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Assessing the impact of windfarm-related disturbance on streamwater carbon, phosphorus and nitrogen dynamics:

A case study of the Whitelee catchments

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Abstract

This research examined the impact which onshore windfarms sited on peat-based soils have on streamwater carbon (C), phosphorus (P) and nitrogen (N) dynamics. Significant disturbance to peatland arises through the excavation of borrow pits, construction of access tracks, insertion of turbine bases and associated deforestation during windfarm development – potentially increasing the transfer of C, P and N from terrestrial stores to the stream network. To identify which impacts occur, streamwater samples from nine catchments draining the Whitelee windfarm, Scotland, Europe's largest onshore windfarm, were collected approximately bi-monthly from October 2007 to September 2010 during and after windfarm construction, building on pre-disturbance data from Waldron *et al.* (2009). The samples were analysed for dissolved organic carbon (DOC), particulate organic carbon (POC), total organic carbon (TOC), soluble reactive phosphorus (SRP), total phosphorus (TP) and nitrate (NO_3^-). Time series were constructed and annual streamwater exports were calculated so that inter-catchment and annual differences could be detected.

DOC concentrations ranged from 2.9 mg L^{-1} to 57.1 mg L^{-1} and DOC exports ranged from 9.0 g m^{-2} yr^{-1} to 42.3 g m^{-2} yr^{-1}. POC concentrations ranged from 0.09 mg L^{-1} to 23.4 mg L^{-1} with POC exports ranging from 0.80 g m^{-2} yr^{-1} to 3.93 g m^{-2} yr^{-1}. DOC exhibited seasonality with maximum concentrations and exports towards the end of each summer. Harmonic regression analysis of the TOC data indicated a slight increase during the maximum phase of the seasonal cycle, coincident with windfarm-related disturbance observed in one catchment only. Regardless of windfarm development, streamwater DOC exports for four peatland-dominated catchments were observed to exceed typical values of C sequestration rate for Scottish peatlands over the four year time series.

SRP concentrations ranged from 1 μg L^{-1} to 289 μg L^{-1} and exports from 12 mg m^{-2} yr^{-1} to 104 mg m^{-2} yr^{-1} with TP concentrations and exports ranging from 2 μg L^{-1} to 328 μg L^{-1} and exports from 25 mg m^{-2} yr^{-1} to 206 mg m^{-2} yr^{-1} respectively. In two catchments where windfarm-related clear-felling and extensive brash mulching were carried out, as much as a tenfold increase was observed from June 2007 in P concentration, coincident with the timings of windfarm-related forestry operations. The water quality status of these two catchments declined from "good" to "moderate" in terms of the Water Framework Directive (2000) UK Technical Advisory Group Environmental Standards for SRP in Rivers, and had still not shown a full recovery after a further two years.

NO_3^- concentrations ranged from 0.001 mg L^{-1} to 2.44 mg L^{-1} and exports from 0.07 g m^{-2} yr^{-1} to 1.64 g m^{-2} yr^{-1}. Harmonic regression analysis indicated a potential impact on streamwater NO_3^- concentration through a change in the seasonal pattern observed in three catchments during 2007-2008, coinciding with windfarm-related disturbance.

To determine the most likely controls of C, P and N, a geographic information system (GIS) analysis was employed to describe the physiography of each catchment and to quantify the extent of windfarm-related disturbance. Multiple linear regression analysis was performed using median concentration and export for a low-disturbance phase from June 2006 to August 2007, and a maximum-disturbance phase from September 2007 until May 2009, with the catchment characteristics from the GIS analysis to identify potential impacts of windfarm-related disturbance.

The percentage of the catchment which was HOST class 15 and 29, both peat-based soil types, was observed to influence streamwater C, with the proportion of the catchment which was pasture observed to influence streamwater N. Windfarm-related disturbances were also found to control streamwater dynamics. The extent of deforestation was observed to greatly increase streamwater P concentration and that there was a smaller increase in C, with consequent impacts on SRP and POC export. The source of this additional C and P resulted most likely from forestry operations, namely, clear-felling large areas of catchment and extensive brash mulching associated with the windfarm habitat restoration, with new organic material available for decomposition and the potential for erosion of the newly-exposed soil surface. Residual fertiliser used to establish the conifer trees, the reduced vegetation uptake of soil P and P release from the roots of the felled trees are three further sources of P in streamwater. The distance to the nearest disturbance was also found to influence streamwater dynamics.

This research has shown that windfarm-related infrastructure can also influence streamwater chemistry, although exerting a less obvious impact: increasing access track length was correlated with decreasing POC and P concentration causing subsequent decreases in export. This is likely to be caused by the effective use of settlement ponds, flocculation blocks and ditch blocking in order to reduce the amount of particulate matter reaching the stream network and potentially through the adsorption of P by the access track construction material. Windfarm-related disturbance did not influence N dynamics; NO_3^- concentration was strongly correlated with HOST class 24 and the proportion of the catchment which was pasture, and NO_3^- exports were influenced by the flow length per catchment area, the percentage of coniferous forest cover and the extent of pasture.

Two recommendations for best practice at future windfarm developments on peatland are made: firstly, monitor C, P and N in streamwater in all catchments before, during and after windfarm construction on C rich soils as part of EIA process in order to ensure that water quality is maintained in rivers, to determine whether discharges from windfarm developments should require to be licensed and to improve the accuracy of C payback time estimates; and secondly, minimise brash-mulching to reduce the impact on streamwater P.

Furthermore, some suggestions for future research were proposed, including: plot studies to determine the best practice mitigation measures for P release in peatland catchments, longitudinal catchment studies, investigation of the relationship between access track construction material and streamwater dynamics, installation of continuous monitoring equipment along with a sampling regime which targets high flow events, examination of the changing stiochiometry, quantification of inorganic C and gaseous forms of C, and measuring catchment C sequestration rates.

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Declaration

I declare that the work described in this thesis has been carried out by myself unless otherwise acknowledged. This thesis is entirely of my own composition and has not, in whole or part, been submitted for any other degree at this or any other university.

Helen S. Murray

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Glossary of Abbreviations

C	carbon
$CaCO_3$	calcium carbonate
CO_2	carbon dioxide
CO_3^{2-}	carbonate
DOC	dissolved organic carbon
EIA	environmental impact assessment
GW	gigawatt
HCO_3^-	bicarbonate
HMP	habitat management plan
MW	megawatt
N	nitrogen
NH_3	ammonia
NO_2^-	nitrite
NO_3^-	nitrate
P	phosphorus
Pg	petagram
POC	particulate organic carbon
Q	discharge
SRP	soluble reactive phosphorus
TP	total phosphorus
TRP	total reactive phosphorus

Square brackets are used to indicate concentration

1. Windfarms on Peatland and Streamwater Chemistry

1.1. Chapter Outline

The aim of this thesis is to examine the impact which onshore windfarms sited on peatland may have on streamwater chemistry. The first part of this introductory chapter gives a brief overview of the scale of peatlands in Scotland as a carbon (C) store, outlines current Scottish Government renewables policy and provides some information about the extent of windfarms situated on highly organic soils and the potential for environmental impact during windfarm development. The speciation, sources and significance of C, phosphorus (P) and nitrogen (N) in streamwater are described next, followed by a section explaining what is meant by windfarm-related disturbance and how it can impact on C, P and N dynamics in streamwater. The Environmental Impact Assessment process required for windfarm developments is briefly reviewed in relation to the potential for impact on streamwater chemistry. The chapter concludes with five research aims and an outline of the thesis structure.

1.2. Windfarms on Peatland

Peatlands are globally critical stores of soil C (Gorham, 1991). In Scotland, with its cool climate, average rainfall of over 1500 mm per annum and an abundant supply of dead organic material which has not fully decomposed, peat has accumulated since the Holocene, covering ~ 14 % of the land area (Bragg, 2002). The C store of Scottish peatlands has been estimated as anywhere between 0.6 Pg (Robertson, 1971) and 16.4 Pg (Howard *et al.,* 1995), with the latest estimates reported as 1.62 Pg (Chapman *et al.,* 2009). Globally, this is small compared to estimates of C stored in peatland in Canada (154 Pg) (Kettles and Tarnocai, 1999) and the former Soviet Union (212 Pg) (Turner *et al.,* 1998), but it is significant locally, representing 56 % of the total C in Scottish soils (Chapman *et al.,* 2009). As climate change continues and C trading markets grow, C sequestered naturally in peatland will gain importance economically and politically, so there is a greater need now more than ever to understand the dynamics of Scotland's C stores to preserve them in the future.

Peatlands in the UK have been under threat for centuries from extraction of peat for use as a fuel or growing medium (Glatzel *et al.,* 2003; Rotherham, 2009), burning (Garnett *et al.,* 2000; Yallop and Clutterbuck, 2009), drainage (Strack *et al.,* 2008; Gibson *et al.,* 2009), grazing (Ward *et al.,* 2007) and afforestation (Grieve, 1994). With the growth of onshore windfarms there is much pressure again in Scotland for development on these C stores. In response to increasing CO_2 concentrations in the atmosphere, the Scottish Government put in place The Climate Change (Scotland) Act (2009), a legislative framework aiming to reduce greenhouse gas emissions associated with the use of fossil fuels and to increase the amount of electricity and heat generated from renewable sources. The Scottish Government has set a target of 100 % of energy generated to be from renewable sources by 2020. With a potential power output of 36.5 GW, Scotland has 25 % of Europe's wind energy resource (http://www.sdi.co.uk/Key%20Industries/Energy/Key%20Facts.aspx) and, as onshore wind turbines are currently the most developed technology and therefore have the lowest manufacturing cost, the bulk of this energy production will come from onshore windfarms. The number of onshore windfarms in Scotland has increased from just 22 in 2004 to 120 in 2011 (http://www.bwea.com/ukwed/index.asp) and they currently supply over 2.61 GW of renewable energy to Scotland.

However, the exposed, less agriculturally productive elevated landscapes which offer the most suitable sites for energy generation from windfarms are also the best for accumulating and storing C. By comparing the two maps in Figure 1 it is evident that onshore windfarms are often sited, or proposed to be sited, on areas of carbon rich soils which hold large stocks of soil C. The visual impact of windfarms on peatland has been much debated, but far less consideration has been given to how the landscape responds to hosting such infrastructure, especially in terms of streamwater chemistry. Disturbance to the soil during the construction of onshore windfarms, which involves the construction of access tracks as well as excavation to install the turbine bases, and can include deforestation, may impact on streamwater chemistry by increasing the transfer of C, P and N from the terrestrial environment to the stream network. This is undesirable for the protection of C stores and the maintenance of good quality streamwater in the usually low nutrient status streams which drain peatland.

