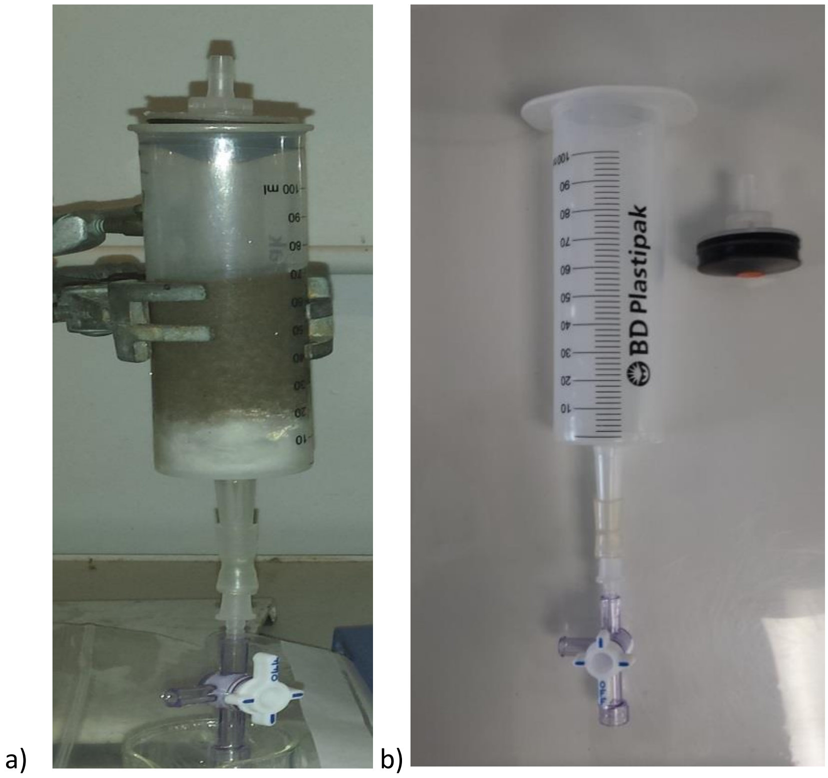


Figure 5.2. Modified 100 ml syringe used for soil columns, a) packed soil column and b) disassembled column

5.2.2.4 *Protocol for column leaching*

The soil solution was added to the column in two 30 ml aliquots, the first aliquot was allowed to percolate through the soil then the second aliquot was added one hour later. The columns were left to drain for 24 hours and the leachate collected in glass beakers. The application of the solution to the soil in the first 24 hours was used to re-wet the dried soils. At the end of the 24 hour re-wetting period (T0), four ml of the leachate was set aside for analysis, the remainder was reintroduced into the column and the drain valve switched off. Four ml of sample was then collected from each column after 24 hours (T1) and 72 hours (T2). Each time the drain valve was closed after the required amount of sample was collected. After 120 hours (T3), the column was allowed to drain completely. The mineral soil used was of the Wilcocks 1 Association with a soil moisture regime class of V or VI, which suggests that it can be wet for between 180-335 days of the year (Jarvis et al., 1984). Due to time constraints and the need for two batches (one for each vegetation source) it was not possible to run the experiment for a length of time that would reflect such long periods of waterlogging. Therefore, the duration of the experiment and leachate sampling times were decided based on times typically reported for batch studies testing the time for sorption equilibrium to be reached between DOC and soils (Moore et al., 1992; You et al., 1999).

5.2.3 Leachate Chemistry

5.2.3.1 *DOC Quantification*

All DOC solutions were analysed for organic carbon content by thermal oxidation using an Analytik Jena Multi N/C 2100S analyser. This equipment uses a differential method to calculate total organic carbon (TOC) in a sample. The total dissolved carbon (TC) is determined by digestion of both organic and inorganic carbon and subsequent detection of the carbon dioxide released. The total inorganic carbon (TIC) from carbonates, hydro-carbonates and free carbon dioxide is measured in a separate TIC reactor. The TIC is subtracted from the TC to give the quantity of TOC in the sample. Since all solution samples analysed in this study were filtered to <0.45 μm, TOC was assumed to equate to DOC. Each batch of analyses included the use of a certified reference material (VKI WW4A) and a standard prepared with the commercially available TIC (1000 ± 10 mg/L, Fluka product 12003-250ML-F) and TOC (1000 ± 10 mg/L, Fluka product 76067-250ML-F) standard solutions. The method detection limit was determined to be 0.25 mg/L using the method of Van Reeuwijk (1998).

5.2.3.2 *Ultra Violet Visible Spectroscopy, pH and conductivity*

To determine if observed differences in DOC retention with time could be explained by differences in aromatic character, samples were analysed for UV–Vis with a Jasco V-630 double beam spectrophotometer at wavelength 254 nm using 10 mm and 2 mm quartz cells (2 mm was used where samples exceeded the instrument range). SUVA was determined for all samples by dividing the absorbance by the sample DOC concentration. The pH of the leachates was also measured using a Mettler Toledo MPH glass electrode pH meter. Leachates were also analysed for conductivity using a Horiba B 173 conductivity meter with a measurement range of 1 µS/cm to 19.9 mS/cm.

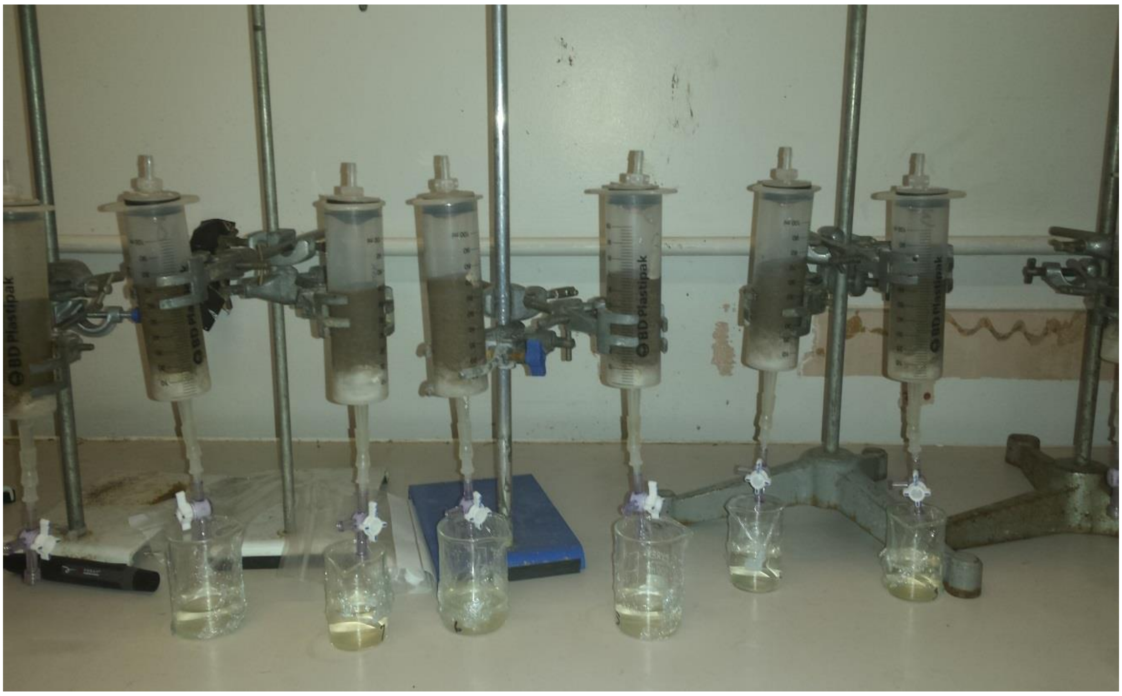


Figure 5.3 . Experimental set-up showing soil columns. Columns containing mineral soil where the DOC solution has been added and the leachate being collected in glass beakers.

5.2.4 Data Analysis

Data analysis was completed in two stages: i) Adsorption and release of DOC in mineral soil after the initial soil rewetting stage (T0); and ii) The effect of retention time on DOC adsorption and release from mineral soil. The data analysis was divided into the two stages to determine and account for the effect of rewetting the mineral soil and the effect of rewetting on the DOC used.

5.2.4.1 *Statistical Analysis*

The statistical package SPSS 22 was used for all analyses. All data were tested for normality using the Kolmogorov–Smirnov test. A two way analysis of variance was carried out for normally distributed data to test for differences between the two DOC sources and among the four concentration treatments. Where normality did not exist, the data were transformed using the following functions: logarithmic, square or square root. None of the transformations was successful in normalising the data therefore non parametric tests were used.

5.2.4.2 *DOC sorption and leachate properties at T0*

A two way analysis of variance (ANOVA) was carried out to test for the differences in DOC sorption between the two DOC sources and among the four concentration treatments. The Scheirer-Ray-Hare test was used to determine if the concentration of DOC in the leachate differed significantly between vegetation covers and among input DOC concentrations. The Scheirer-Ray-Hare test is an extension of the Kruskal Wallace test; it allows a two way analysis of variance to be done using ranks similar to the Kruskal Wallace test (Dytham, 2011). Scheirer-Ray-Hare is considered a suitable alternative to the two way ANOVA in cases where data do not meet the assumptions for ANOVA (Dytham, 2011).

The Wilcoxon Sign Rank test was used to determine if the pH and conductivity of the leachate differed significantly from the pH and conductivity of the initial DOC solutions. The data was then analysed with the Scheirer-Ray-Hare test to determine if the conductivity and pH of the leachate varied significantly between vegetation and among concentrations.

5.2.4.3 *Effect of retention time on DOC sorption to mineral soil and DOC leached from soil columns*

Of the solutions collected at (T0) and subsequently added back into the columns a concentration of 88 mg/kg was common to both DOC sources. Therefore data collected from columns with the 88 mg/kg treatment were analysed for significant effects of DOC source on DOC sorption to mineral soil and DOC leached from soil columns. The sorption data for the 88 mg/kg treatment was normally distributed so a two way ANOVA was used to test if there were significant influences of retention time and vegetation source on the amount of DOC adsorbed or desorbed.

Non parametric tests were used for all other analyses since the rest of the data was not normally distributed. The Scheirer-Ray-Hare test was used to determine the following:

- Were there significant influences of retention time and input DOC concentration on the amount of DOC adsorbed to mineral soil?
- Were there significant influences of retention time and input DOC concentration on the amount of DOC leached from soil columns?
- Were there significant influences of retention time and DOC source on the amount of DOC leached from soil columns?
- Did the pH, conductivity and SUVA of the leachates vary significantly between vegetation types and among concentrations?

5.3 Results

5.3.1 Mineral soil properties

The mineral soil was an acidic (pH in 4.87) sandy loam with low carbon content (8.43 mg/g). Details of its mineral composition are given in table 5.2.

Table 5.2. Properties of the mineral soil. All soil measurements are means of triplicate samples with the standard error of the mean given in brackets. Al_p pyrophosphate extractable aluminium, Al_o oxalate extractable aluminium, Al_{CD} citrate dithionite extractable aluminium, Fe_p pyrophosphate extractable iron, Fe_o oxalate extractable iron, Fe_{CD} dithionite extractable iron.

Soil property	
Carbon (mg/g)	8.43 (0.03)
C/N	8.97 (0.2)
pH_{H2O}	4.87 (0.01)
Al_p mg/g	1.19 (0.01)
Al_o mg/g	1.9 (0.04)
Al_{CD} mg/g	1.09 (0.01)
Fe_p mg/g	2.76 (0.07)
Fe_o mg/g	10.39 (0.44)
Fe_{CD} mg/g	13.61 (0.6)
Texture	Sandy Loam

5.3.2 Adsorption and release of DOC in mineral soil after initial soil rewetting stage (T0)

5.3.2.1 *The amount of DOC adsorbed*

The amount of DOC adsorbed varied significantly between the two sources of DOC ($F_{1,31}$ = 320.5 , $p < 0.001$); greater adsorption of DOC occurred for the DOC solutions extracted from peat covered with grass (amount sorbed ranged from -86 mg/kg to 42.6 mg/kg) than heather (amount sorbed ranged from -85.5 mg/kg to 7 mg/kg ; Figure 5.4). Negative values indicate desorption.

The concentration of DOC in the solutions added to the mineral soil also had a significant effect on the sorption of DOC by the mineral soil ($F_{3,31}$ = 901.8 , $p < 0.001$). At low concentrations of added DOC net desorption was observed while at higher concentrations of added DOC net adsorption was seen (Figure 5.4). The two sources of DOC vary significantly in their sorption response to changes in concentration ($F_{3,31}$ = 39.6 , $p < 0.001$). The concentration at which adsorption begins to occur between the mineral soil and the DOC added is much lower for the DOC solutions from the grass (>47 mg/kg) than from the heather (>95.6 mg/kg) (Figure 5.4).