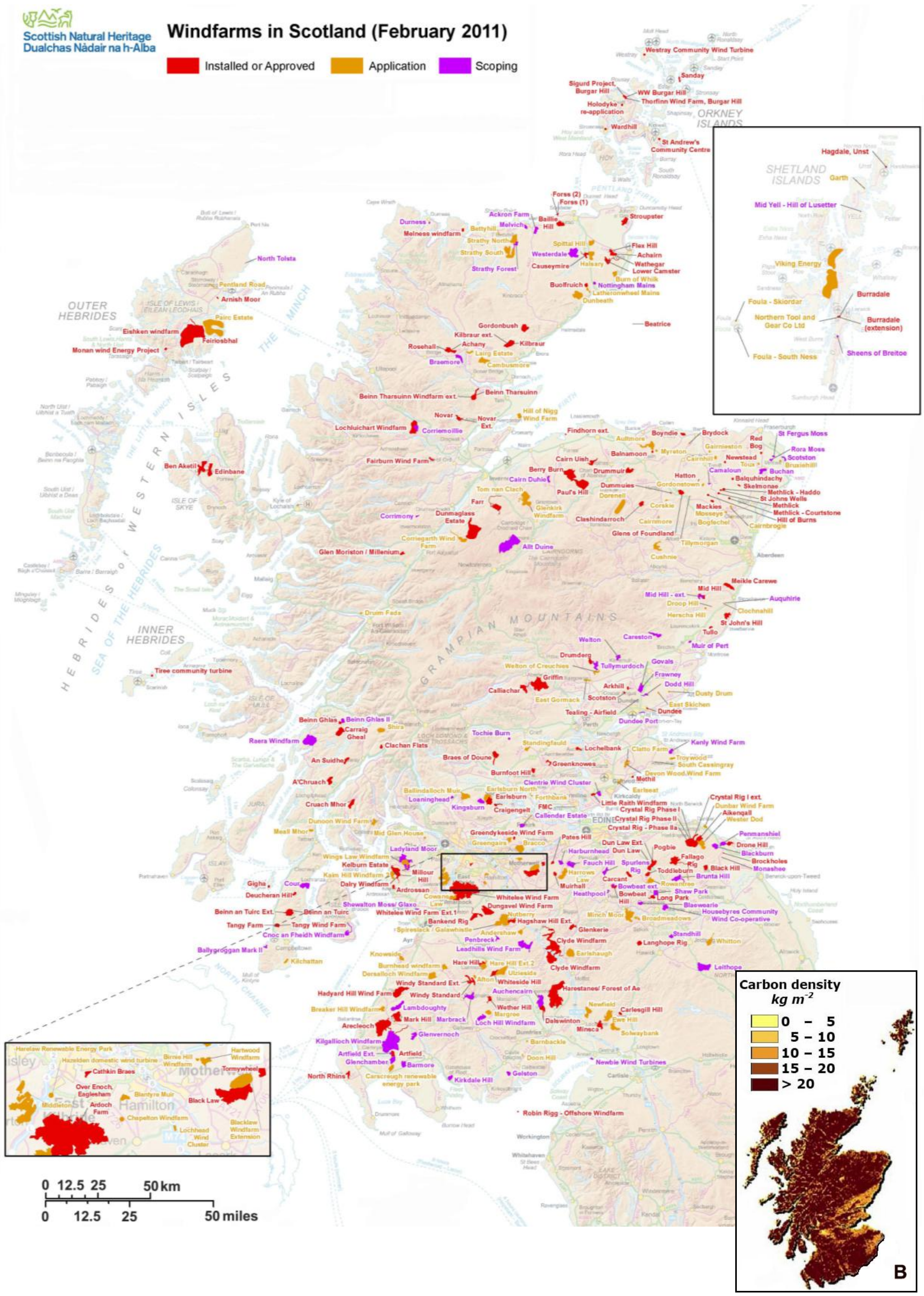


Figure 1. Locations of windfarms in Scotland courtesy of Scottish Natural Heritage. Inset Figure 1B. Map of carbon rich topsoils in Scotland which, when presented beside windfarm locations, shows windfarms are often sited on carbon rich soils. Map in 1B adapted from Bradley *et al.* (2005).

1.3. Carbon, Phosphorus and Nitrogen in Streamwater

This section outlines the speciation, sources and significance of C, P and N in streamwater, with particular emphasis on peatland streams.

1.3.1. Carbon

Three forms of streamwater C, encompassing both organic and inorganic species, are commonly identified: (i) dissolved i.e. dissolved organic carbon (DOC), bicarbonate ions (HCO_3^-) and carbonate ions (CO_3^{2-}) (ii) particulate organic carbon (POC), and (iii) gaseous, such as free CO_2 or CH_4 (Stumm and Morgan, 1981). In peatlands, DOC and POC are important components of streamwaters (e.g. Grieve, 1991; Hope *et al.,* 1997a) and are mainly derived from terrestrial sources, for example, from soil organic matter, fragmented plant material and microbial processes (Vannote *et al.,* 1980; Fiebig *et al.,* 1990; Brooks *et al.,* 1999). The relative proportions of the inorganic forms of C present in streamwater are dependent on pH and, to a lesser extent, temperature, and are mainly derived from weathering and dissolution of CO_3^{2-} containing minerals. In peatland streams which are characterised by low pH and drain catchments where the underlying parent material is usually CO_3^{2-}-poor, the concentration of CO_3^{2-} ions is negligible (Stumm and Morgan, 1981).

Organic C present in freshwater covers a size spectrum ranging from free monomers, fulvic and humic acids via macromolecules such as proteins and colloids, to aggregates and large particles (Thurman, 1985) (Figure 2). POC is generally defined as the fraction of organic C which is retained on a 0.7 μm pore size filter (e.g. Dawson *et al.,* 2004; Dinsmore *et al.,* 2010). POC in streamwaters draining Scottish peatlands generally represents a much smaller component of C export than DOC (e.g. Dinsmore *et al.,* 2010). DOC concentrations – concentration hereafter indicated by square brackets, e.g. [DOC] – and exports in streamwater have been strongly positively related to the size of the soil C pool and the percentage of peat cover (e.g. Hope *et al.,* 1994; Hope *et al.,* 1997a,b; Dillon and Molot, 1997; Aitkenhead *et al.,* 1999; Eckhardt and Moore, 1990; Mattsson *et al.,* 2005; Xie *et al.,* 2005; Kortelainen *et al.,* 2006). Other catchment variables such as discharge (Clark *et al.,* 2007; Austnes *et al.,* 2010), slope (Ludwig *et al.,* 1996; Grieve and Marsden, 2001) and catchment size (Russell *et al.,* 1998; Mattsson *et al.,* 2005; Billett *et al.,* 2006) have all been found to influence streamwater [DOC]. [POC] is highly variable temporally in relation to high flow events, and spatially due to the patchiness of soil erosion within catchments (Hope *et al.,* 1997a).

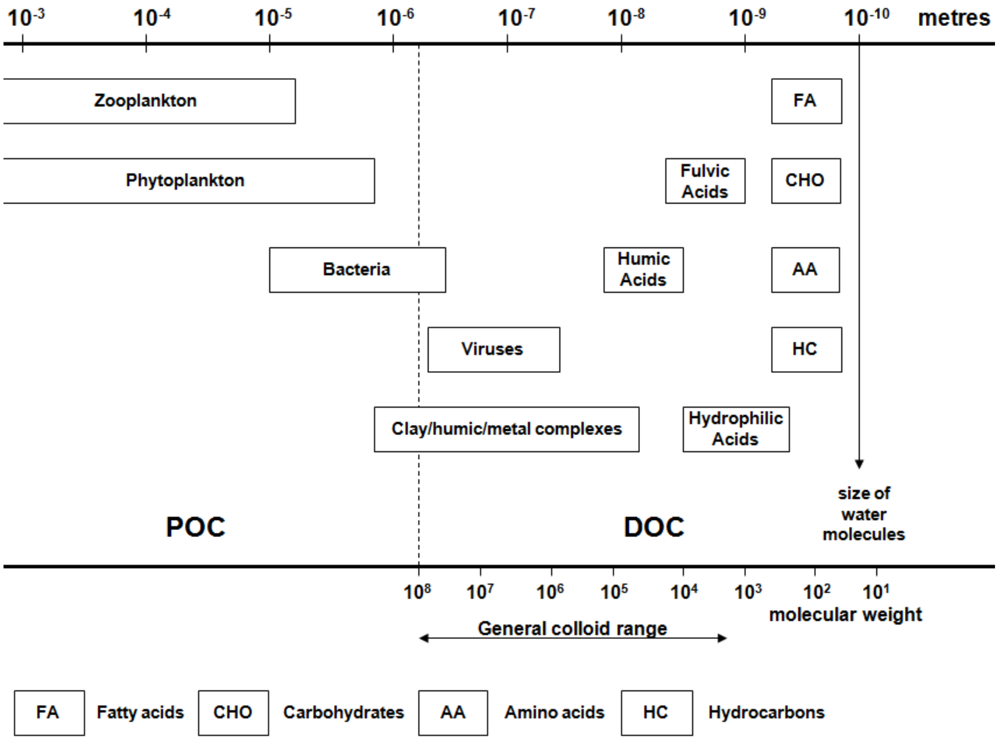


Figure 2. Continuum of organic carbon in freshwater. From Robards *et al.* (1994).

C is an important source of energy to stream ecosystems (Fisher and Likens, 1973; Wetzel, 1992). The transport of DOC in peatland streams, although small compared to other terrestrial C fluxes and reservoirs (Kempe, 1979), is a major transfer pathway between the terrestrial and ocean C pools (*c.f.* Ludwig *et al.,* 1996). In streamwater, in-stream processes cycle and recycle C continually (*c.f.* Dawson *et al.,* 2001a; Dawson *et al.,* 2004) and additional C inputs are acquired as streams flow downstream into coastal environments and then the ocean. Isotopic studies have suggested that the majority of headwater terrestrial-derived DOC is from relatively young, decadal, ^{14}C post-nuclear testing sources (Schiff *et al.,* 1997; Palmer *et al.,* 2001). In larger rivers, a combination of young and old DOC and predominantly old POC (> 1000 years) from terrestrial sources is observed (Raymond and Bauer, 2001). Younger, more labile DOC is respired selectively leaving an older organic matter component to enter oceanic C pools (Raymond and Bauer, 2001). Respiration (e.g. Lennon, 2004), degassing of soil-derived CO_2 from headwaters (e.g. Hope *et al.,* 2004), and UV-oxidation (e.g. Osburn *et al.,* 2001) of DOC, resulting in $CO_{2(aq)}$ over-saturation and degassing (Cole *et al.,* 2007) means that streamwaters, especially peatland streams, are potentially important conduits of C transfer to the atmosphere from the soil C pool (Kling *et al.,* 1991; Cole *et al.,* 1994; Cole and Caraco, 2001; Cole *et al.,* 2007).

Aquatic C exports from peatland have a pivotal influence in terms of C balance (Siemens, 2003), with aquatic C exports from undisturbed peatland rivers reported to equal C sequestration in the peatland (Billett *et al.,* 2004). Anthropogenic activity, such as the development of windfarms on peatland, has the potential to increase aquatic C export and may cause the peatland to shift from being in C balance or a C sink to being a source of C. The assessment of the impacts of disturbance associated with the construction of windfarm infrastructure on peatland appears to have received little attention from the scientific community. Change in streamwater chemistry due to peatland disturbance can be difficult to identify as it occurs in the wider context of other components of environmental variability which drive streamwater dynamics and is set against a background of already increasing [DOC] in freshwaters across northern temperate latitudes (Monteith *et al.,* 2007). For example, in the UK, increasing trends in freshwater DOC were reported on a regional scale, with significant increases in [DOC] observed in all 22 UK Acid Waters Monitoring Network catchments, ranging from 0.06 to 0.51 mg L^{-1} yr^{-1} (Evans *et al.,* 2005). In two catchments in northern England, one, Broken Scar (catchment area 818 km^2) had a significant increase in the levels of water colour based on a 30 year data set with a median annual [DOC] increase of 0.11 mg L^{-1} yr^{-1} and at the other, Warkworth (589 km^2) there was a significant but much smaller median annual [DOC] increase of 0.026 mg L^{-1} yr^{-1}, based on a 39 year dataset (Worrall *et al.,* 2004a). In another study, 77 % of 198 sites, comprising 29 lakes, 8 water supply reservoirs and 161 rivers, there was an upward trend in [DOC] with the average annual increase in [DOC] of 0.17 mg L^{-1} yr^{-1} (Worrall *et al.,* 2004b). More variable trends have been reported in [TOC] in Scotland. In 39 of 58 river sites with long-term data, significant upward trends in [TOC] were observed and the rate of [TOC] increase averaged across all sites was 0.12 mg L^{-1} yr^{-1} (SEPA, 2007).