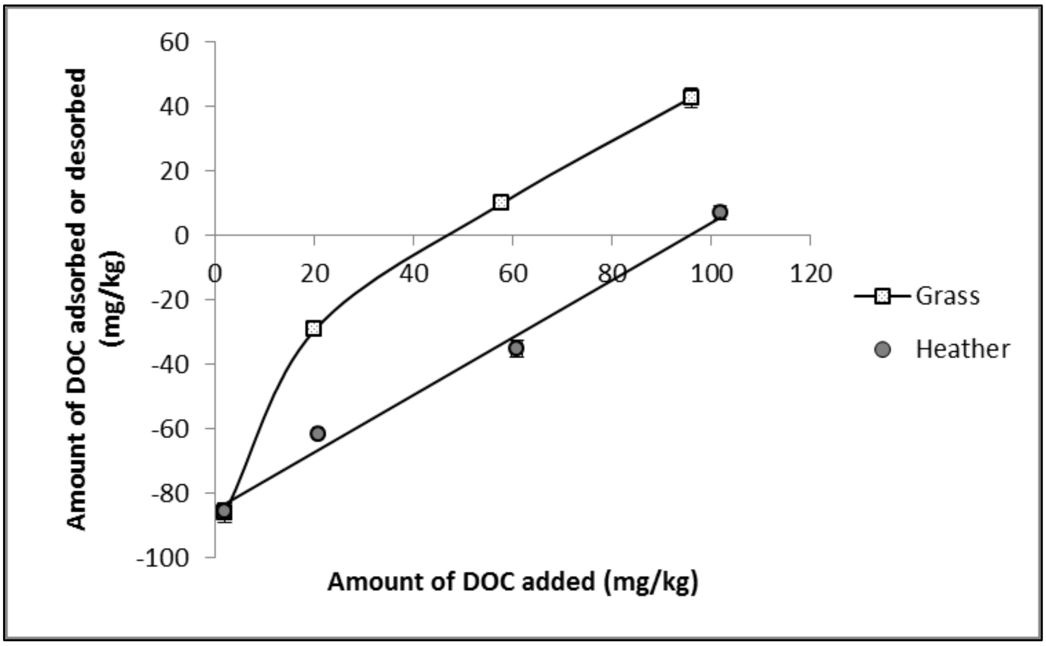


Figure 5.4. Comparison of DOC sorption to mineral soil for DOC sourced from peat collected beneath heather and grass after re-wetting soil for 24 hours. Negative values indicate desorption and positive values indicate adsorption. Standard error bars are smaller than the symbol size for all mean values, n=4.

5.3.2.2 *DOC leached from soil columns*

The amount of DOC in the leachates after 24 hours varied significantly (H (1) =15, $p < 0.001$) between the two sources of DOC. The leachates collected from columns treated with GDOC had a much lower DOC concentration (average = 59.6 ± 9.5 mg/kg) than those treated with HDOC (average = 90.1 ± 3.2 mg/kg) (Figure 5.5).

The initial concentration of HDOC added to the mineral soil had no significant effect on the concentration of DOC in the leachates at T0. The leachates from the 2 mg/kg GDOC treatment (median = 86.8 mg/ kg) were significantly higher than leachates from columns treated with 20 mg/kg (median = 49.5 mg/kg, U = 0, p = 0.029), 60 mg/kg (median = 47.5 mg/ kg, U = 0, p = 0.029) and 100 mg/ kg (median = 51.4 mg/ kg, U = 0, p = 0.029) of GDOC. There were no significant differences in the leachates from columns treated with 20 mg/kg, 60 mg/kg or 100 mg/kg of GDOC.

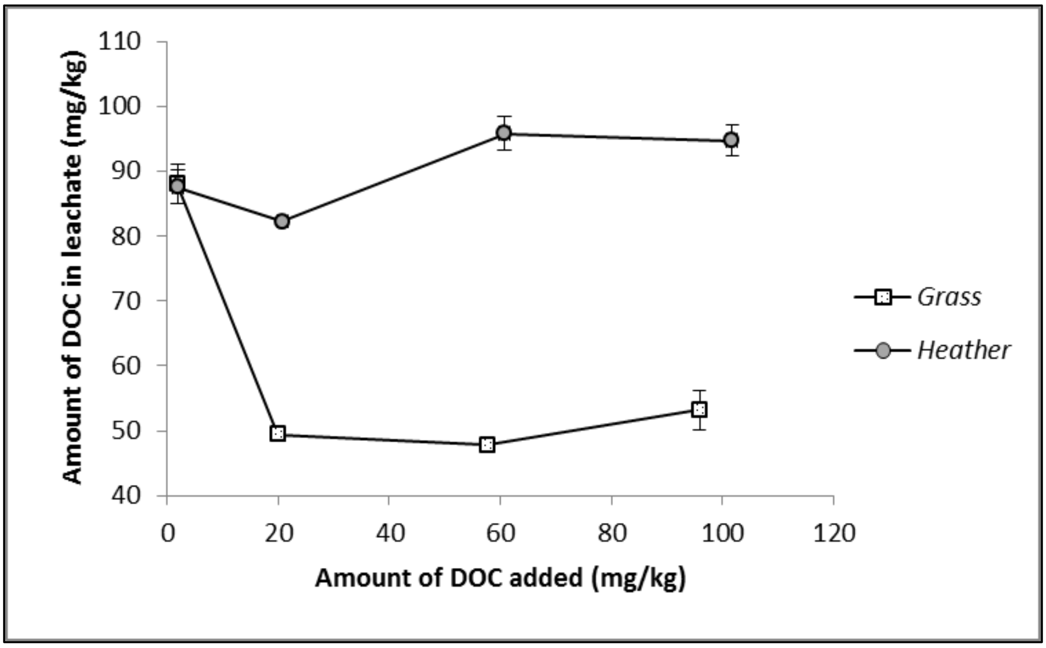


Figure 5.5. Comparison of DOC in leachate after 24 hours (T0) of contact between mineral soil and DOC sourced from O horizon soil beneath heather and grass. Error bars show standard error of the mean, for some means error bars were smaller than the symbol size, n=4.

5.3.2.3 *Change in pH and conductivity of leachates*

The leachates showed a significant increase in pH (Z = -4.938, p < 0.001) at T0 when compared to the pH of the original DOC solutions The GDOC treatment solutions ranged in pH from 4.07 to 5.20 while the pH of the GDOC column leachates ranged from 7.00 to 7.88 (Figure 5.6). The HDOC treatment solutions ranged in pH from 3.65 to 5.06 while the pH of the HDOC column leachates ranged from 7.44 to 7.87 (Figure 5.7). The conductivity also increased significantly (Z = -4.940, p < 0.001) in the leachates at T0 (Figures 5.8 and 5.9). The GDOC treatment solutions ranged in conductivity from 4.0 µS/cm to 85 µS/cm while the conductivity of the GDOC column leachates ranged from 90 µS/cm to 190 µS/cm (Figure 5.8). The HDOC treatment solutions ranged in conductivity from 5 µS/cm to 136 µS/cm while the conductivity of the HDOC column leachates ranged from 172 µS/cm to 210 µS/cm (Figure 5.9). There was a vegetation influence on both the pH (H(1) = 10.32, p < 0.001) and the conductivity of the leachates (H(1) = 16.81, p < 0.001).The effect of vegetation on these properties was significantly influenced by the input concentration of DOC; pH (H(3) = 8.76, p = 0.03), conductivity (H(3) = 7.21, p = 0.07). The 2 mg/kg treatment behaved similarly for the two DOC sources. When the input concentration of GDOC was increased from 2 mg/kg to 20 mg/kg the Leachate pH decreased from 7.76 to 7.03 (Figure 5.6) and the leachate conductivity decreased from 178.8 µS/cm to 92.8 µS/cm (Figure 5.8). At input concentrations above 20 mg/kg there were no significant further changes to pH or conductivity for the GDOC leachates (Figures 5.6 and 5.8). The pH and conductivity of the leachates from columns treated with HDOC were similar among the 4 treatment concentrations (Figures 5.7 and 5.9).

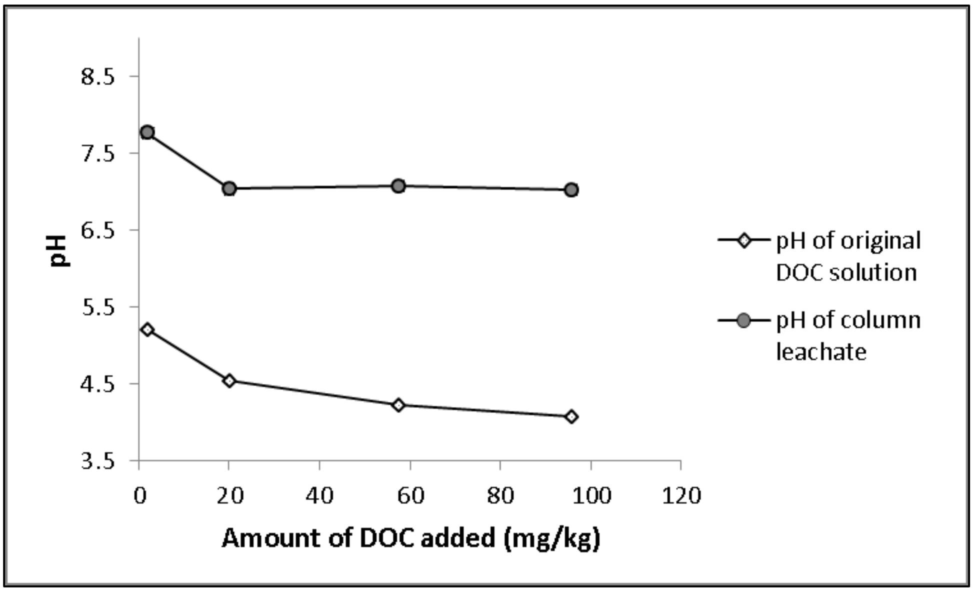


Figure 5.6. Change in pH of DOC in leachate after 24 hours (T0) of contact between mineral soil and DOC sourced from O horizon soil beneath grass for increasing concentrations of DOC added to the soil columns. Standard error bars are smaller than the symbol size for all mean values, n=4.

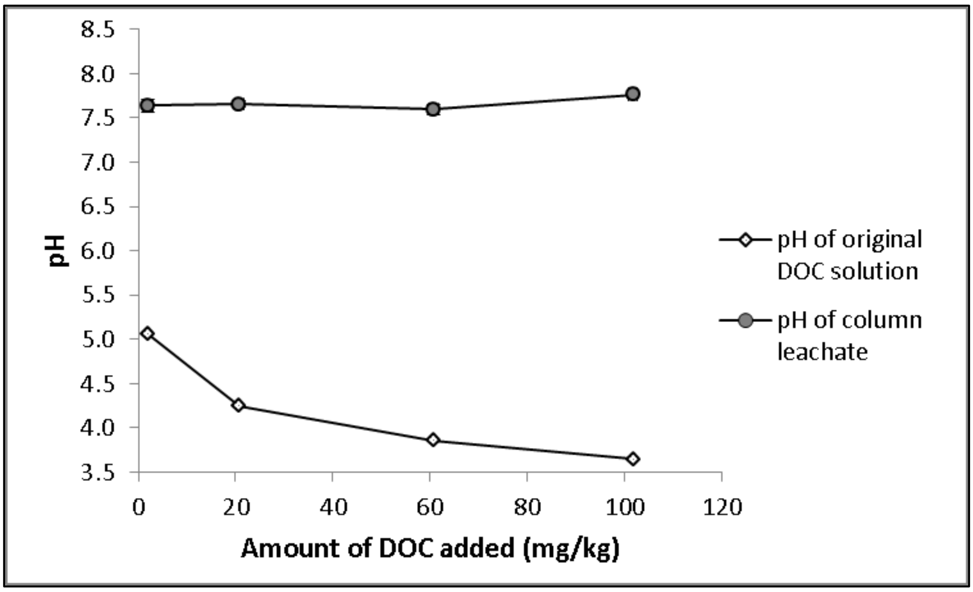


Figure 5.7. Change in pH of DOC in leachate after 24 hours (T0) of contact between mineral soil and DOC sourced from O horizon soil beneath heather for increasing concentrations of DOC added to the soil columns. Standard error bars are smaller than the symbol size for all mean values, n=4.

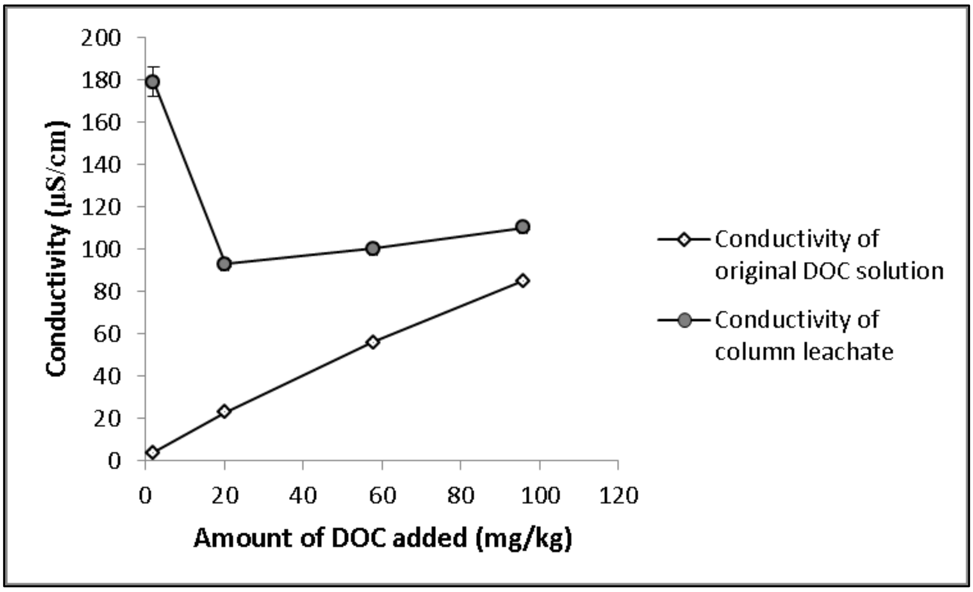


Figure 5.8. Change in conductivity of DOC in leachate after 24 hours (T0) of contact between mineral soil and DOC sourced from O horizon soil beneath grass for increasing concentrations of DOC added to the soil columns. Error bars show standard error of the mean, for some means error bars were smaller than the symbol size, n=4.

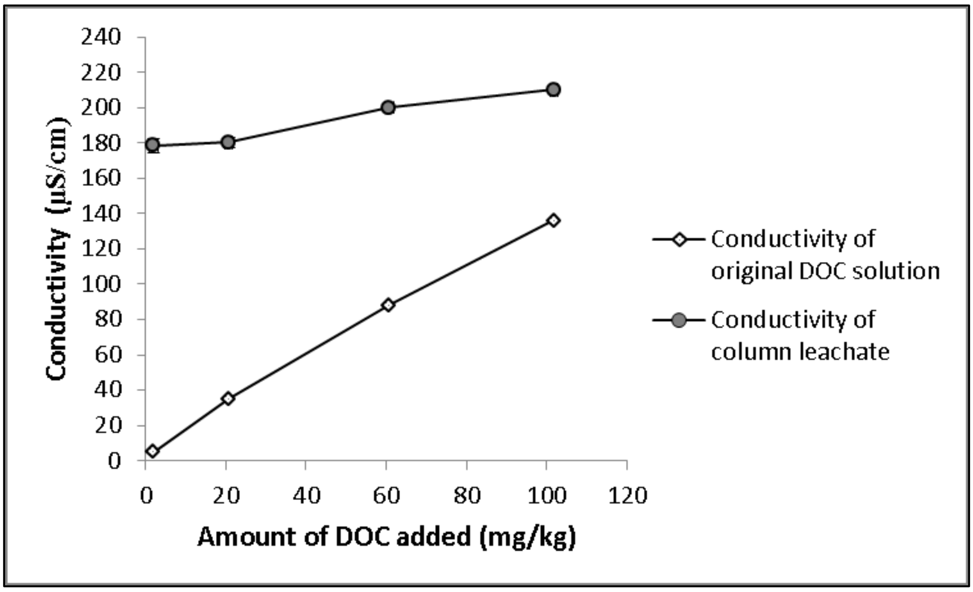


Figure 5.9. Change in conductivity of DOC in leachate after 24 hours (T0) of contact between mineral soil and DOC sourced from O horizon soil beneath heather for increasing concentrations of DOC added to the soil columns. Standard error bars are smaller than the symbol size for all mean values, n=4.

5.3.3 Effect of retention time on DOC sorption

5.3.3.1 *The amount of DOC adsorbed*

There was no significant effect of retention time on the amount of DOC adsorbed by or desorbed from the mineral soil. In contrast, the input concentration significantly affected the amount of DOC adsorbed or desorbed for both sources of DOC; GDOC (H(3) = 30.64, p < 0.001), HDOC (H(3) = 14.08, p < 0.001). For the soil columns treated with GDOC, low concentrations of added DOC (48 – 53 mg/kg) resulted in net desorption while the highest concentration (88 mg/kg) resulted in net adsorption (Figure 5.10). For the soil columns treated with HDOC, a narrower range of concentrations (82−96 mg/kg) was applied to the soil columns and only net adsorption was seen (Figure 5.11). However, it was observed that with increasing concentration, the amount of DOC adsorbed also increased (Figure 5.11).

Of the solutions added to the soil columns a concentration of 88 mg/kg was common to both DOC sources. For this concentration of DOC there were no significant changes in the amount of DOC adsorbed with increasing retention time and no significant effect of DOC source on the amount of DOC adsorbed with time. The DOC from both sources was adsorbed in similar quantities by the mineral soil; an average of 44.4 ± 2.3 mg/kg for GDOC and 45.3 ± 2.0 mg/kg for HDOC.

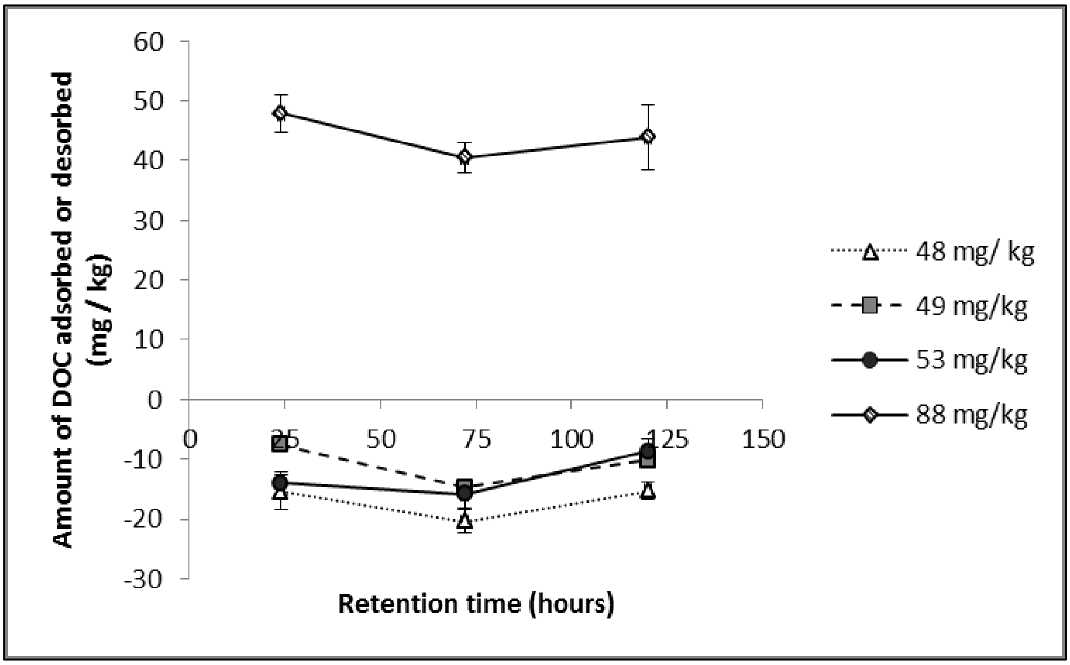


Figure 5.10. Change in DOC adsorption with time for differing amounts of added DOC extracted from O-horizon soil beneath grass. Error bars show standard error of the mean, for some means the error bars are smaller than the symbol size, (n=4).

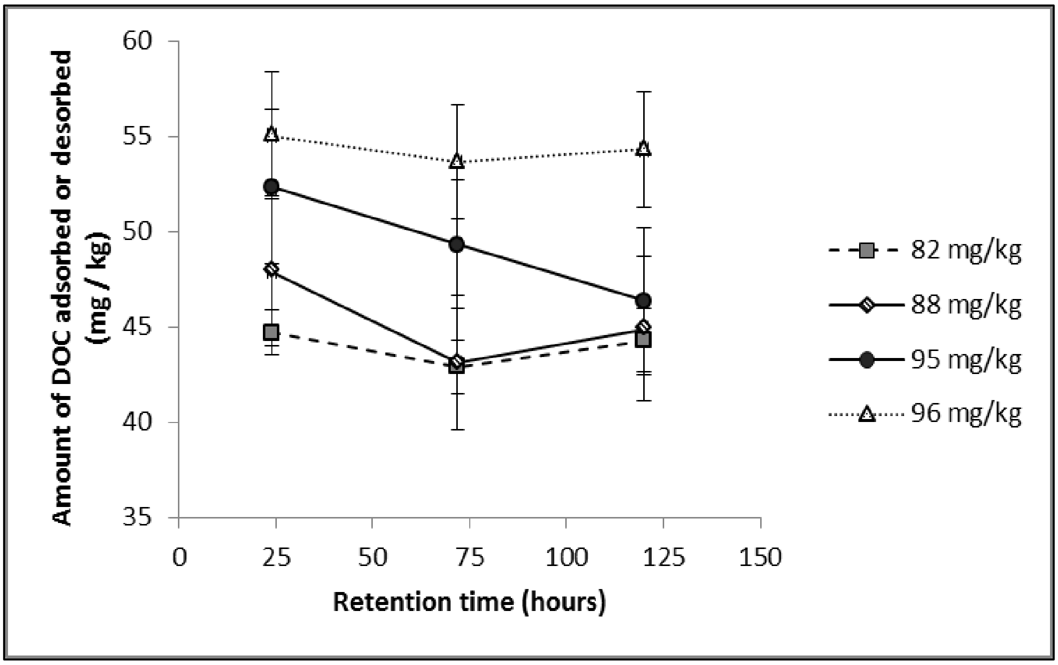


Figure 5.11. Change in DOC adsorption with time for differing amounts of added DOC extracted from O-horizon soil beneath heather. Error bars show standard error of the mean (n=4)

5.3.3.2 *Changes in pH and conductivity of leachates*

For both DOC sources, the pH of the leachates collected at T1, T2 and T3 were lower than the pH of the initial solution added back into the columns (T0 leachate) (Figures 5.12 and 5.13). The pH of the leachate collected from the soil columns treated with GDOC was significantly affected by retention time of the soil solution (H(2) = 9.71, p = 0.01) and the input concentration of the DOC (H(3) = 27.35, p < 0.001). The 48, 49 and 53 mg/kg treatments all decreased in pH between T1 (24 hours) and T2 (72 hours) then increased between T2 (72 hours) and T3 (120 hours). The 88 mg/ kg treatment showed decreasing pH throughout the duration of the experiment. The pH of leachates collected from the soil columns treated with HDOC decreased with increasing retention time for the duration of the experiments with the exception of the 96 mg/kg treatment which decreased from pH 7.47 at T1 to pH 7.15 at T2, then increased slightly to pH 7.19 at T3. The changes in leachate pH with time for columns treated with HDOC were statistically significant (H(2) = 26.66, p < 0.001).