The cause of the observed increases in [DOC] has been subject to debate (*c.f.* SNIFFER, 2011 for a detailed review of drivers of change in [DOC]). Freeman *et al.* (2001a) suggested that increased activity of the enzyme phenol oxidase, proposed to regulate C store in peatlands (Freeman *et al.,* 2001b), due to a rise in temperature caused increased DOC production and recalcitrance. DOC accumulates and there is therefore a larger available DOC store. Changes in hydrology have also been suggested as causes, with Worrall *et al.* (2006) attributing the increases in [DOC] to enhanced DOC production in post-drought periods whereas Tranvik and Jansson (2002) proposed that these increases were due to higher runoff volumes, resulting in greater export with more flow occurring through surficial pathways where DOC is more available. Other studies relate the increases in riverwater [DOC] to changes in atmospheric conditions. Freeman *et al.* (2004) proposed that the [DOC] increases were caused by elevated atmospheric CO_2 which in turn increased terrestrial productivity and litter production and hence the available terrestrial DOC store. Findlay (2005) hypothesised that a doubling in [DOC] in the Hudson River, New York, over 16 years was caused by increased soil microbial activity and consequent effects on plant and decomposer C dynamics stimulated by increased atmospheric N deposition, resulting in a larger terrestrial store of available DOC and therefore a greater export has been observed. Evans *et al.* (2008) suggest that it is the form of N deposition, not just the total amount of N deposition which is an important control on acidity and therefore [DOC]. Monteith *et al.* (2007) found that widespread increases in [DOC] in surface waters across eastern North America, northern and central Europe to be strongly correlated with a gradual decline in the sulphate content of atmospheric deposition which increased organic matter solubility and thus increasing [DOC]. Clark *et al.* (2010) comment that the increase in freshwater [DOC] is likely to be caused by a range of these different drivers and that the exact importance of a particular driver varies between locations.

The potential loss of DOC and POC from soils to watercourses due to windfarm development, in addition to already increasing [DOC] in freshwater drainage systems, could present some benefits for aquatic ecosystems as discussed in Freeman *et al.* (2004). Increased [DOC] would create additional substrates for microbial food chains (Wetzel *et al.,* 1992) as DOC can account for up to 30 – 75 % of the total in-stream energy inputs (Fisher and Likens, 1972) and the quantity of bacterial biomass is often controlled by the amount of C availability as well as source quality (Bott *et al.,* 1984). Increased [DOC] also attenuates UV-light to protect organisms from harmful wavelengths (Schindler *et al.* 1997; Roulet and Moore, 2006). However, discolouration of water reduces light levels in the water column and on the stream bed which may decrease the amount of food for heterotrophic organisms by reducing primary productivity (Grieve and Gilvear, 2008). Further to ecological impacts, the quality and cost of treating drinking water supplies are of great concern (Roulet and Moore, 2006; Chapman *et al.,* 2010) because the incomplete removal of DOC in water supplies leads to low residual chlorine thus limiting protection against biological contamination. The chlorination of DOC-rich water can produce potential carcinogens as a by-product of water treatment (Worrall *et al.,* 2003). Consequently water suppliers have to investigate other more costly means of water treatment, such as UV irradiation or ozonation, which are also less effective than chlorination in protecting against biological contamination within the water distribution system.

1.3.2. Phosphorus

When studying P, one of the major nutrients necessary for bacterial and plant growth, in water it is useful to categorise the P compounds present into types. From combinations of different physical (total, particulate and dissolved) and chemical (orthophosphate, inorganic and total) fractions there are at least 12 forms of P in water (Figure 3). Particulate P includes living and dead plankton, precipitates of P, P adsorbed to particulates, and amorphous P (Broberg and Persson, 1988). The dissolved forms include inorganic P and organic P. P in streams is usually found in the form of phosphates (MEWAM, 1992). Phosphates can be bound to organic matter, contained within organic matter, or inorganic, including polyphosphates and orthophosphates (MEWAM, 1992). P is highly chemically and biologically active in streamwater, undergoing numerous transformations and moving between the particulate and dissolved phases, between the sediment and water column, and between the biota and abiotic environment (Mainstone and Parr, 2002). Processes occurring in the aquatic system may either consume P, e.g. through sedimentation, sorption onto suspended solids or sediment, algal uptake, or produce P, e.g. through desorption, biological degradation or re-suspension (Robards *et al.,* 1994). Polyphosphates, also known as metaphosphates or condensed phosphates, are unstable in water and will eventually convert to orthophosphate (Eaton *et al.,* 2005). Orthophosphate is the most stable form of phosphate, and is the form used by in-stream biota since it is available immediately without any extracellular processing (Eaton *et al.,* 2005). Orthophosphate is commonly referred to as "reactive P”. The term “reactive” in this research is defined by the analytical methods for P meaning that P reacts in the acid molybdate reaction to produce the blue colour without prior hydrolysis or oxidation treatments.

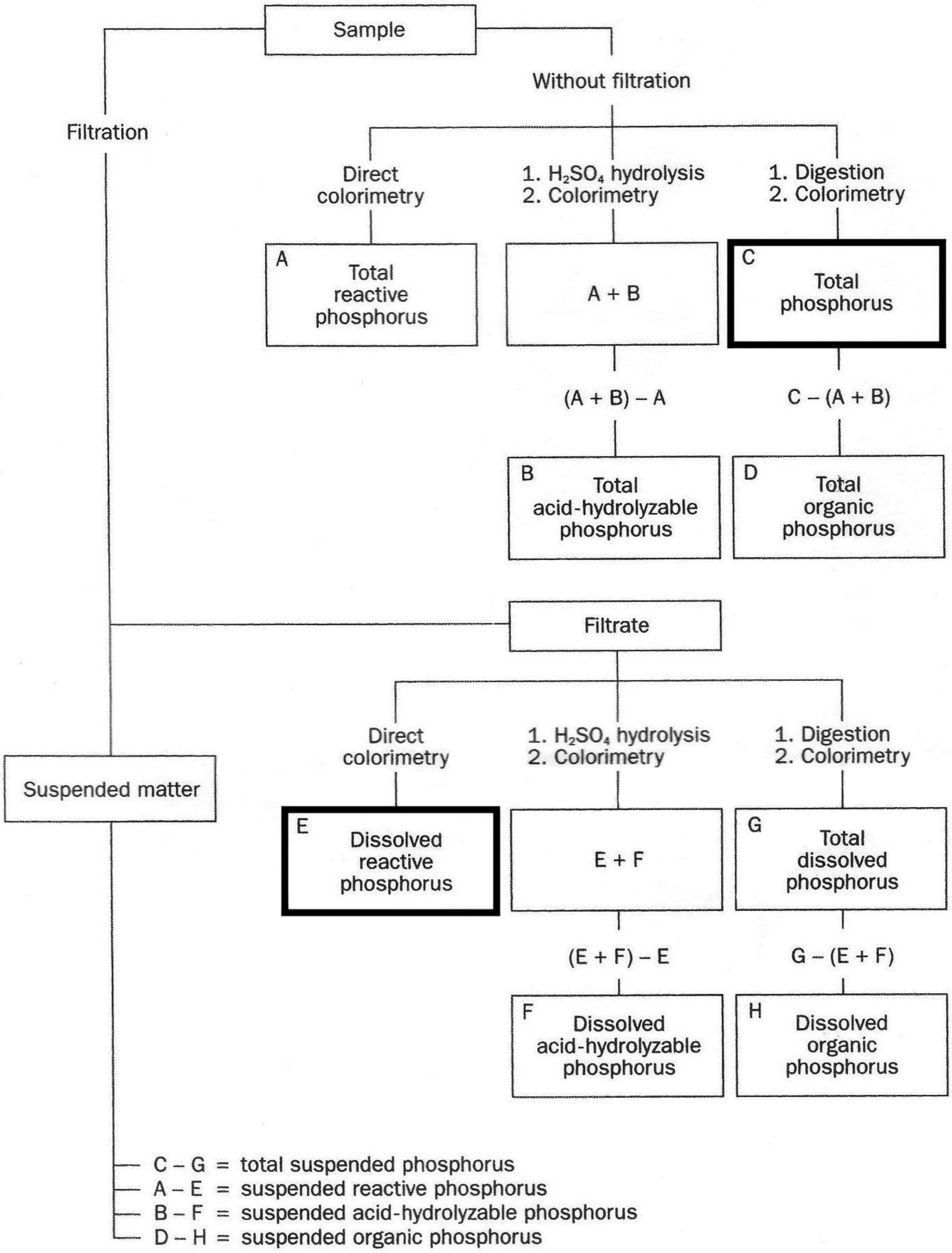


Figure 3. Schematic of analytically defined particulate and dissolved phosphorus fractions. From Eaton *et al.* (2005) p.4.147. The forms of P which this research focuses on are indicated by the boxes with black thick lines. Dissolved reactive phosphorus (box E) in this research is termed soluble reactive phosphorus (SRP).

Of the several forms of P (Figure 3) which can be measured this research will focus on total phosphorus (TP), a measure of all the forms of P, dissolved or particulate, which are found in a water sample and also soluble reactive phosphorus (SRP), a measure of the filterable inorganic fraction of P, the form directly taken up by in-stream biological processes. SRP is a measure of orthophosphate but also includes any labile condensed and organic phosphate which is hydrolysed during the analytical measurement (Robards *et al.,* 1994).

P in streamwater arises from many sources, including the effluents of domestic or industrial origin, in particular from sewage and from diffuse inputs from agricultural land due to inorganic fertilizer use, organic manure application and natural deposits from grazing animals (Robards *et al.,* 1994). In peat-dominated catchments where there is a low human influence, the leaching and weathering of igneous and sedimentary rocks, the decomposition of organic matter containing P compounds either weakly associated with the organic material or chemically bound within it, P from atmospheric deposition and soil/river bank erosion and P mobilised from in-stream sediments during high flow events are more influential sources than P from sewage effluents (Robards *et al.,* 1994).

The ‘average’ area-normalized TP and SRP exports to watercourses in Great Britain are approximately 240 mg P m^{-2} yr^{-1} and 180 mg P m^{-2} yr^{-1}, respectively (White and Hammond, 2009). These values were calculated using inventories of industrial P exports and estimates of P exports from sewage treatment works and diffuse sources. From this the annual TP and SRP exports to British waters are estimated to be 60 and 47 kt P yr^{-1} respectively, of which households contribute 73 / 78 % (TP / SRP), agriculture contributes 20 / 13 %, industry contributes 3 / 4 %, and 4 / 6 % comes from background sources (White and Hammond, 2009). Background sources are defined as atmospheric deposition, orchards, woodlands, forests, wetlands including bogs, fens, marshes and swamps (White and Hammond, 2009) and are generally low since P is not abundantly available from most British geologies (Mainstone and Parr, 2002). Estimates of rates of background P export to rivers vary widely, partly due to methodological differences in estimations and partly due to natural differences in catchment conditions. The majority of estimates range between 5 and 65 mg P m^{-2} yr^{-1} (e.g. Vighi and Chiaudani, 1985; Billen *et al.,* 1991) and Withers and Jarvie (2008) more recently estimated the background input of P to rivers to be generally < 10 mg P m^{-2} yr^{-1}.

Peatland streamwaters are generally classed as oligotrophic due to the fact they are characterised by extremely low nutrient concentrations, with P often the growth-limiting nutrient (Mainstone and Parr, 2002). The addition of excess P to freshwater environments may eventually result in eutrophication – the accumulation of nutrients – resulting in algae and aquatic plants in large quantities (Isermann, 1990; Mainstone and Parr, 2002). When these die, bacterial decomposition uses up dissolved oxygen which can result in fish kills (Nisbet, 2001). Whilst eutrophication can occur naturally, it is in many instances associated with anthropogenic sources of P which increase the rate at which P enters the water. The control of P loss is therefore important in mitigating the eutrophication of streamwaters. Peatland streams are highly sensitive to small increases in P availability, so even enrichment of the order of 10 μg L^{-1} is of concern (Mainstone and Parr, 2002).

Environmental standards set for [SRP] in rivers in the UK to comply with the European Community Water Framework Directive (2000) use annual mean [SRP] in different river types based on annual mean alkalinity in the form of [$CaCO_3$] to determine the water quality status (UKTAG, 2008) (Table 1 and Table 2). The directive specified that substances which contribute to eutrophication, in particular phosphates, are priority pollutants. Not only are [P] important in terms of water quality and streamwater trophic status, but contemporaneous P availability with C will influence the connection of streamwater and atmospheric C cycles. Ecological stiochiometric theory predicts that the potential for DOC to be respired to CO_2 is influenced strongly by availability of P (Frost *et al.,* 2005; Cross *et al.,* 2005) suggesting that a stoichiometric perspective could also be useful to investigate the fate of DOC. This is a simplistic overview of the interaction of C and P in streamwaters, since it is also influenced by environmental conditions and community structure, but ultimately nutrient availability will influence the fate of exported C (Dodds, 2006).

Table 1. Typology for nutrient conditions for rivers, sourced from Water Framework Directive UK Technical Advisory Group Environmental Standards and Conditions Final Report p.28. (UKTAG, 2008).

Altitude	**Annual mean alkalinity (mg L^{-1} $CaCO_3$)**	
	< 50	**> 50**
Under 80 m	Type 1n	Type 3n
Over 80 m	Type 2n	Type 4n

Table 2. Standards for phosphorus in rivers based on [SRP], sourced from Water Framework Directive UK Technical Advisory Group Environmental Standards and Conditions Final Report p.29. (UKTAG, 2008).

River type	Annual mean [SRP], µg L^{-1}			
	High	Good	Moderate	Poor
1n	30	50	150	500
2n	20	40	150	500
3n	50	120	250	1000
4n	50	120	250	1000

1.3.3. Nitrogen

In streamwaters the forms of N of greatest interest are, in order of decreasing oxidation state, total oxidised N, ammonia (NH_3) and organic N, all of which, as well as N_2 gas, are biochemically inter-convertible (Robards *et al.,* 1994) (Figure 4). Organic N includes proteins and peptides, nucleic acids and ureas, and numerous synthetic organic materials (Eaton *et al.,* 2005). The concentration of NH_4^+ is generally low in streamwaters as it adsorbs to soil and clay particles and is not leached readily from soils (Eaton *et al.,* 2005). Total oxidised N (TON) consists of nitrate (NO_3^-) and nitrite (NO_2^-). NO_2^- is an intermediate oxidation state of N, both in the oxidation of NH_3 to NO_3^- and in the reduction of NO_3^- (Eaton *et al.,* 2005), which occurs naturally in streamwaters.

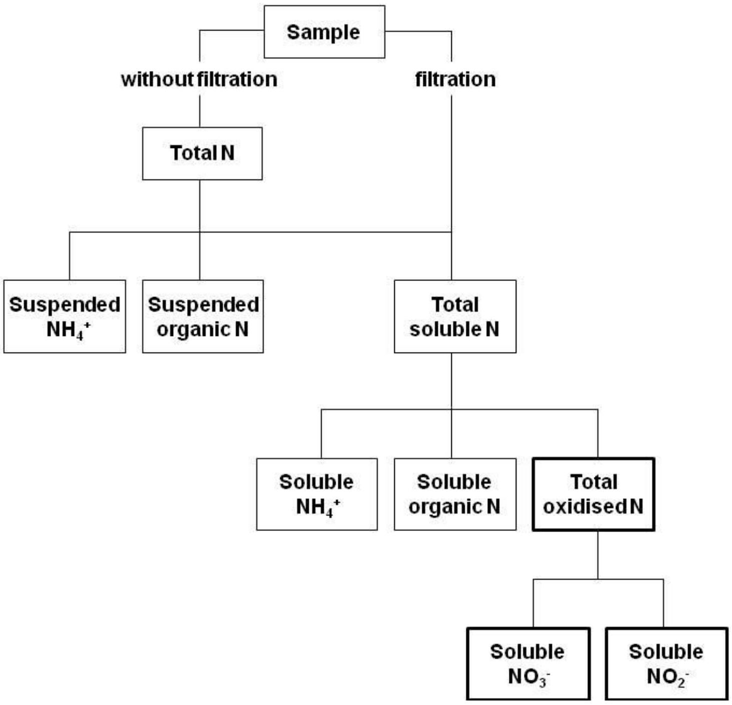


Figure 4. Schematic of nitrogen forms in streamwater. The forms this research focuses on are shown in the boxes with thick black line.

The concentration in streamwater of these species varies widely depending on the geographical location, local geology and land use but NO_3^- is usually the most important in waters (Neal *et al.,* 2003). NO_3^- generally occurs in low concentration in peatland streamwaters, and increases with the amount of agricultural land within a catchment (Chapman *et al.,* 2001). Apart from the input of N in rainfall, some of which is N from fossil fuel combustion (Neal *et al.,* 2003), the main inputs of NO_3^- into freshwater come from slurry, mainly as NH_4^+ until nitrified, and fertiliser applied to agricultural land, via wastewater point discharges or through diffuse runoff (Robards *et al.,* 1994). NO_3^- is an essential nutrient for most photosynthetic autotrophs and [N] in streamwater is also important because, as with P, increasing concentrations are linked to excessive algal growth (Robards *et al.,* 1994). NO_3^- is identified in Annex VIII of the Water Framework Directive (2000) as a priority pollutant which contributes to eutrophication. Further to this, in excessive amounts NO_3^- is linked to the illness known as methaemoglobinemia in infants and to gastric and stomach cancers (Magee, 1977). The EU Drinking Water Directive sets a maximum admissible concentration of 11.3 mg L^{-1} for NO_3^--N in drinking water to avoid methaemoglobinemia in infants. Rather than assess the potential clinical effects, the measurement of TON and NO_2^-, and the subsequent calculation of $[NO_3^-]$ (see Chapter 3.3.2.3) were conducted in this research in order to assess whether disturbance due to windfarm construction increases the transfer of NO_3^- from soils to the aquatic system. Increases in NO_3^- could impact on streamwater trophic status and, since NO_3^- is the form of N most readily available for take-up by in-stream biota, could also affect the extent to which in-stream C is respired to CO_2 (Lennon and Pfaff, 2005).

1.4. Windfarm-Related Disturbance

Windfarm-related disturbance to peatland can be separated into two types – windfarm construction activities associated with hosting the windfarm infrastructure, and forestry operations to improve air flow or to meet habitat management plan (HMP) requirements. A HMP usually has the objective of restoring commercial conifer plantation to peatland habitat through the re-establishment of bog forming plant species, often as part of measures to mitigate the impact of a windfarm on wildlife, particularly for the benefit of peatland breeding and wintering birds. The need for deforestation is especially apparent at Scottish windfarm developments where the large areas of commercial conifer forest planted after World War Two through to the 1980s on less productive upland soils provided a strategic timber reserve. Between c.1947 and c.1988, the area of blanket peat in Scotland is estimated to have declined by 21 % (Mackey *et al.,* 1998). Half of the reduction in the blanket peatland area (51 %) was due to afforestation and much of the remainder was drained (44 %), mainly in preparation for forest planting (Mackey *et al.,* 1998).

1.4.1. Windfarm Construction Activities

During windfarm construction disturbance to the soil is unavoidable. Disturbance arises from the excavation of borrow pits (onsite quarries), construction of access roads, insertion of turbine foundations and associated drainage channels at turbine bases and beside roads (see Appendix 1). Windfarm construction activities are likely to lead to the exposure, compaction and dewatering of peat, potentially impacting on [C] in streamwater, and are also likely to enhance peat decomposition rates and increase CO_2 emissions. Construction activities especially those related to drainage could also affect C exports due to changes in hydrological pathways. The scale and impact of these activities are thought to be similar to disturbances associated with peat harvesting which has been shown to increase aquatic C exports, with DOC exports from harvested peatlands in Canada found to be approximately twice those from undisturbed peatlands (Glatzel *et al.,* 2003).

The few early concerns about windfarms on peatland centred on the risk of peat slides following the slide in 2003 during construction of the Derrybrien windfarm in County Galway, Ireland, where 70 ha of peat and conifer plantation slid downhill conveying 450,000 tonnes of peat into surrounding watercourses. As a result of this incident, guidance is now extensive on mitigating slide risk and the EIA process in Scotland includes peat stability reports which should be conducted according to guidance in “Peat Landslide Hazard and Risk Assessments – Best Practice Guide for Proposed Electricity Generation Developments” (Scottish Government, 2007). This requirement has the added benefit of enforcing an extensive peat survey indicating areas of deep peat best avoided for construction. A detailed report on the Derrybrien windfarm peat slides (Lindsay and Bragg, 2005) did not focus solely on the peat slide but also highlighted the importance of losses of C through drainage and the oxidation of peat during windfarm construction in the overall C budget of the site.

One of the only two published papers sourced after an extensive literature search on the impact of windfarm development on streamwater chemistry included exports of DOC and suspended sediment calculated during the period immediately following the completion of construction of a windfarm on peatland in Scotland (Grieve and Gilvear, 2008). Six streams draining the Braes of Doune windfarm near Stirling, and three control streams were sampled on the same dates on seven occasions from October 2006 to February 2008. [DOC] in the streams draining the windfarm were always greater than those in the control streams, with mean differences ranging from 2 to around 5 mg L^{-1} and maximum concentrations in excess of 30 mg L^{-1} during high flow events. Suspended sediment concentrations were found to be elevated markedly in the disturbed streams with maximum concentrations in event flow four to five times greater than in the controls. Comparing flow-weighted mean [DOC] between the disturbed and control catchments, DOC export attributed to windfarm-related disturbance was estimated at 5 g m^{-2} (Grieve and Gilvear, 2008). The second paper published regarding the impact of windfarm development on streamwater chemistry took a stiochiometric perspective on C, P and N export in streamwater before and during windfarm construction in peat-dominated catchments. C, P and N exports were reported to increase in a stoichiometric manner which supports aquatic respiration rather than promotes an increase in microbial biomass, thus greater CO_2 degassing may prevail (Waldron *et al.,* 2009). Hence, disturbance of terrestrial C stores may impact both the aquatic and gaseous C cycle (Waldron *et al.,* 2009).