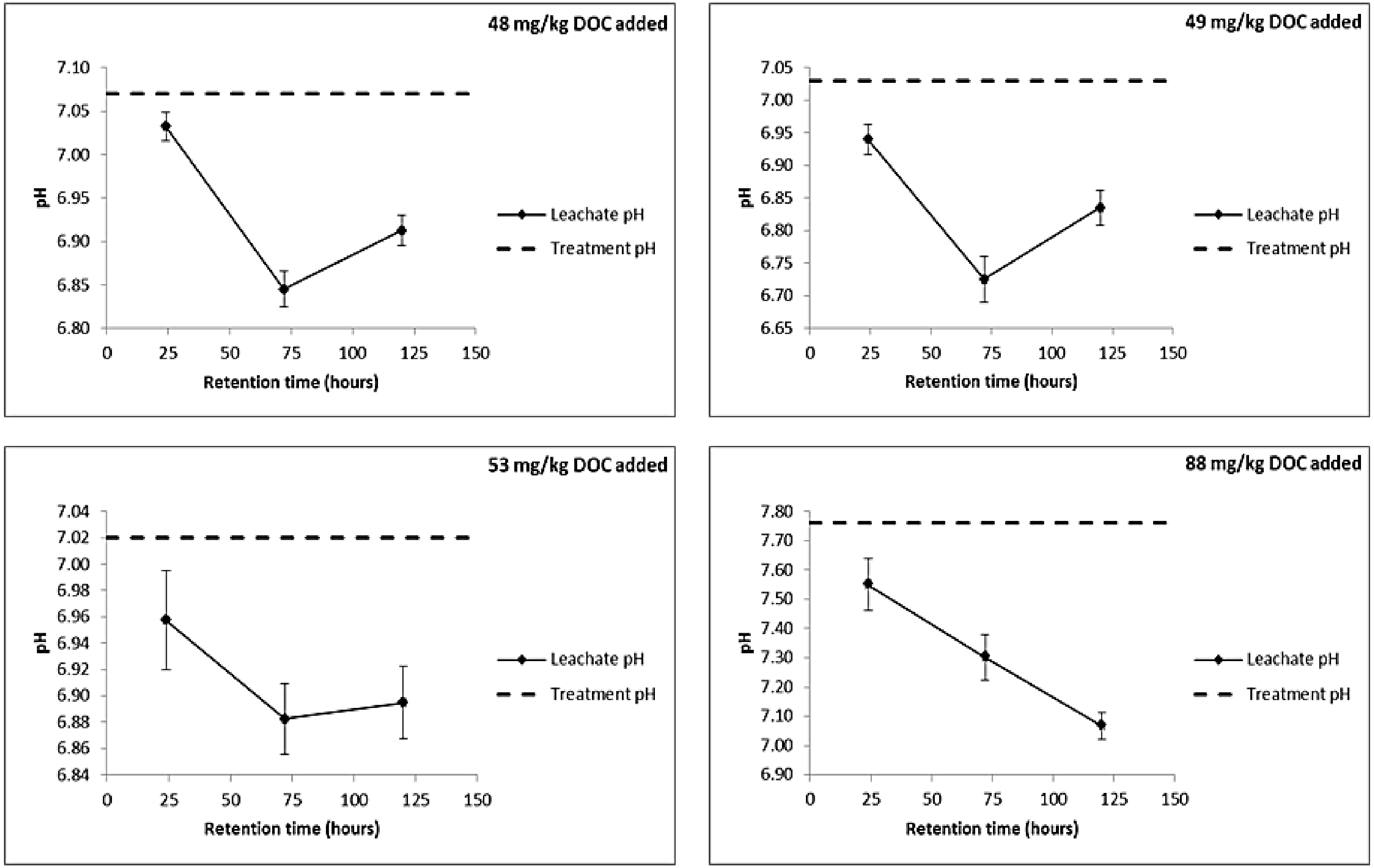


Figure 5.12. Influence of retention time on pH of leachates from O horizon soil beneath grass after contact with mineral soil. Error bars show standard error of the mean, n=4.

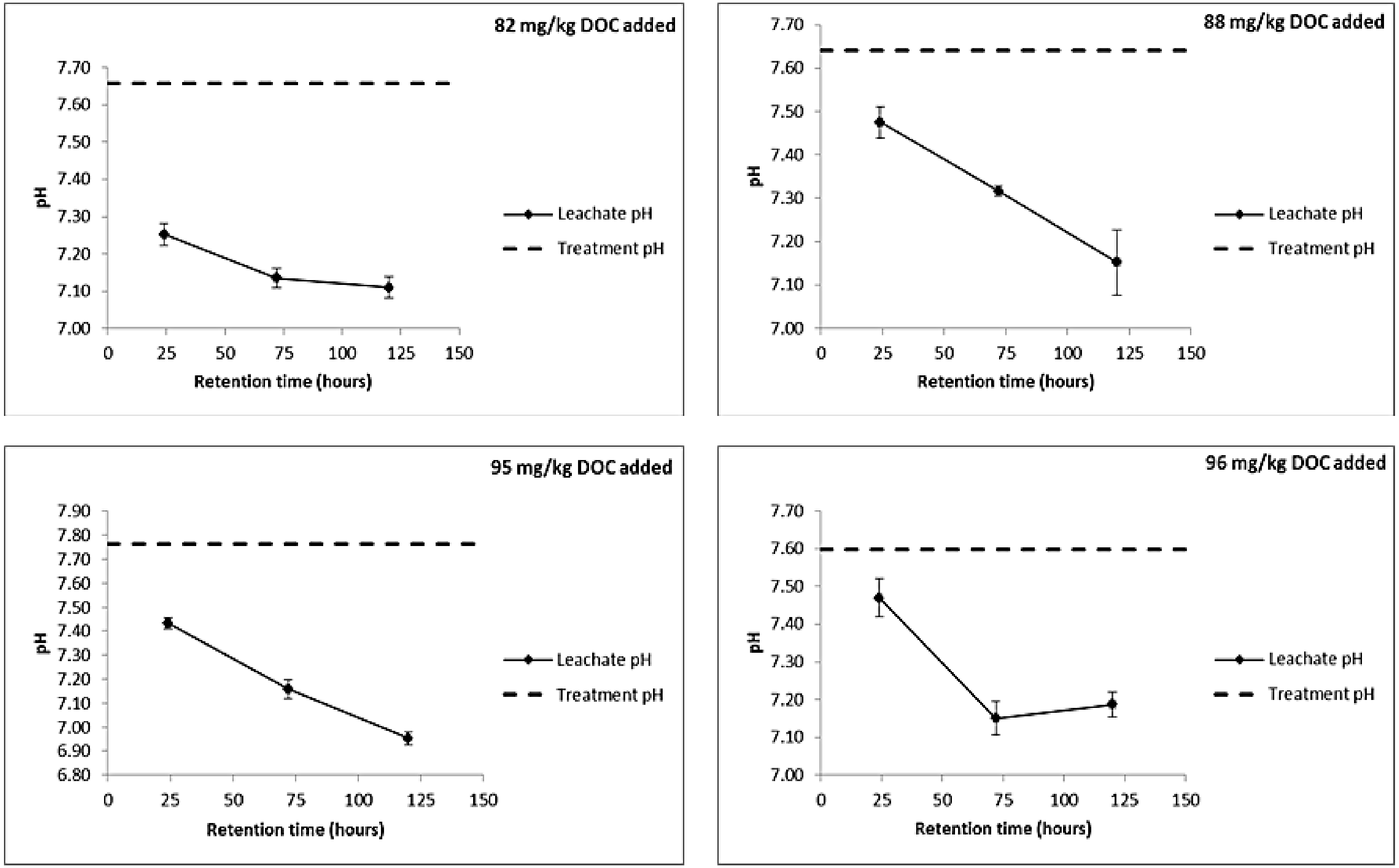


Figure 5.13. Influence of retention time on pH of leachates from O horizon soil beneath heather after contact with mineral soil. Error bars show standard error of the mean, n=4.

The conductivity of the leachates collected from the soil columns treated with GDOC was significantly (H(3) = 24.99, $p < 0.001$) affected by the input concentration of the DOC. For the lower concentrations of added DOC the conductivity of the leachates increased from that of the added DOC solution at T0, while for the highest concentration of added DOC (88 mg/kg) the leachates showed a decrease in conductivity from that of the treatment solution (T0 leachate) added to the columns (Figure 5.14). The conductivity of leachates collected from soil columns treated with HDOC was significantly affected by retention time (H(2) = 7.69, $p = 0.02$) and the concentration of added DOC (H(3) = 23.84, $p < 0.001$). The range of conductivities observed for the leachates of the 95 mg/kg treatment (127 µS/cm to 137 µS/cm) was higher than that of the other treatments (82 mg/kg treatment = 97 µS/cm to 115 µS/cm; 88 mg/kg treatment = 102 µS/cm to 121 µS/cm; 96 mg/kg treatment = 113 µS/cm to 126 µS/cm; Figure 5.15).

5.3.3.3 *Quality of the DOC in the leachate as determined by SUVA.*

The Wilcoxon signed rank test showed that there was a significant decrease in the SUVA between the original soil solutions and the leachate collected at 120 hrs for treatment solutions sourced from both vegetation types, (Z= -3.516, $p <0.001$). SUVA decreased most in the leachates derived from beneath the heather (5.05 ± 0.06 L m/mg to 0.33 ± 0.02 L m/mg) than those sourced from beneath the grass (4.69 ± 0.10 L m/mg to 0.32 ± 0.04 L m/mg; Figure 5.16). However, for both DOC sources there was no significant difference between the SUVA of the solutions at the very start of the experiments and the leachates at the end (120 hours). The input DOC concentration also had no significant effect on the SUVA of the leachate collected after 120 hrs.

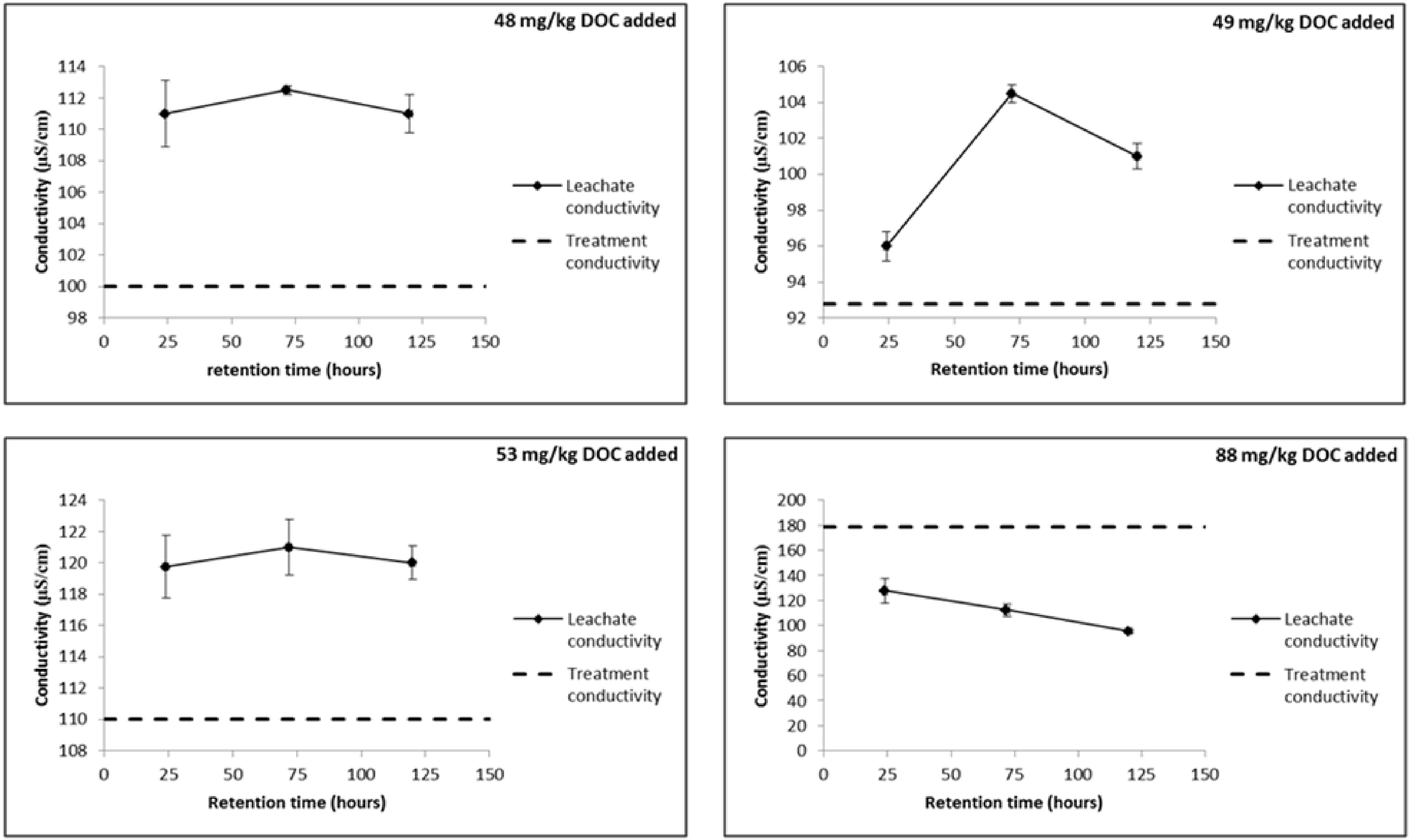


Figure 5.14. Influence of retention time on conductivity of leachates from O horizon soil beneath grass after contact with mineral soil. Error bars show standard error of the mean, n=4.