1.4.2. Forestry Operations

Disturbance to the soil can also be caused by the forestry operations required for some windfarm developments to improve airflow and to reduce wind turbulence thereby increasing windfarm output, and for HMPs. Tree harvesting is a major disruption of the catchment nutrient cycle. The Forests and Water Guidelines (Forestry Commission, 2003) – the best practice guidelines in the UK for forest management and design – indicate that forestry operations can impact on C, P and N dynamics in streamwater. Four types of forestry operations are commonly carried out at windfarm developments: clear-felling, key-holing, whole-tree mulching and brash mulching. Clear-felling is deforestation where all merchantable trees within a coup (area of plantation) are harvested and no significant tree cover remains. Statistically significant increases in streamwater [DOC] have been reported after clear-felling (Cummins and Farrell, 2003a, Tetzlaff *et al.,* 2007, see Table 3). In both cases the increases were superimposed on the seasonal cycle of streamwater [DOC] and observed only during the maximum phase of the season cycle. A number of studies have documented large increases in streamwater [P] (Ahtiainen and Huttunen, 1999, Cummins and Farrell, 2003b and Rodgers *et al.,* 2010) and [NO_3^-] (Reynolds *et al.,*

Table 3. Summary of impacts of clear-felling on streamwater carbon, phosphorus and nitrogen.

Catchment Area (km^2)	Area Felled (%)	Summary of Main Observations	Reference
4.94	58	Four-fold increases in [TP] to 142 μg L^{-1}. Five-fold increases in [SRP] to 97.2 μg L^{-1} taking four years for [P] to recover to pre-clear-fell levels	Ahtiainen & Huttunen, 1999
0.9 1.4	39, 37 23, 23	Slight increases in [DOC] during the maximum phase of the seasonal cycle observed after felling in peaty and humic gley dominated catchments. Elevated [NO_3^-] for four years after felling with accentuated annual cycles of NO_3^-, with highest [NO_3^-] occurring in autumn and winter when temperatures and biological uptake are lower. [NO_3^-] increased initially for two years, before declining.	Tetzlaff *et al.,* 2007
1.15 1.60	33 66	Statistically significant increases in [DOC] superimposed on the strong seasonal cycle compared to control catchment after clear-felling on peatland. [TRP] (defined in Figure 3, Chapter 1.3.2) were 9 μg L^{-1} prior to felling and increased to 265 μg L^{-1} after felling. Declining tail the following 20 weeks over summer to winter, followed by a second increase of similar magnitude the next summer.	Cummins & Farrell, 2003a,b
0.25	23	Increase in [TRP] from 6 μg L^{-1} to a peak of 429 μg L^{-1} 13 months after felling on peat commenced. Four years after clear-felling, [TRP] returned to pre-clear-felling levels.	Rodgers *et al.,* 2010
Plynlimon 0.06 Beddgelert 0.01 Beddgelert 0.06	100 62 28	Maximum [NO_3^-] of 3.2 mg L^{-1} observed at Plynlimon about one year after the start of felling, declining to control stream values (0.5 mg L^{-1}) after 5 years. [NO_3^-] in the Beddgelert catchments remained above the control catchment for three years before declining.	Reynolds *et al.,* 1994
0.35 0.34	25 50	In streams draining podzols, [NO_3^-] were up to an order of magnitude higher for the first few years after felling. For forested gley soils, felling resulted in an order of magnitude increase in [NO_3^-] in a small drainage ditch, but not in the main stream channel. No clear response for [SRP].	Neal *et al.,* 2003a,b

1994, Neal *et al.,* 2003a) following tree harvesting. The Forests and Water Guidelines state that elevated [P] in peatland streamwaters last 12 to 18 months after clear-felling (Forestry Commission, 2003) and elevated [NO_3^-] may last 2 to 5 years (Forestry Commission, 2003), depending upon the rate of re-vegetation (Stevens and Hornung, 1990; Emmett *et al.,* 1991b).

The second type of forestry operation commonly carried out at windfarm developments is ‘key-holing’ in which minimal tree removal is conducted from a short distance around locations, for example a strip of 30 m of plantation removed either side along windfarm tracks and a 50 m radius removed around turbine bases. This felling type reduces wind turbulence around turbines in forested areas. Due to its smaller scale, disturbance from forestry ‘key-holing’ is less likely to impact on streamwater chemistry.

In areas of forest where trees are too small to be merchantable or the ground is too wet for conventional felling machinery, whole-tree mulching may be employed. This is where standing trees are reduced to small chips which are left in-situ to degrade, from which a pulse of labile nutrients may be released to adjacent watercourses. Whole-tree mulching is conducted generally on a less extensive scale than clear-felling since it is carried out only where necessary due to the lack of economic return for the trees.

Where clear-felling is conducted, the above-ground parts of the tree unacceptable for conventional timber processing, usually the tops of trees, branches and conifer needles as well as small dead trees – collectively termed ‘brash’ – are left on the ground. Some of this material is used to form a ‘brash mat’ to help protect the underling peat from physical damage, such as rutting, liquefaction, compaction and erosion, caused by the heavy felling machinery. Brash contains much higher nutrient concentrations than stem wood and is, therefore, an important source of leachable nutrients (Nisbet *et al.,* 1997). Furthermore, although not directly comparable to fertiliser inputs, brash may contain approximately half the concentration of P and potassium recommended in fertiliser prescriptions and double the normal N application rate for conifer plantations (Taylor, 1991). When brash is retained intact on site once felling is complete it returns nutrients to the soil over time. Stevens *et al.* (1995) presented evidence that brash is a source of P to drainage waters, showing that in the year after felling of a UK upland conifer plantation around one third of the total amount of P present in brash leached into soil water, which could potentially impact on streamwater.

If the brash is not left in-situ but mulched on site, the increased decomposition rate of the material has been shown to impact on water quality through the increased likelihood of leaching of labile nutrients (Titus and Malcolm, 1999; Moffat *et al.,* 2006). Peatland streams are particularly sensitive to nutrient leaching from brash mulching because they are naturally nutrient-poor with biological activity usually P-limited. Brash mulching is known to lead to P enrichment and disruption of the stream ecosystem (Forestry Commission, 2003).

1.5. Environmental Impact Assessment and Streamwater Chemistry

Proposals to construct, extend or operate an onshore windfarm in Scotland with a generation capacity under 50 MW are submitted to the local planning authority. Under Section 36 of the 1989 Electricity Act, onshore windfarm proposals in excess of 50 MW require the consent of the Scottish Government. In either case an Environmental Impact Assessment (EIA) must be prepared in accordance with The Electricity Works (Environmental Impact Assessment) (Scotland) Regulations 2000 in advance of a consultation and the planning decision. The EIA usually includes a description of the physical characteristics of the windfarm and land use requirements during construction and operation and discusses aspects of the environment likely to be affected by the development including, population, flora, fauna, soil, water, air, climate, archaeology and landscape. The EIA also includes a summary of likely significant impacts of the development on the environment, whether they are direct, indirect, secondary, cumulative, short-, medium-, long-term, permanent, temporary, positive or negative, and a description of the mitigation measures designed to prevent, reduce and where possible offset any significant adverse effects.

Although EIA usually mention possible impact on water quality, it is often in terms of maintaining public and private water supply or fish stocks and the eutrophication of lochs and reservoirs, rather than the potential for impact on the trophic status of streamwater draining disturbed peatlands, which are usually nutrient poor. Further to this, at present streamwater C export is not considered to cause a significant environmental impact and the link between peatland streams and the atmospheric C cycle (*c.f* Cole *et al.,* 2007) does not appear to be considered in EIA. This is due to the paucity of data for peatland catchments subject to windfarm-related disturbance as there are no data available to assess whether or not there is an impact. This is an idea brought to the fore in Waldron *et al.* (2009).

1.6. Research Aims

In the past five years, the impact of onshore renewables on peatland C stores has been attracting attention from the public, a growing awareness in political communities, and more gradual interest from the scientific arena (*c.f.* Grieve and Gilvear, 2008, Waldron *et al.,* 2009). The basic premise of the research for this thesis which started in October 2007 is to build on the preliminary data published by Waldron *et al.* (2009), to explore the effects of different windfarm disturbance activities on streamwater chemistry and thereby increase the accuracy of export estimates. Rather than adopting the same stiochiometric approach as Waldron *et al.* (2009), the focus of this research is to identify what impacts on streamwater C, P and N occur during and after windfarm development as there are currently knowledge gaps about how peatland streamwaters respond to windfarm construction and associated forestry operations. The research thus serves to inform windfarm developers, land managers, policy makers and environmental regulators about the impacts of windfarm-related disturbance on streamwater chemistry and will provide, based on the impacts observed, recommendations for best practice at future windfarm developments. The management of peatland C stores is important and, although the development and operation of onshore windfarms is currently the predominant form of disturbance to peatland, this research is also relevant to any type of development on peatland which shares the same disturbance mechanisms.

This research aims to:

1. Observe streamwater C, P and N concentrations in catchments draining a windfarm sited on peatland during and after windfarm construction to identify what impacts occur, examine the magnitude of any impacts and quantify the recovery time from these impacts;
2. Quantify streamwater exports of C, P and N;
3. Compare the magnitude of streamwater C exports to suggested peatland C sequestration rates;
4. Use a geographic information system (GIS)-based analysis to describe catchment characteristics and to identify the controls on streamwater C, P and N concentrations and exports and to assess the impact of windfarm-related disturbance on these; and
5. Make recommendations for best practice with regards to minimising impacts on C, P and N concentrations and exports at future windfarm developments on peatland.

1.7. Thesis Structure

The thesis consists of six further chapters. Chapter 2 covers the field methodology and describes the field site, windfarm development, catchments and water sampling points. It also includes the water sampling procedure, a description of the deployment and use of a continuous water depth and water quality logger, the hydrograph during the study period and the flow duration curve of the nearest long-term SEPA gauged catchment. Chapter 3 outlines the methodology for the laboratory analysis of concentrations in the water samples. The choice of filter procedure and filter pore size is discussed and the impact of different sample storage procedures on return from the field on [C] is examined.

To address aim 1, the C, P and N time series of concentration from the approximate bi-monthly sampling are presented in Chapter 4. For each parameter, whether there is an impact of disturbance detectable at the sampling points outwith the immediate area of disturbance is assessed through a harmonic regression analysis on the C and N time series and by referring to the UK Technical Advisory Group Environmental Standards in the case of the SRP time series. Inter-catchment and annual differences were identified and from these differences, the main controls on streamwater chemistry were inferred.

In Chapter 5 the monthly and annual streamwater C, P and N exports for before, during and after windfarm construction are presented, interpreted and compared with estimates from a range of other catchments to address aim 2. The generation of long-term half-hourly estimates of Q by three methods is described and the choice of the most suitable method of estimation of Q for each catchment is explained. To deliver aim 3, the C exports for the catchments are compared to estimated C sequestration rates for the Whitelee peatland.

In the penultimate chapter the controls on streamwater chemistry are investigated in relation to windfarm-related disturbance through the creation of a GIS to describe the physiography of each catchment and to quantify the extent of windfarm-related disturbance classified into low- and maximum- disturbance phases to address aim 4. Next, multiple linear regression analysis between median concentration and export for each parameter during each disturbance phase is described with the aim of identifying the most likely controls on C, P and N in streamwater. Chapter 6 concludes with an assessment of the impact of windfarm-related disturbance on streamwater chemistry and exports.

In the final chapter the key results are summarised in relation to research aims 1-4. Next the impacts of windfarm-related disturbance are synthesised to address the fifth aim and two recommendations are suggested for minimising the impact on streamwater chemistry in future windfarm developments. In conclusion specific proposals are made for further research into streamwater chemistry at windfarm developments hosted on peatlands, based on the findings of this research.