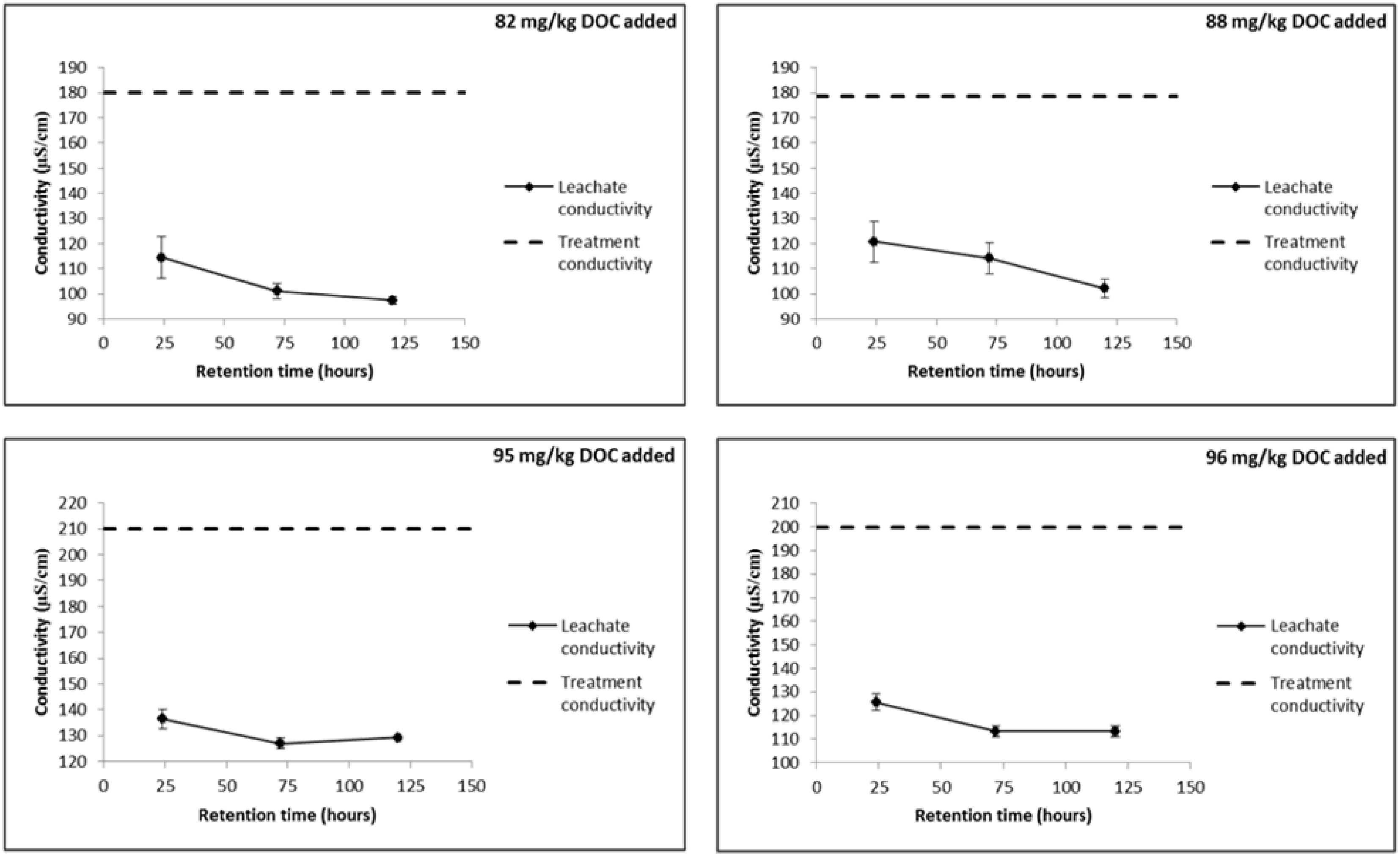


Figure 5.15. Influence of retention time on conductivity of leachates from O horizon soil beneath heather after contact with mineral soil. Error bars show standard error of the mean, n=4.

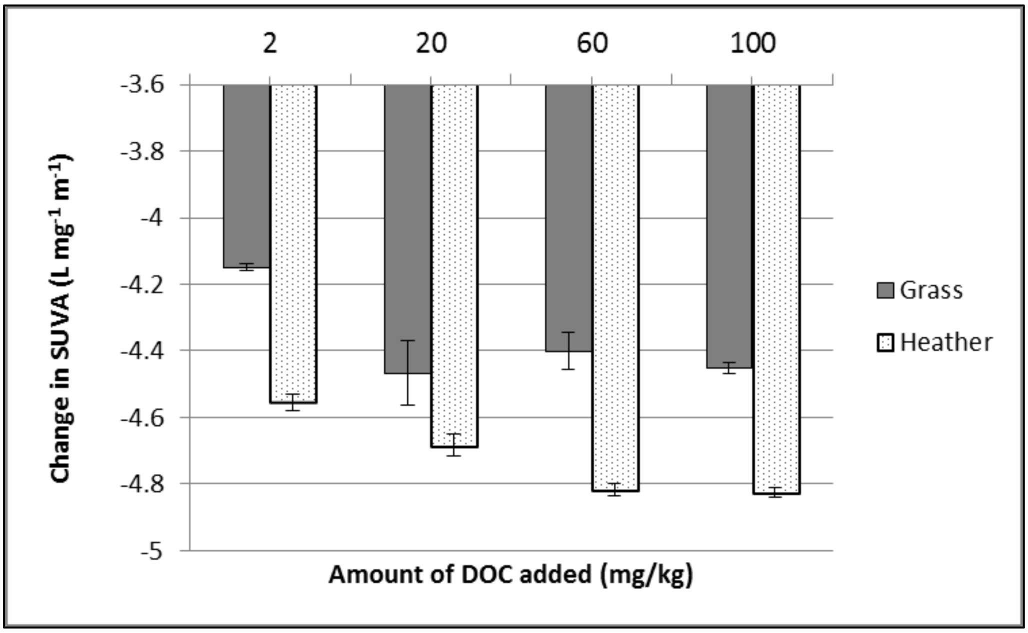


Figure 5.16 Change in SUVA between pre and post adsorption DOC solutions of grass and heather. Error bars show standard error of the mean, n=4.

Using the equation presented by Weishaar et al. (2003) that links SUVA to percent aromaticity (% aromaticity = 6.52*SUVA + 3.63), the difference in aromaticity of the two DOC sources was small. The solution derived from the peat beneath grass contained 34 ± 1 % aromatic carbon compounds, whereas solution derived from the peat beneath heather contained 37 ± 0 % aromatic compounds. After 120 hrs the post-adsorption leachate derived from peat beneath grass contained 8 ± 1 % aromatic carbon compounds, whereas leachate derived from the peat beneath heather contained 6 ± 0 % aromatic compounds.

5.4 Discussion

The work described in this chapter shows that sorption equilibrium between the mineral soils and soil solution is reached within 24 hours of the soil solution entering the mineral layer. Adsorption within the mineral soil is influenced by DOC concentration and source. There is an active exchange of carbon between the soil and the soil solution which results in the exchange of high aromatic DOC for low aromatic DOC (as inferred by SUVA). Additionally it was observed that there is a fixed equilibrium which exists between the soil and DOC which differs by DOC source. These main findings and their implications for DOC dynamics within upland catchments will be discussed further in this section.

5.4.1 The dynamics of the interaction between added DOC and mineral soil following the re-wetting stage.

5.4.1.1 *Input concentration controls DOC adsorption and desorption to mineral soil but has no effect on DOC export from the mineral horizon*

The results show that there is a concentration effect on the adsorption and desorption of DOC from mineral soil; addition of low concentrations of DOC resulted in net desorption while higher concentrations resulted in net adsorption. This concentration effect is most likely a reflection of the null point of the soil for these solutions. The null point is the point at which adsorption and desorption are in equilibrium (Kerr and Eimers, 2012). At concentrations above the null point adsorption occurs and at concentrations below the null point desorption occurs (see section 3.4.2). The observation of adsorption at the higher concentrations within this study does support the theory that the observation of net desorption in chapter three for similarly sourced DOC was due to the lower concentration ranges (heather = 5 -49 mg/L; grass = 4.5 -31 mg/L; see section 3.4.2).

The DOC source influenced the concentration effect; for HDOC adsorption was seen only in the 100 mg/kg treatment while for GDOC adsorption was observed in the 60 and 100 mg/kg treatments. The concentrations of DOC in the leachates were not significantly different among the four treatments, for grass the average DOC was 90.1 ± 3.2 mg/kg and for heather the average DOC was 59.6 ± 9.5 mg/kg. This suggests that there is a fixed equilibrium DOC concentration which exists between the soil solution and leachate and that this equilibrium is specific to the DOC source. This concept is shown in figure 5.17. This is an interesting finding because the amount of sorption observed has been interpreted as a measure of soils’ ability to limit the export of DOC (Nelson et al., 1992). Nelson et al. (1992) studied two adjacent catchments with similar land use, climate, vegetation and topography but different soils. These researchers observed that the amount of DOC exported to streams was lower in the catchment with soils which had higher clay contents. (Nelson et al., 1992). It was also observed that the soils with the higher clay contents had a greater adsorption capacity for forest DOC (Nelson et al., 1992). It was therefore suggested the lower stream water DOC in the catchment dominated by soils with high clay contents was due to the greater adsorption capacity of the soils (Nelson et al., 1992). The results presented in this chapter however suggest that the DOC adsorption capacity of a soil may not be reflective of the potential to limit DOC export from a soil.

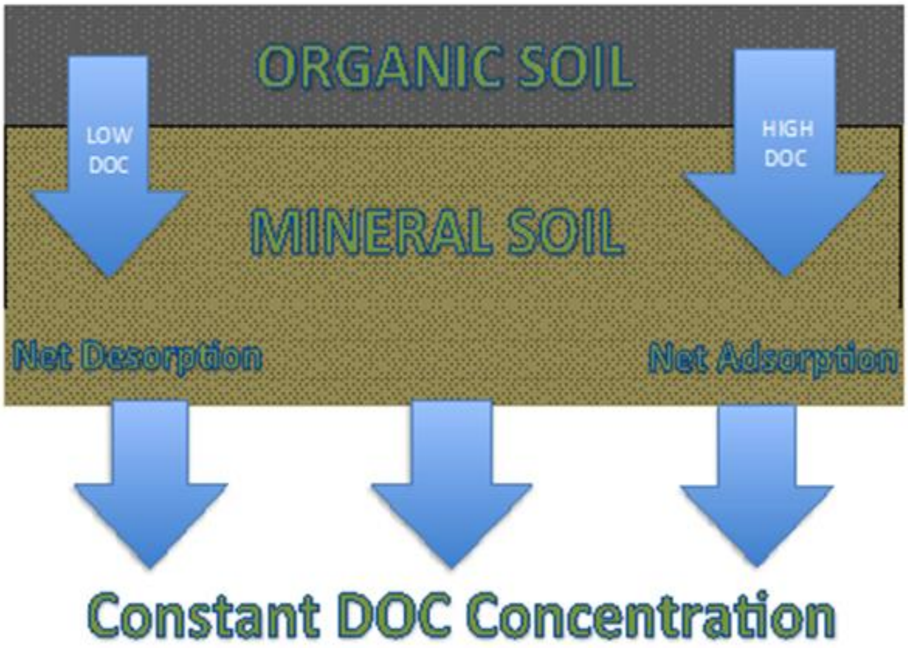


Figure 5.17. Conceptual model of the relationship between DOC sorption in mineral soils and its export from mineral soils.

There was a clear influence of DOC source on DOC sorption; the concentration at which adsorption begins to occur between the mineral soil and the DOC added is much lower for GDOC (>47 mg/kg) than HDOC (>95.6 mg/kg). It is surprising that GDOC is sorbed more readily by the soil because GDOC had a lower SUVA (4.69 ± 0.1 L m/mg) than HDOC (5.05 ± 0.1 L m/mg). SUVA is often used as a measure of the aromatic composition of DOC, with higher SUVA values indicating higher aromatic content (Weishaar et al., 2003). It is the high aromatic DOC which is thought to be favoured for sorption to mineral soils (Kaiser et al., 1996). Therefore HDOC would be expected to be more readily adsorbed by the mineral soil. The fact that this did not occur is showing that the mineral soil used in this study has a greater affinity for GDOC. This also suggests that DOC sorption is insensitive to subtle differences in SUVA.

This work presented in this chapter supports the work presented in chapter three of this thesis, where differences in the sorption characteristics of DOC derived from the organic horizons beneath grass, heather and forest were observed. However, the two chapters contradict each other in the order in which net desorption is favoured. In chapter three greater net desorption after 24 hours was seen from the mineral soils treated with DOC sourced from beneath grass (GDOC), while the results from this chapter show greater net desorption when the added DOC is sourced from beneath heather (HDOC). Differences in the experimental methods could be the likely cause of differences between the work described in chapter 3 and the work described here. Chapter three was a batch study, and in batch studies soil particles may be broken into smaller pieces during the shaking, resulting in greater surface area of the solid being exposed to the solution (Mon et al., 2006; Qualls and Haines, 1992). This would provide a greater surface area available for adsorption of solutes from the solution or there can be greater desorption from the mineral surface (Qualls and Haines, 1992). Conversely in column studies due to compaction of the soil, there may be some surfaces on the sorbent which are isolated from contact with the solution as it flows through the column (Qualls and Haines, 1992). The two studies also differed in their soil to solution ratios and it has been shown by Kaiser et al. (2001b) that with increasing soil to solution ratio there is increased release of DOC from the mineral soil. This would explain why greater desorption was seen for the two DOC sources in the batch study than in the column study. The differences in methodology do not easily explain why the order in which desorption is favoured between the two DOC sources differs between the column and batch studies.

Another possible explanation of the differences between the batch and column studies is that the character of the added DOC and or the properties of the mineral soils differed since the two studies were conducted on soils sourced from two different locations in the UK. The mineral soils used in both experiments are classed as cambic stagnohumic gleys, however comparison of the properties of the two soils (Table 5.3) shows that the Marsden soil has a higher content of the metal oxides (Al_p = 1.19 mg/g; Al_o = 1.9 mg/g; Fe_p = 2.76 mg/g; Fe_o = 10.39 mg/g) than the Kielder mineral soil used in the batch study (Al_p = 1.01mg/g; Al_o = 1.53 mg/g; Fe_p = 2.36 mg/g; Fe_o = 5.65 mg/g). While the Kielder mineral soil had a higher clay content (14.5 %) than the Marsden soil (7.2 %). The higher metal oxide content of the Marsden soil may be a controlling factor in its greater affinity for the DOC derived from grass; while the higher clay content of the Kielder soil may be a controlling factor in the higher affinity for DOC derived from peat soil covered with heather.

Table 5.3. Comparison between the Marsden and Kielder mineral soils of soil properties commonly associated with sorption of DOC to mineral soils.

Soil property	Site where soil was collected	
	Marsden	Kielder
Carbon (mg/g)	8.43 (0.03)	19.4 7.1 (after treatment with NaOCl)
C/N	8.97 (0.2)	23.85 (0.25)
pH H_2O	4.87 (0.01)	4.64 (0.03)
Al_p mg/g	1.19 (0.01)	1.01 (0.01)
Al_o mg/g	1.90 (0.04)	1.53 (0.04)
Fe_p mg/g	2.76 (0.07)	2.36 (0.05)
Fe_o mg/g	10.39 (0.44)	5.65 (0.20)
Clay (%)	7.2	14.5

The greater affinity of the soil for GDOC may be a reflection of the more decomposed state of the DOC from grass. The grass with its nutrient rich, lignin poor litter would have been degraded more readily than the recalcitrant woody litter of heather (De Deyn et al., 2008). Grass therefore could have more products of microbial metabolism. Spielvogel et al. (2008) found there was a significant positive ($p \leq 0.05$) relationship between microbial derived sugars and poorly crystalline (Fe_o) iron oxides of Bw horizon soils of a laxic cambisol. Spielvogel et al. (2008) examined the chemical composition of carbon associated with A, B and C horizons from three soils (a laxic cambisol rich in sesquioxides; a skeletic cambisol poor in sesquioxides; and an entic podzol). The microbially derived sugars increased with increases in poorly crystalline Fe (Fe_o) ($R^2 = 0.88$) while no significant relationship was seen between Fe_o and plant derived sugars or lignin (Spielvogel et al., 2008). The findings of Spielvogel et al. (2008) might explain why greater sorption of GDOC is seen in the research described in this chapter. Considering that the organic carbon produced by grass is more readily degraded than that of heather, it is likely that DOC derived from peat covered by grass will have more products of microbial metabolism SOM. Therefore the higher Fe_o content of the mineral soil in this study readily sorbs these products of microbial origin.

The possibility of a greater affinity of iron oxides for GDOC over HDOC is still contrary to previous findings in the literature. Previous studies have shown that sorption of DOC rich in aromatic moieties is favoured by synthesized iron oxides (Gu et al., 1994; Kaiser, 2003) as well as soils rich in iron oxides (Kaiser et al., 1997; Ussiri and Johnson, 2004). In addition to reporting that sorption to mineral surfaces is favoured by aromatic carbon, some of the previous studies also reported that sorption was related to the carboxylic acid functional groups in the DOC (Gu et al., 1994; Sanderman et al., 2014; Ussiri and Johnson, 2004). Using UV-visible spectroscopy, Nuclear Magnetic Resonance spectroscopy, Infrared spectroscopy and high performance size exclusion chromatography, Kang and Xing (2008) observed that the sorption of DOC derived from a soil humic acid to the crystalline iron oxide, goethite, resulted in the sorption of polar alkyl carbon compounds, and that high molecular weight aromatics were left in the equilibrium solution. Kang and Xing (2008) also observed that goethite had sorption sites for carboxylic acid. Comparison of the research of (Kang and Xing, 2008) with previous studies in the literature (Gu et al., 1994; Ussiri and Johnson, 2004) indicates that it is the reactive functional group in DOC which is significant in sorption rather than the degree of aromaticity. Therefore although the HDOC used in this study was more aromatic than the GDOC it is possible that differences in the reactive functional groups could have led to the greater affinity of the soil for GDOC. However, without knowledge of the specific chemical composition of each of the DOC sources used in this study it is not possible to confirm that the soil is showing affinity for specific functional groups.

A fixed DOC equilibrium concentration for soil solution may seem contradictory to previous research which has shown seasonal variations in DOC concentrations in soil solution and catchment surface waters (Tipping et al., 1999; van den Berg et al., 2012). However, this may not be the case and the two observations may in fact work well together in explaining seasonal DOC dynamics. In this study the equilibrium concentration at T0 differed between the two DOC sources. Seasonal changes in DOC quality have been reported in the literature. For example, Kaiser et al. (2001a) reported seasonal changes in the DOC released from organic floor layers of Scots Pine and European Beech forest. Summer samples were more hydrophobic with increased aromatic, aliphatic and carboxyl groups as well as lignin degradation products (Kaiser et al., 2001a). The variation was attributed to warm moist conditions of summer/autumn favouring increased microbial activity (Kaiser et al., 2001a). Therefore if the DOC equilibrium concentration is prone to change when the quality of the input DOC changes, then it is possible that seasonal changes in the input DOC will cause that shift leading to the observed seasonal variation in DOC exported to catchment waters.

5.4.1.2 *Leachate characteristics indicate adsorption occurs by Ligand exchange*

The observed increases in pH and conductivity with increasing concentrations of added DOC are indicative of the release of ions into the solution. This suggests that ligand exchange is the dominant mechanism by which DOC is being adsorbed to the soil. Carboxyl groups are a major constituent of DOC (Steinberg, 2003), and therefore it is possible that the pH increase is the result of the soil's surface OH^- groups being displaced by the carboxyl groups in DOC when DOC is adsorbed. Kothawala et al. (2009) and Sodano et al. (2016) both report post adsorption pH increases in DOC solutions, however their pH increases were much lower than those seen in this study. These differences may be explained by differences in the amount of poorly crystalline Fe and Al oxides among the three studies. Sodano et al. (2016) precipitated different amounts of Fe (hydr)oxides onto vermiculate and conducted sorption studies with paddy soil DOC; the authors found that DOC sorption was improved by the presence of Fe (hydr)oxides. By using FTIR Sodano et al. (2016) also showed that the interaction between DOC and Fe (hydr)oxides was through ligand exchange involving the carboxylic group. Kothawala et al. (2009) studied DOC sorption to 52 Canadian mineral soils and determined there was a statistical relationship between the amount of DOC adsorbed by soils and the amount of poorly crystalline oxides in soils. The soil used in the column experiments described in this chapter had a much higher poorly crystalline metal oxide content (Al_o =1.9 mg/g ± 0.04 and Fe_o= 10.39 mg/g ±0.44) than any of the soils used in the study by Kothawala et al. (2009), who reported averages of 0.0009 mg/ g – 0.0227 mg/ g for Al_o and 0.001 mg/g – 0.0198 mg/g for Fe_o. This indicates a greater amount of sites for ligand exchange in the Marsden soil used here and therefore greater potential for organic anion exchange for OH^-, leading to a substantial increase in pH in post adsorption.

5.4.2 The effects of increasing retention time of DOC soil solution on the dynamics of the interaction between added DOC and mineral soil.

5.4.2.1 *Sorption equilibrium between DOC and mineral soil is established within the first 24 hours of contact*

When the leachate was added back into the soil columns after the re-wetting stage (T0) it was observed that the concentration of DOC in the leachate collected 24 hours later (T1) differed significantly from the amount of DOC added. Increasing the retention time of the soil solution in the soil columns beyond 24 hours had no effect on the amount of DOC adsorbed by the mineral soil or leached from the soil column. This would suggest that sorption equilibrium between the DOC in the soil solution and the mineral soil is reached within 24 hours. This finding supports the work of previous batch studies which have shown that DOC sorption/desorption occurs within the first 24 hours (Moore et al., 1992; You et al., 1999). Moore et al. (1992) found that >90% of the DOC sorption which occurred in 48 hours took place in the first 24 hours of the batch experiment. You et al. (1999) conducted timed SOM desorption equilibrium experiments at a range on water:soil ratios (25:1, 5:1 and 1:1) for between 4 and 72 hours and found that the DOC concentration stabilised after 24 hours. The results of this chapter, along with the batch studies referred to above confirm that most of the DOC sorption to mineral soils occurs within 24 hours and justifies the use of 24 hours as an appropriate length of time for studying DOC sorption in both batch and column experiments.

5.4.2.2 *Input DOC concentration affects the amount of DOC adsorbed and may or may not affect the concentration of DOC leached*

Similar to the results of the re-wetting step (T0), it was found that the concentration of DOC in the input solution had an effect on the amount of DOC adsorbed or desorbed from the mineral soil. However, contrary to the re-wetting step it was found that the input concentration also influenced the amount of DOC leached from the soil column. For GDOC, the addition of DOC in the concentration range 48 – 53 mg /kg resulted in leachates with higher DOC concentrations, while the addition of the highest concentration (88 mg/kg) resulted in leachates of a lower DOC concentration. In contrast, HDOC had a narrower range of DOC concentrations (82-96 mg/kg) but the amount of DOC in the leachates differed significantly with concentration ($p < 0.001$).

The observation of a concentration effect on the amount of DOC in the leachates collected beyond T0 is most likely due to changes that occurred in the characteristics of the soil solution DOC during the re-wetting stage. To reach the fixed equilibrium concentration some treatments resulted in greater net desorption of DOC than others, and this could have led to compositional differences in the DOC collected from the various treatments at T0, if the composition of the DOC that desorbed differed markedly to that in soil solution. If as suggested in section 5.4.1.1 leachate DOC concentration is dependent on DOC quality, then the compositional differences in the DOC collected at T0 would lead to differences in the way the DOC interacts with the mineral soil when reapplied to the soil columns. For leachates collected beyond T0 the effects of differences in DOC composition may have been disguised as concentration effects. A limitation of this experiment is that the quality of the DOC in the leachate at T0 was not assessed due to low sample volume, and therefore the possibility of compositional changes between the treatment solutions at the start of the experiments and the leachates at T0 cannot be confirmed.

5.4.2.3 *Leachate characteristics indicate aromatic carbon is adsorbed.*

There was a significant decrease in SUVA between the initial DOC solutions derived from the organic horizon beneath the two vegetation types and the leachates obtained at the end of the experiment (i.e. after 120 hours). Since SUVA is used as a proxy for aromatic carbon content (Weishaar et al., 2003), the observed change in SUVA indicates that the mineral soil preferentially adsorbed the aromatic carbon in the soil solutions. This finding is similar to previous studies which have shown it is the hydrophobic fraction or aromatic carbon that is preferentially adsorbed to mineral soil surface (Kaiser et al., 1996; Ussiri and Johnson, 2004). Therefore, the observed change in SUVA values is indicating that there is an active exchange of DOC between the soil solution and the soil matrix.