2. Field Methodology

2.1. Chapter Outline

This chapter covers the field methodology and describes the field site, windfarm development, catchments and water sampling points. It also includes a description of the water sampling procedure and the deployment and use of a continuous water depth and water quality logger.

2.2. Description of Field Site

To examine the five research aims (see Chapter 1.6), a field site with rivers draining C-rich soils, subject to disturbance, was sought. A peatland plateau, Whitelee, 30 km to the south of the city of Glasgow, central Scotland (55^{o} 40’ 24” N, 04^{o} 16’ 00” W), was selected (Figure 5). Here Europe’s largest onshore windfarm, comprising of 140 turbines and covering an area of 55 km^2, was under construction during the research period. The attributes of this field site are representative of many peatlands under consideration for windfarm developments therefore the results of research will be applicable to peatlands across the UK. This fieldsite has relatively low human population densities so anthropogenic sources of C are low for almost all the catchments making them ideal for this kind of impact study.

The Whitelee plateau has a maximum altitude of 376 m above sea level and is mainly covered with commercial plantations of Sitka spruce (*Picea sitchensis*) (Figure 6). For the history of the transformation of the Whitelee plateau moorland into the conifer forest see Tittensor (2009). There are three small water supply reservoirs, Lochgoin, Dunwan Dam and Craigendunton, to the west of the Whitelee Forest. The predominant land-use other than commercial forestry is rough grazing of sheep and cattle on the areas of open moorland (acid grassland and rush pastures), although there are some areas of improved pasture and arable land on the lower slopes to the north of the Whitelee plateau. A summary of meteorological data from the Whitelee area is included in Table 4 to indicates that the climate of the field site can be summarised as cool and moist.

Figure 5. Map of UK showing location of field site.

Table 4. Meteorological data from the nearest meteorological station to the Whitelee catchments, Saughall (G.R. NS 259841 636403), 3 km west of sampling point 1. Data courtesy of Michael Chalton, Saughall Meteorological Station.

Meteorological Data Saughall		
Altitude	221 m	
Mean annual rainfall (1975-2005)	1342 mm	
Mean annual air temperature (1998-2005)	Max 11.5 °C	Min 4.2 °C
Mean actual sunshine (1961-1990)	3.61 hours/day	
Mean days of air frost per annum (1988-2005)	72.8	
Mean no. of gales per annum (1988-1997)	9.4	
Mean winter soil temperature @ 30 cm depth (1988-2005)	2.69 °C	
Mean summer soil temperature @ 30 cm depth (1988-2005)	13.5 °C	

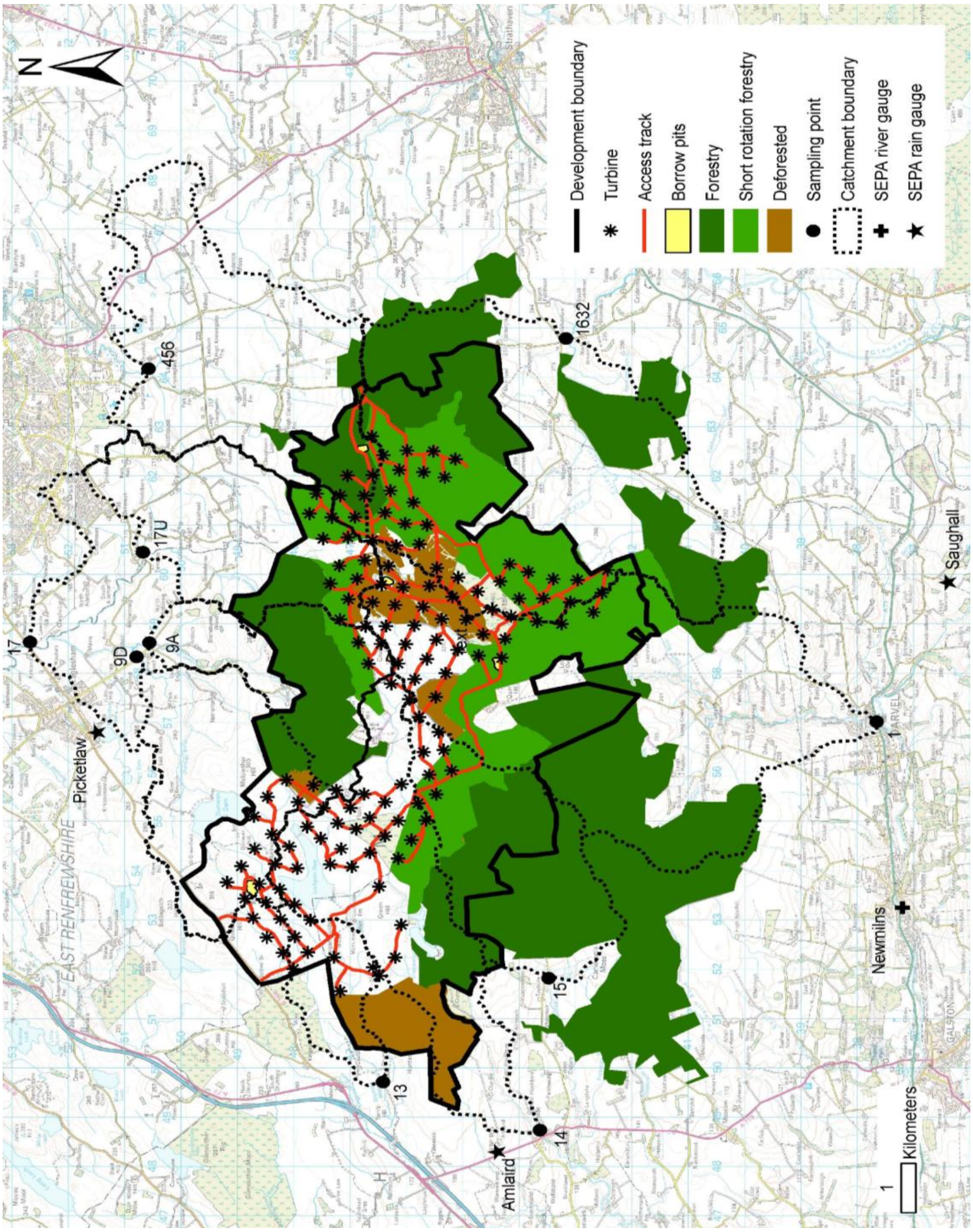


Figure 6. Map of Whitelee plateau showing the access tracks, turbines, borrow pits and forestry management associated with the windfarm development. The ten sampling points used during the research and catchment boundaries are also shown.

The dominant soil type across the Whitelee plateau is peat (Figure 7). Peat depth was measured (by Ritchies on behalf of CRE Energy) at 161 locations across the windfarm development. Depths ranged from 5 cm to over 8 m, with a mean depth of 190 cm (± 134.7 cm 1 S.D.). The peat across much of the area has been affected by the commercial forestry operations, although relatively undisturbed areas of peat also exist. Adjacent to the peat are poorly drained non-calcareous gleys, peaty podzols which are freely draining below the iron pan, freely draining brown earth forest soils, imperfectly draining brown forest soils, very poorly drained humic gleys and poorly drained peaty gleys (Figure 7). The slopes of the Whitelee plateau are composed of very poorly draining humic gleys and imperfectly and poorly drained non-calcareous gleys (Figure 7). On the lower hillslopes and in association with stream channels there are freely draining brown forest soils of low base status and freely draining peaty podzols.

The following description of the Whitelee plateau geology is sourced from the Environmental Impact Statement (EIS) prepared by Scottish Power for planning consent for the windfarm (CRE Energy, 2002). The underlying geology is dominated by carboniferous micro to macroporphyritic basalts of the Clyde plateau volcanic group of the calciferous sandstone series. There are small areas of basaltic tuffs and trachytes. Volcanic detritus deposits are present in many areas. The extrusive igneous rocks are associated with intrusive igneous bodies of trachyandesite, which also date to the Calciferous Sandstone age. The area is cut by major north-west – south-east trending andesite and andesitic quartz-dolerite dykes, which date from the Tertiary. The area has undergone some minor folding and is likely to have undergone some minor localised thermal metamorphism associated with the igneous activity. The bedrock is overlain generally by approximately 3 m of glacial and recent drift deposits but does outcrop in small areas throughout the field site. An area of earthy and sandy angular moraine is present in the centre of the field site. Drumlins are present in the south west of the field site in the till.

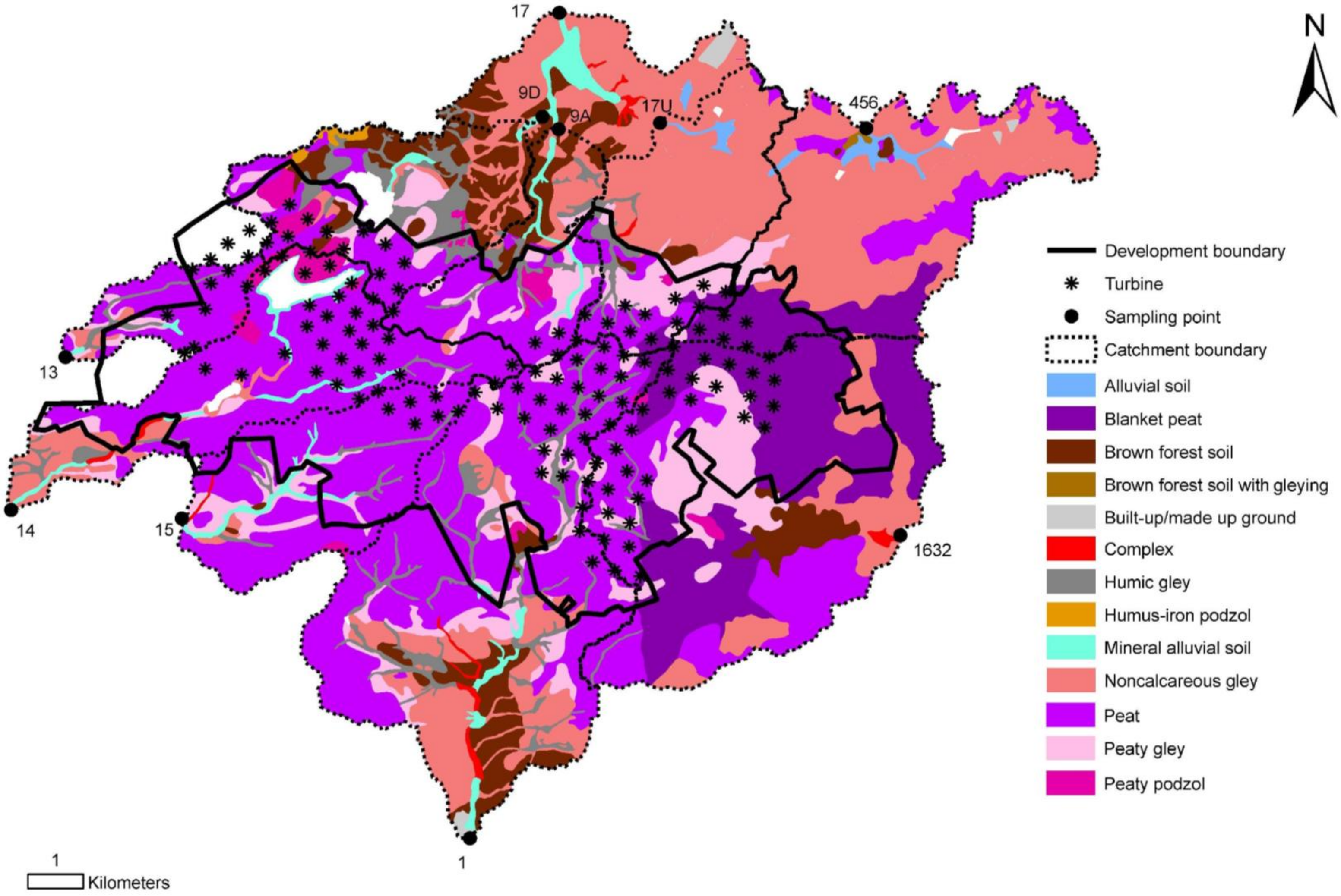


Figure 7. Soil map of the field site showing the catchment boundaries and locations of water sampling points and windfarm development. For more detailed information on soil type per catchment see Chapter 6.2.3.1.2. Soil data courtesy of Macaulay Land Use Research Institute.

2.3. Whitelee Windfarm Development

Whitelee is Europe's largest onshore windfarm in terms of capacity with the potential to generate 322 MW and comprises 140 turbines. Construction began in October 2006 and Whitelee became fully operational in May 2009. It is estimated that Whitelee avoids more than 542,400 tonnes of CO_2 emissions per annum, based on the direct replacement of energy production from coal-fired power stations (CRE Energy, 2002). The C payback time of the windfarm – the time of operation required to accumulate sufficient carbon savings to balance the carbon losses due to its development (*c.f.* Nayak *et al.,* 2010) – is estimated to be three years, whilst the windfarm lifespan is 25 years (personal communication with Scottish Power Renewables).

The following descriptions of the development of tracks, turbines and borrow pits have been sourced from the Environmental Impact Statement (CRE Energy, 2002) and through personal communication with Scottish Power Renewables. As well as the windfarm infrastructure much of the windfarm area was forested with plantations of Sitka spruce so felling of large areas of commercial forestry, owned by The Forestry Commission and adjacent private forestry holdings, was required for windfarm construction and operation. The locations, timings and likely extent of disturbance of felling activities were obtained from the Forestry Commission and Forest Enterprise.

2.3.1. Access Tracks

Prior to construction, there were no roads in the area of the windfarm, apart from forest tracks and a few access lanes to the scattered farms extending onto the higher ground. Only the main accesses to the windfarm development (< 1 km) were tarmac roads. 86 km of non-tarmac access track was required to link the turbines and control compound (Figure 6). The tracks were laid from west to east across the plateau from a 17 km non-tarmac "spine road" (Appendix 1). Construction of the tracks began in October 2006 and was completed by June 2007. The majority of the tracks (70 %) were floating, constructed by first laying a geotextile mat on top of the heather, followed by a geogrid which is a plastic grid designed to interlock with road construction aggregates to stabilise the road while coping with tensile forces. A 6.5 m wide, 600 mm deep fill of graded rock was placed over this, with the rocks sized to fit through the holes in the geogrid to lock it in place. This was rolled, and 200 mm of crushed rock was laid over a second geogrid to form the surface. The tracks were built in short lengths and designed so that roadside drainage was limited to small areas and disruption to the existing drainage regime was believed to be mitigated or wholly avoided. Water is able to permeate through the tracks into the underlying soil. The track layout was designed to use existing tracks as far as possible and to minimise the length of track required and adverse effects on landscape, ecology and archaeology, while maintaining appropriate gradients for construction vehicles. The tracks were aligned to reflect contours and field boundaries and avoided wherever possible areas of deep peat, cross-slopes and cuttings into existing terrain. There were over 200 water crossings, and runoff from roads and construction work was collected by drainage ditches into settlement ponds in which alum blocks were placed to encourage flocculation and settlement of suspended material prior to discharge into watercourses.

2.3.2. Turbines

Three-bladed horizontal axis turbines were erected on the Whitelee ridge, a location where the long-term average wind speed is approximately 8 m s^{-1} at a height of 70 m above the ground (CRE Energy, 2002). The turbine locations are shown in Figure 6. The following information regarding the construction of the turbine foundations was obtained through personal communication with John Buick, Project Engineer for Scottish Power Renewable Energy Ltd. The turbine bases consisted of a 3.1 m deep reinforced concrete base above granulated fill of stone obtained on-site, which varied in depth depending on the distance to the hardstanding below. The foundations vary in diameter from 15.85 m to 16.75 m, with the wider bases used over deeper and more fluid peat. If the foundation was situated in fibrous peat, construction was straightforward, with a 50 m wide hole excavated to the hardstanding, granulated fill inserted and a layer of blinding concrete poured to form a solid base. The bases constructed in fluid peat required a different excavation technique, as the hole fills up with fluid peat during excavation. The “rock doughnut” technique was used. An excavator was used to punch large rocks in a circle through the fluid peat to the depth of the underlying glacial till. This was backfilled with smaller rock. The resulting circle of punched rock held the fluid peat back so that the middle could be scooped out and the base constructed. In both cases, the surface vegetation was reinstated following construction. Drainage was constructed around the turbine bases to provide extra stability.

Approximately 77 km of buried cabling connects the turbines to the on-site substation at the eastern end of the windfarm development. This mostly follows the routes of the tracks in trenches of approximately 1 m depth. After cable-laying, the trenches were backfilled with the original excavated material, and the original turf and topsoil placed on top. A further 6.5 km underground cabling carries the electricity generated from the substation at the east of the windfarm development (G.R NS 637 468) to a grid connection point at East Kilbride South transformer station (G.R NS 695 530).

2.3.3. Borrow Pits

In order to minimise transport movements on main and local roads, on-site borrow pits were used to source the majority of the inert material for track construction, turbine hardstandings, backfill on the turbine bases and temporary turbine construction platforms at each turbine to support the crane used to erect the wind turbine. In excess of 300,000 m^3 of peat were excavated to extract hard core from six on-site borrow pits (Figure 6 and Appendix 1). On-site and imported construction materials were analysed to check that they were inert in terms of leaching and would not impact later on soil and water chemistry. The position, size and shape of the borrow pits were chosen to minimise the impact on ecology, hydrology and views and to facilitate reinstatement. The areal size of the borrow pits in relation to the whole windfarm development is very small. After the extraction of hard core, the borrow pits were backfilled with surplus excavated peat and the stripped top layer of turf re-used for restoration to form stable profiles similar to the existing natural landform. The backfilled areas were firmed and the re-located turf lightly compacted to remove air pockets and to attach the turf to underlying peat, apart from at one borrow pit where turf was not available, and the backfilled area was seeded with a native grass seed mix containing some heather (Cameron Ecology, personal communication).

2.3.4. Windfarm-Related Forestry Operations

An overview of the impacts of clear-felling on peatland is given in Chapter 1.4.2. Felling took place from winter 2006, five months after water sampling commenced, and forestry operations were completed during July 2008. Felling was carried out in two phases in parallel with the other construction activities. The initial phase was localised felling to facilitate construction of the tracks, turbine bases, substation, and cable installation. “Keyhole” felling of an area of 100 m diameter was carried out around individual turbines located within retained areas of forestry. Access tracks required additional felling of approximately 30 m either side of the tracks although tracks were, as far as possible, located on existing forestry rides to minimise the amount of felling required and the risk of windthrow.

The second phase involved larger areas of tree removal to create the area to be retained as open ground for the life of the windfarm. The locations of this felling are shown in Figure 6. The nature, extent and timings of these large-scale felling activities are summarised in Table 5. Deforestation is required to improve airflow, reduce wind turbulence and thereby increase windfarm output. Deforestation was also required outwith the main area of turbines as part of the HMP with the objective of restoring commercial conifer plantation to bog as part of mitigation measures for the impact of windfarms on wildlife, particularly for the benefit of upland breeding and wintering birds.

In total for both phases of felling 1042 ha of forest was clear-felled. In addition, and on-going during the lifespan of the windfarm, 1999 ha of forest is managed on a short rotation to ensure that the average tree height does not exceed 10 m. Trees taller than this height can impede air flow and therefore have a negative impact on wind speed, strength and direction and power generation by the wind turbines. When the mean tree height reaches 10 m the trees will be felled and each coupe will be restocked according to standard forest practice at the time. The extent of short rotation forestry areas can be seen in Figure 6.

2.4. Description of Water Sampling Points

As Whitelee windfarm is located on an elevated plateau surrounded by lower land there is a radial drainage pattern which constitutes several catchments. This research used the same water sampling points of the outlets at the nine catchments draining the Whitelee windfarm as Waldron *et al.* (2009) (Figure 8). The nine sampling points are outwith the windfarm boundary and are at different distances downstream from windfarm-related disturbance in order to assess how far downstream any impact of disturbance may be detectable. It was not possible to carry out longitudinal sampling due to access issues, time and logistical constraints. No control catchment exists because the catchments are subject to varying types and amounts of windfarm-related disturbance and through comparison it is possible to attribute an impact to a specific type of disturbance.

Catchments 456, 9A, 9D and 17 are north draining and the remaining five, catchments 13, 14, 15, 1 and 1632, are south draining (hereafter termed N-draining and S-draining respectively). The catchment names are those used in the EIS (CRE Energy, 2002). In August 2008, sampling was discontinued at catchment 17 due to the construction upstream of a flood storage facility which was considered to alter the flow regime and the water chemistry at this location.

Table 5. Nature, extent and timings of forestry operations at Whitelee windfarm development.

Forest Name	Year Planted	Main Tree Type	Catchment	Area Felled (km^2)	Deforestation practice	Year of Felling	Future Management
Whitelee	1962-1992	Sitka spruce	1, 1632, 9A, 17/17U	4.70	1.73 km^2 clear felled + brash mat mulching 2.97 km^2 whole tree mulching	South + East coupes = 2008 West coupes = spring 2009 North coupes = 2007	Permanently open for improved wind flow
Cleughearn	1972-1979	Sitka spruce	9D, 17/17U	2.04	Clear-felled	2008	Permanently open for improved wind flow
Flow Moss “Triangle”	1977	Lodgepole pine	14	0.64	Whole tree mulching	2007	Permanently open for improved wind flow
Drumtee/ Clanfin	1991	Sitka spruce	13, 14	3.04	2.67 km^2 clear-felled + brash mat mulching 0.37 km^2 whole tree mulching	Clear-felling = Nov 06 – Jan 08 Whole tree mulching = May 07 – Feb 08 Brash mulching = May 07 – July 08	Bog restorations as part of offsite Habitat Management Plan

Therefore in August 2008, 17U, 3.7 km upstream of sampling point 17, was added as an alternative to the discontinued sampling point. The grid references of the sampling points are given in Table 6 and an image of each sampling point is in Appendix 2. The streams draining the nine study catchments coalesce to form tributaries to the larger rivers of the area, with the N-draining catchments flowing into the White Cart Water, and the S-draining catchments feeding into the River Irvine. A stage board and a continuous water quality logger were deployed at sampling point 13 during the period of research (see Chapter 2.5).

2.4.1. Description of Catchments

Table 6 includes the catchment area and length of the maximum flow path upstream of each sampling point calculated using ArcGIS, the elevation of each sample point generated from digital elevation data and the stream order at each sampling point generated using the Strahler ordering method (see Chapter 6.2.3.1.1). The ecological classification of the surface waters for the EU Water Framework Directive according to the SEPA River Basin Management Plan Interactive Map (www.sepa.org.uk/water/ river_basin_planning.aspx#Interactivemap) and the main land use data from Coordination of Information on the Environment (CORINE) Land Cover Map for 2000 (see Chapter 6.2.3.1.3) are also included in Table 5. An overview of windfarm-related disturbance and forestry operations in each catchment is presented in Table 7.