5.5 Conclusion

This study sought to understand the influence of soil solution retention time on DOC adsorption to mineral soil. The findings reported here have shown that regardless of the DOC source and DOC concentration sorption equilibrium is reached between the soil and soil solution within 24 hours. This suggests that in soils prone to seasonal waterlogging sorption equilibrium between the soil and DOC in soil solution would be reached within 24 hours.

Additionally this study has shown that the DOC source does affect the amount of DOC adsorbed by the mineral soil; the soil used in this study had a greater affinity for GDOC (DOC extracted from peat dominated by grass) than for HDOC (DOC extracted from peat dominated by heather). There was also an exchange of DOC between the mineral soil and soil solution as indicated by the decreased SUVA in the leachates collected at the end of the experiments when compared to the SUVA of the treatments. This suggests that DOC of a low aromatic character will be released from mineral soil in catchments dominated by heather and grass.

This study has also shown that there may be a sorption equilibrium concentration which exists between DOC and mineral soil and that this sorption equilibrium is only affected by the composition of the DOC source. This would suggest that should predicted climate changes lead to increased production of DOC the soil will buffer the DOC increases by releasing or adsorbing DOC to maintain that sorption equilibrium.

6 Synthesis

This chapter discusses the relationship between the main findings of this thesis and the implications of these findings for the retention and release of DOC in mineral soils of upland catchments. First a summary of the main findings of the previous three chapters is presented followed by a discussion of their implications and the presentation of a conceptual model which gives an overview of sorption processes in upland catchments. Finally suggestions for future research are proposed.

6.1 Summary of the main findings

6.1.1 The effects of vegetation cover on the sorption of DOC to mineral soils

Chapter three sought to determine if there were differences in the composition (quality) and adsorptive properties of DOC leached from surface peat developed under different types of vegetation (objective 1). The results indicated that the DOC produced in O-horizon soil beneath heather, grass and forest differs in its quality and sorptive properties. Using SUVA as a proxy for aromaticity it was observed that the heather DOC was most aromatic while the grass DOC was the least aromatic. Net adsorption was seen in mineral soil treated with forest DOC, while net desorption was seen in the same mineral soil treated with heather and grass DOC. Despite the observation of net desorption when the soil was treated with heather and grass DOC, there was clearly an exchange of DOC between the mineral soil and DOC solutions, evidenced by a decrease in SUVA following sorption. Treatment SUVA was no indicator of whether or not DOC was adsorbed, since the forest DOC had a SUVA value which was midway between that of the heather and forest DOC, and yet forest consistently showed adsorption with no significant change in SUVA. Additionally, Treatment SUVA was no indicator of whether or not exchange occurred between the mineral soil and the DOC solution. This was shown by the observation that grass and heather which had quite different treatment SUVA both decreased dramatically in the desorbed solutions. The observed differences in the quality of the leachate collected after mineral soil from the same location was treated with the three sources of DOC therefore suggests that vegetation cover will also affect the quality of DOC exported from mineral soils.

6.1.2 The capacity of Upland mineral soils to retain DOC and the soil properties which influence sorption.

Chapter four sought to determine the total capacities of UK upland soils to adsorb DOC (objective 2) and the soil properties which influence sorption within these soils (objective

3). The modified Langmuir isotherm was used to estimate the maximum adsorption capacity (Q_{max}) of 20 mineral soils and the estimated Q_{max} values ranged from 835 mg/kg to 6002 mg/kg. The measured soil organic carbon (SOC) contents of the soils ranged from 9.1 g/kg to 81.6 g/kg .The experimentally measured sorption at the highest concentration of added DOC (RE_{112}) showed there was a positive relationship between sorption and the iron oxides. The modelled Q_{max} showed no relationship with the extractable iron in these soils, this suggests the modelled sorption capacities (Q_{max}) may not be reflective of the true sorption capacity of these soils. The results of this study also show that the UK upland mineral soils are not currently saturated as suggested by the observation of net adsorption in all soils across the experimental range of added DOC concentrations. Of the properties measured the dominant control on desorption in these soils was the amorphous forms of Al (which accounted for 31% of the variation in desorption). Desorption decreased with increasing amounts of amorphous Al. The dominant controls on the capacity to adsorb DOC in these soils were the amount of amorphous Al_o (explaining 39 % of the variability), pH (explaining 34 % of the variability) and clay content (explaining 20.8% of the variability). No significant differences were observed by horizon or soil type. However, mineral soils vegetated with graminoids were found to retain large amounts of DOC compared to mineral soils beneath forest or shrubs. A major part of the variability in sorption was not accounted for by the properties measured which would suggest that there is some additional control on the adsorption and desorption of DOC in these soils. However this additional control was not identifiable within the scope of this thesis.

6.1.3 The influence of retention time on the adsorption of dissolved organic carbon to mineral soil.

Chapter five sought to determine whether soil solution retention time within the mineral soil had an impact on the amount of DOC adsorbed or released (objective 4). Using a column study it was found that beyond 24 hours there was no significant change in the amount of DOC adsorbed or desorbed from mineral soil. Additionally the results of chapter five revealed that there was a fixed equilibrium concentration between the DOC and mineral soil and that the equilibrium concentration differed according to the DOC source. This was inferred from the observation that the concentration of DOC in the leachates did not differ significantly between the treatments but did differ between the DOC sourced from peat beneath heather and grass. There was also an exchange of DOC between the mineral soil and soil solution as suggested by the decreased SUVA in the leachates collected at the end of the experiments when compared to SUVA of the treatments.

6.2 Implications of these findings

This thesis has expanded the knowledge of the factors controlling the sorption of DOC in upland organo mineral soils. Emerging from this thesis are six major findings with regards to retention and release of DOC in UK upland organo-mineral soils: i) The hydrophobic or aromatic character of DOC as determined by SUVA is no indicator of sorption behaviour of DOC to mineral soils; ii) vegetation cover greatly influences the quality of DOC leached from the organic horizons and the subsequent sorption of that DOC to mineral soils; iii)there is a fixed equilibrium concentration between the mineral soil and DOC solution which varies by DOC source; iv) despite the presence of large amounts of iron oxides within these soils, iron oxides are not among the dominant controls of DOC sorption within these soils; v) despite containing a large amount of organic carbon, UK upland organo-mineral soils are not carbon saturated and have the ability to retain more DOC; vi) soil pH is a major control on the adsorption of DOC within these soils.

Firstly, the observation that the aromatic character of DOC as measured with SUVA was not an indicator of whether or not sorption would occur in the mineral soil was intriguing. It is generally accepted within the literature that hydrophobic or highly aromatic compounds are favoured for adsorption to mineral soils (Kaiser et al., 1996; Kalbitz et al., 2005) . However the findings of chapters three and five of this thesis suggest that depending on their mineral make-up soils may show specificity for some DOC substrates over others. This specificity is not dependent on the overall hydrophobic or aromatic character of the DOC but may be related to the specific chemical composition of that DOC. For example in chapter three it was seen that sorption of the forest DOC was favoured over the more aromatic (as inferred from SUVA) DOC of heather. While, in chapter five it was found that the mineral soil exhibited a higher affinity for grass DOC over the more aromatic (as inferred from SUVA) DOC from heather. Within the scope of this thesis it was not possible to determine the specific properties that would cause one type of DOC to be favoured over the other. However the results here are consistent with the conclusions of a few published studies that implicate lignin composition as a determinant in the sorption of DOC (Guggenberger and Zech, 1994; Hernes et al., 2007). This suggests that vegetation cover can be used as a management strategy to control DOC behaviour in upland catchments. However as this thesis used laboratory experiments further work is needed before drawing conclusions on applications at field scale. It should be noted that the work of chapters three and five differed in the affinity of the soils for DOC sourced beneath grass and heather. The stagnohumic gley sourced from Kielder forest which was used in the experiments described in chapter three showed a greater affinity for DOC from heather.

While the stagnohumic gley sourced from Marsden Moor which was used in the experiments described in chapter five showed a greater affinity for grass. While it is not possible to rule out that these differences might be due to differences in methodology, it is also likely that the differences could be due to differences in the mineral make-up of the soils. The soil used in chapter three had a higher clay content than the soil used in chapter five. While the soil used in chapter five had a higher Fe_o content. This indicates that when selecting vegetation to control DOC dynamics some consideration should also be given to the mineralogy of the dominant soil types in the catchment.

This thesis focussed on DOC extracted from peat soils beneath different vegetation covers as this is considered to be the major source of DOC to the mineral horizons whose sorption properties were being investigated. However, organic horizons will not be the only sources of DOC within the catchment. Vegetation litter also contributes to the DOC exported to surface waters and a greater amount of DOC is typically leached from fresh litter than from peat soils (Ritson et al., 2014a; Tang et al., 2013). Therefore if vegetation were to be considered as a management strategy for the control of DOC in catchment waters, consideration should be given to the quantity and quality of DOC produced by vegetation litter. Dependent on the hydrological pathway of water in the catchment litter sources may be a significant contributor to the DOC seen in surface waters. Further work is needed to determine the sorption parameters of different litters.

The observation of a fixed equilibrium concentration between the mineral soil and the DOC which varied with DOC source was interesting. Sorption of DOC to mineral soils is considered to be an indicator of amount of DOC that will be exported (Nelson et al., 1992; Ussiri and Johnson, 2004). However the results of chapter five indicate that amount sorbed may not truly reflect the amount of DOC that will be released from the soils. The attainment of that equilibrium concentration will be dependent on the soil and soil solution being in contact for the time required to reach sorption equilibrium. In chapter five of this thesis as well as within the literature (You et al., 1999) sorption equilibrium was reached within 24 hours. However in freely draining soils such as podzols or during storm events the flow of soil solution through the soils may be more rapid and so sorption equilibrium may not be reached and as such this equilibrium concentration may not be reflected in DOC exported from these soils.

What is also interesting about this equilibrium concentration is that whether adsorption or desorption dominated both the quantity and the quality of the DOC released from the soil was the same. The quality as measured with SUVA always showed a reduction in aromaticity indicating an active exchange of DOC between the soil and soil solution. Considering that these soils have a finite capacity for the retention of DOC (Chapter 4), and that the DOC bonded to the dominant sorption sites is irreversibly bound (Kaiser and Zech, 1999), the question then arises, how will this equilibrium concentration be affected once the soils are saturated? It is possible there could be a ‘breakthrough’ of the DOC solution where it is completely unchanged as it passes through the mineral layer leading to the export of more aromatic and highly coloured DOC. However it is not possible to determine this within the scope of this thesis and so the effects of saturation on the sorption equilibrium would need to be investigated in future studies.

Land uses, such as livestock grazing, which can cause shifts in the dominant vegetation cover, could also impact on the DOC sorption in mineral soils. There is a long history of sheep grazing in the UK uplands which dates back to the 1700s with significant increases occurring between the 1950s and 1990s due to the introduction of subsidies (Holden et al., 2007; Lilly et al., 2009). Sites where heavy grazing is prevalent can show a decline in the cover of heather and other shrubs, and their replacement with graminoid species (Lilly et al., 2009). Based on the findings of this thesis a shift in the dominant vegetation to graminoids could result in greater export of DOC from the mineral horizons but that DOC would have a low SUVA and by inference a low hydrophobic or aromatic character.

The soils investigated in this research are currently not saturated with carbon (Chapter 4). However they do appear to have a limited number of binding sites for the retention of carbon (Chapter 4), therefore they can become saturated and potentially leach greater amounts of DOC. However the results presented in this thesis have shown that the attainment of a saturated state can be limited by the choice of vegetation cover. With forest and heather dominated sites potentially resulting in greater adsorption of DOC and thus soils will potentially reach saturation quicker (Figure 6.1). While sites dominated by grasses will adsorb less DOC due to a reduced affinity for DOC from this source (Chapter 3) and so will take longer to reach saturation, they will have a greater amount of available sorption sites and as such will be perceived to have a greater capacity for the retention of DOC than other vegetation covers (Chapter 4; Figure 6.1).

It should be noted that none of the measured soil properties could explain the difference in sorption behaviour of graminoid dominated soils, which suggests that sorption in these soils is controlled by other factors. Within this thesis non-sterile soils were used. By using non sterile soils more realistic estimates of the contribution of soil properties are likely to be attained. However the microbial community also plays a significant role in the processing of DOC within these soils. For example Jagadamma et al. (2012) observed that greater apparent adsorption was seen in non-sterilized soils than in sterilized soils when the substrates used were glucose and L-alanine, indicating that not all of the substrate was sorbed to the mineral soil but instead some was utilised by the microbes. While the use of the lignin precursor sinapyl alcohol showed no significant difference in sorption between sterile and non-sterile soils due to the lignin being more difficult to degrade by microbes (Jagadamma et al., 2012). Considering that fast growing plants such as grasses produce nutrient rich litter that is readily broken down (De Deyn et al., 2008), it is possible that the apparent increased sorption capacity reflects a greater utilisation of the DOC by microbes, resulting in less sorption and thus the availability of more sorption sites.

It was found that the dominant sites for adsorption are the amorphous forms of aluminium and the clay fraction which possibly indicates the involvement of the crystalline clay minerals. Surprisingly iron content had minor influence on DOC maximum sorption capacity within these soils. This could point to these sites being saturated with DOC. However, the observation of a minor correlation with the measured sorption at the highest concentration of added DOC (RE_{112}) suggests that Fe sites are not totally saturated with carbon. Another explanation for the lack of correlation between Q_{max} and the Fe contents is that there is great variability in the available Fe sorption sites due to the redox activity of iron in soils. Some upland soils such as the stagnogleys used in this study are prone to seasonal waterlogging (Avery, 1980) . Under waterlogged conditions iron in soils is reduced (Grybos et al., 2009; Stumm and Sulzberger, 1992) which results in the release of any associated adsorbates such as DOC (Grybos et al., 2009). As the soils dry and become aerated again the iron is oxidised once more and has the ability to adsorb DOC being leached into the mineral horizons. Due to this redox activity and the associated variable retention and release of DOC, a soil's ability to adsorb DOC may not be reflective of its Fe content.

Soil pH was found to be a major control on the adsorption of DOC to the mineral soils. However, the work in chapter four suggests that it is a decreasing pH (increasing acidity) that favours desorption of DOC in these soils. Considering that the deposition of acid ions is decreasing (Monteith et al., 2014; Monteith et al., 2007), it seems unlikely that increasing acidity would be the driver for increased DOC export from these soils. The findings of chapter four are also contrary to the current theory that DOC export to surface waters is due to a decrease in acidity of soils within the catchments as a result of decreasing acid deposition (Ekström et al., 2011; Evans et al., 2006; Evans et al., 2012; Monteith et al., 2007). Past research has shown that there is a pH optimum for DOC adsorption to mineral soils which occurs around pH 4 -4.5 (Jardine et al., 1989; Kennedy et al., 1996). Adsorption decreases at pHs above and below the optimum pH (Jardine et al., 1989). The soils used in this thesis were highly acidic and below the optimum pH for adsorption, therefore it is likely that recovery from acidification (increasing pH) is having the effect of enhancing DOC adsorption to these soils. The work of this thesis suggests that although pH is controlling the adsorption of DOC to the mineral soils, it is not driving the increased export of DOC from these soils. It could be that the increased export of DOC is being driven by increases in DOC production/release in organic horizons (Sawicka et al., 2016; Stutter et al., 2011; Vanguelova et al., 2010). Increased production in the organic horizon would mean increased input of DOC to the mineral horizons in catchments where longitudinal flow dominates. The mineral horizons in the highly acidic catchments (pH <4) are likely to be actively adsorbing DOC since they do have available sorption sites (see Chapter 4) and their existing pHs would allow adsorption. However, the amounts retained by the soil may not be enough to compensate for the increased inputs from the organic horizon. Furthermore, it is likely that if the mineral soils recover beyond their pH for optimum adsorption, their ability to retain DOC will be reduced and greater increases in DOC could be observed in soil solutions and surface waters of upland catchments.

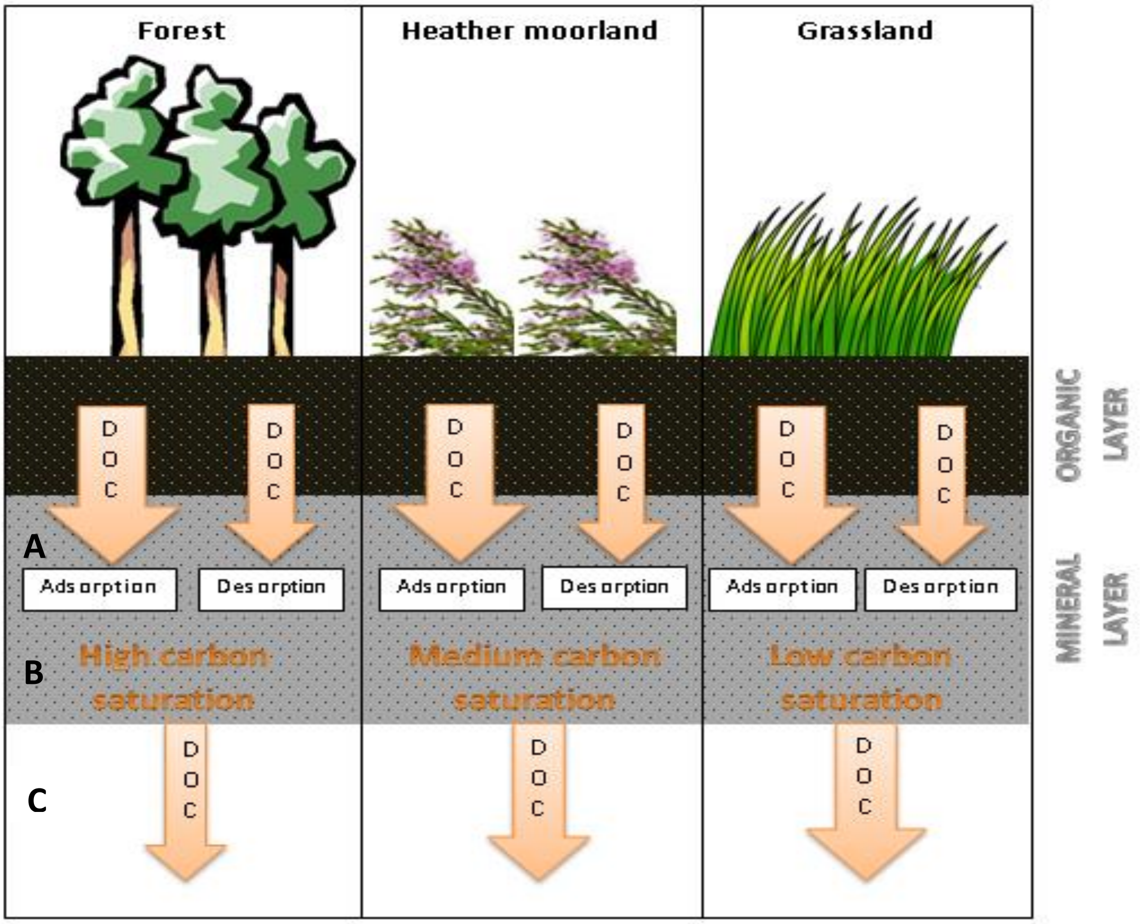


Figure 6.1. Conceptual model of the sorption processes occurring in mineral soils with DOC leached from organic horizons under different types of vegetation as investigated in this thesis: the size of the arrows indicate the relative concentrations of DOC, large arrows indicate high concentrations and small arrows indicate low concentrations. A) When DOC concentrations entering the mineral layer are high, DOC is adsorbed by the soil; when concentrations are low DOC is desorbed from the soil (Chapters 3 and 5). B) Soils beneath graminoids (which include grasses) have the capacity to retain greater amounts of DOC than soils beneath shrubs and forest (Chapter 4) and so are likely to be less saturated. Soils show a greater affinity for forest DOC (chapter 3) and so have the potential to be more saturated with carbon. While the soils show less affinity for the DOC sourced beneath heather and grass (Chapter 3) and so these are likely to become less saturated than the forest soils. C) Regardless of whether adsorption or desorption dominates in the mineral layer a fixed concentration of DOC is exported (Chapter 5.); this fixed concentration differs by DOC source (chapter 5; forest DOC was not tested in this chapter but it was assumed that a unique sorption equilibrium concentration would also have been reached with DOC from this source and so the findings have been extrapolated to include forest).

6.4 Future work

The findings of this thesis clearly showed differences in the sorption behaviour of DOC sourced from beneath forest, heather and grass, possibly due to differences in the sorptive properties of the DOC from each source. Within the scope of this thesis it was not possible to fully characterise the DOC from the three vegetation sources. Therefore future work should focus on identifying the chemical constituents of the DOC from these vegetation sources. Once the major chemical constituents have been identified it would be useful to study the sorptive properties of the pure forms of the dominant compounds to identify which compounds control sorption of DOC from these sources. Additionally the DOC leached from soils treated with the various chemical compounds should also be fully characterised to determine how the quality of DOC released from these soils differs according to the DOC source. Fourier transform ion cyclotron resonance mass spectroscopy (FT-ICR MS) is a method which could be employed in the molecular characterisation of DOC from different vegetation sources. FT-ICR MS has been successfully used to characterise humic acids before and after adsorption to alumina (Galindo and Del Nero, 2015) as well as the fractionation of DOM by a mineral soil (Avneri-Katz et al., 2017). Avneri-Katz et al. (2017) were able to determine that polyphenols and compounds with carboxylic groups were preferentially adsorbed following the adsorptive fractionation of DOM by a clay rich mineral soil. Therefore this technique could prove useful in studying the adsorption processes of DOC originating from heather, grass and forest at the molecular level.

The discovery of a fixed equilibrium concentration between the soil and soil solution should be studied further. This discovery emerged out of experiments designed to investigate how retention time affects the sorption of DOC from different sources (Chapter 5), as the focus was on time and DOC source, only one mineral soil was used. Therefore it would be useful to investigate the sorption equilibrium using a wider range of mineral horizons from stagnopodzols and stagnogleys. Also, since these soils seem to have a finite capacity for DOC (Chapter 4), knowledge of how the equilibrium concentration is likely to change once soils become carbon saturated would be of value. It would also be of value to examine how the intact soil structure impacts this sorption equilibrium. This would allow for better understanding of how the DOC and soils are likely to behave in the field.

The results of this thesis have indicated that soil properties do not fully explain the variability in DOC sorption within mineral soils and that DOC composition is a major control on DOC sorption. Therefore to aid with better prediction of DOC sorption behaviour in mineral soils, future research should move away from the traditional statistical regression models using only soil properties and look towards the development of physical models which integrate the properties of the DOC solution and properties of the soils.

The observed differences in the quality of DOC released from mineral soils treated with different sources of DOC can potentially impact the effective treatment of waters to which the DOC is exported. Therefore it would be useful to conduct experiments looking at the reactivity of DOC sourced from mineral horizons beneath these three vegetation covers towards the formation of disinfection by products. This could be done using methods similar to Ritson et al. (2014a) who looked at the treatability of DOC sourced from heather, sphagnum and peat. Ritson et al. (2014a) assessed the efficiency of the coagulation process for the removal of DOC from heather, sphagnum and peat. The reactivity of the post coagulation product to the formation of disinfection by-products was then investigated. The DOC sources investigated in the work of Ritson et al. (2014a) are representative of DOC at the points of production. This would be applicable in catchments where there is a greater amount of hydrological flow through surficial layers. However, in catchments where flow through the mineral horizons contributes greater to the DOC exported to surface waters knowledge of the reactivity of DOC released from mineral horizons would be of value.

The work described in this thesis was conducted in the laboratory using batch and column studies and as such some variables seen in the field were not accounted for. For example, the batch studies and repacked columns used in this work would not have accounted for the soil structure. Soil structure can refer to the arrangements of soil particles, the strength of particle aggregation and the features of the pore spaces (Elliot et al., 1999). Soil structure is important because it controls the storage and flow of fluids and heat through the soil (Elliot et al., 1999). The gentle grinding and sifting of the soils used in this thesis would have disrupted soil structure. Furthermore, the use of batch studies and packed soil columns would not have allowed soil structure to be maintained. Further work is therefore needed to determine if the observations made in this thesis are likely to occur in the field. Intact organo-mineral soil cores could be collected from under different vegetation covers and used in a leaching experiment in the laboratory to further investigate the sorptive behaviour of the DOC as it moves along the soil profile. Use of soil cores would allow soil structure to be maintained but conducting the experiments in the laboratory would control for climatic variables. Therefore to account for climatic variables and give a true representation of what would occur in the field, lysimeters could be placed in successive horizons along the soil profile under different vegetation covers and the soil solutions could be collected and analysed for changes in DOC quantity and quality.

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