The Water Framework Directive (2000) UK Technical Advisory Group Environmental Standards for [SRP] require the classification of river type based on thresholds of altitude and alkalinity in the form of [$CaCO_3$] (UKTAG, 2008) (Table 8); thus alkalinity analysis was carried out for one hydrologic year from October 2009. All the S-draining catchments and N-draining catchments 9A and 9D have annual mean alkalinity of < 50 mg L^{-1} $CaCO_3$ at an altitude of > 80 m (Table 9) which classifies these rivers as Type 2n. Catchments 456 and 17U have annual mean alkalinity of > 50 mg L^{-1} $CaCO_3$ at an altitude of > 80 m (Table 9) which classifies these rivers as Type 4n.

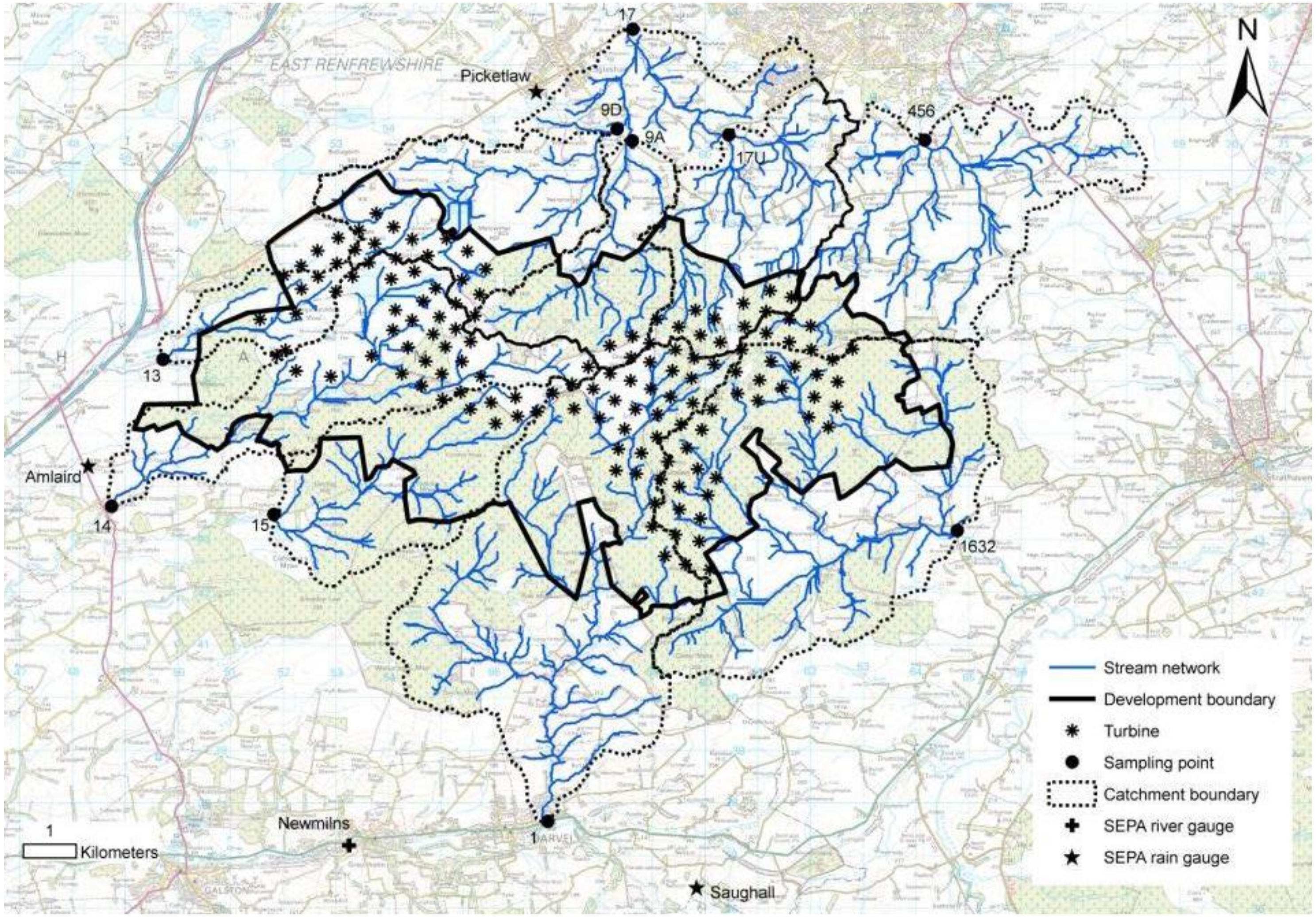


Figure 8. Stream network of the Whitelee catchments and sampling points. Catchments 9A and 9D are nested in catchment 17. The location of SEPA river gauging station on the River Irvine in Newmilns and locations of SEPA rainfall gauges are also shown.

Table 6. Summary of sampling point locations and catchment characteristics derived as explained in the text.

Catchment	Catchment Area (km^2)	Grid reference (NS grid square)	Flow length upstream (km)	Elevation (m a.s.l)	Stream order	SEPA ecological classification	Main Land Use
13	9.4	249659 646430	5.3	238.3	3rd	not available	Rough grazing, open moorland, commercial forestry
14	14.4	248734 643689	8.1	167.4	4th	poor	Rough grazing, open moorland, commercial forestry, 59 ha reservoir in upper catchment
15	13.4	251817 643400	6.0	165.0	4th	poor	Rough grazing, open moorland, commercial forestry
1	29.4	256909 637655	11.4	103.5	5th	good	Rough grazing, open moorland, commercial forestry
1632	30.0	264812 643100	10.8	206.1	4th	poor	Rough grazing, open moorland, commercial forestry
456	11.7	264069 650683	9.3	180.9	5th	moderate	Grazing – sheep and cattle, golf course
9A	7.9	258539 650603	5.9	146.7	4th	not available	Grazing – sheep and cattle
9D	11.6	258166 650680	6.8	145.8	4th	good/heavily modified	Rough grazing, open moorland, commercial forestry, 52 ha reservoir in upper catchment
17	34.5	258550 652664	12.8	116.2	6th	moderate	Grazing – sheep and cattle
17U	12.0	260391 656670	7.1	150.6	5th	moderate	Grazing – sheep and cattle

Table 7. Overview of disturbance, percentage peat-based soils and percentage pasture across the catchments. Peat, blanket peat (> 1m depth), peaty gleys and peaty podzols were grouped together and classed as peat-based soils (for detailed soil data see Chapter 6.2.3.1.2).

Catchment	% catchment deforested	Track length (km)	No. of turbines	Flow length upstream to nearest disturbance (km)	% peat-based soil	% pasture
13	12.2	4.3	6	1.0	84.5	10.9
14	10.3	15.1	30	1.8	74.8	16.1
15	3.5	4.7	6	4.2	89.6	7.1
1	10.7	16.8	30	7.3	53.0	31.7
1632	13.2	21.8	29	4.6	34.5	18.0
456	0.8	5.1	5	4.9	16.0	72.3
9A	0.5	1.8	4	4.8	48.1	32.3
9D	2.3	6.7	14	5.2	17.9	36.6
17	2.0	13.9	29	7.9	32.1	55.6
17U	3.9	10.7	11	4.8	4.1	65.8

Table 8. River type thresholds required to determine SRP standards.

Altitude	**Annual mean alkalinity (as mg L^{-1} [$CaCO_3$])**	
	< 50	**> 50**
< 80 m	Type 1n	Type 3n
> 80 m	Type 2n	Type 4n

Table 9. Mean annual alkalinity for the Whitelee catchments for the hydrologic year 2009-2010. The altitude of all the catchment sampling points was > 80 m.

Catchment	**Altitude (m)**	**Annual mean alkalinity (mg L^{-1} $CaCO_3$)**	**Type**
13	238	33.3 ± 27.4	2n
14	167	27.1 ± 14.5	2n
15	195	13.5 ± 10.4	2n
1	104	37.3 ± 20.0	2n
1632	206	28.7 ± 17.0	2n
456	181	56.6 ± 20.8	4n
9A	147	37.9 ± 20.2	2n
9D	146	37.2 ± 20.2	2n
17U	151	52.2 ± 22.9	4n

2.4.2. Water Sampling Procedure

In this research sampling of surface river water was carried out approximately every two to three weeks commencing in October 2007 and continued until September 2010 using the same sampling points as Waldron *et al.* (2009) to build on the five month baseline monitoring period prior to this research. Approximately bi-monthly sampling was favoured in the present research because, although still likely to miss the detail of high flow event transfers, the higher temporal resolution than monthly sampling allowed a more accurate estimation of C, P and N exports from the study catchments.

At each sampling point samples were collected at approximately 2 cm below the surface of flowing water. On each occasion a 1 L polythene bottle was filled for C analysis and 100 mL polypropylene vials were filled, one each for P, N and alkalinity analysis, the latter being added to the routine sampling regime during the research. New vials were always used for the P, N and alkalinity samples, whilst the same bottles, dedicated to each sampling point, were re-used for sample collection for C determination. Care was taken to sample upstream of any particulate matter disturbed upon entering the river and upstream of any visible pipes or drains from roads, fields and houses. The containers and tops were all rinsed twice with river water at the site to remove potential contaminants from the inside of the containers, with rinsings disposed of downstream from the sampling point, and then filled completely with sample.

On each sampling occasion all catchments were sampled within a five hour time period. The time at which each water sample was collected was recorded along with the water depth. At sampling points 13 and 1632 water depth was noted from the installed stage boards whilst at the other sampling points stage height was measured using a metre rule at the same predetermined location each time so that depth could be compared between sampling occasions as an indicator of whether baseflows or high flows were being sampled.

Between sample collection and analysis there is the potential for physical, chemical and biological processes to change the water quality characteristics (Kotlash and Chessman, 1998). This was minimised by the storage of samples in a cool box containing ice packs until arrival in the laboratory, and refrigeration at 4 °C upon arrival there for the short period of time, typically less than 3 hours, until filtration (see Chapter 3.3.1).

2.5. Water Quality Logger

An In-situ Inc. multi-parameter Troll 9000 water quality logger was installed from September 2007 to June 2010 in S-draining catchment 13 since this catchment was closest to windfarm-related disturbance, had amongst the highest percentage area deforested and percentage peat-based soils. The probes attached to the logger measured temperature, pH, specific conductivity, absolute pressure and barometric pressure. These parameters were measured every 30 minutes, offering an opportunity to characterize water quality in catchment 13 and to calculate stage height from pressure data which can be used to provide a continuous river flow record (see Chapter 5.2.3). Half-hourly data collection was chosen to strike a balance between gaining a better understanding of changes during event flow, and the time required to manage and analyse large quantities of data.

2.5.1. Water Quality Logger Maintenance

Approximately every two months the probes attached to the logger were cleaned and calibrated and the data downloaded using Win-Situ 4 software. The conductivity sensor was calibrated with 147 μs cm^{-1} KCl solution (0.037275 g KCl in 500 mL de-ionised water). The reference electrolyte solution in the pH probe was refilled and the probe recalibrated with pH 4.0 and 7.0 buffers – an appropriate range for the pH in these river systems. Prior to recalibration, the performance of the probes was tested using the standard solutions to assess for drift during the preceding two months.

The absolute pressure data, measured using an unvented sensor was corrected for the barometric pressure and then converted to depth taking account of gravitational acceleration calculated in Win-Situ software from the logger latitude (55º) and elevation above sea level (238 m) and assuming that the water has a density of 0.998 g cm^{-3}. It was 9 cm above the streambed for the period 4th September 2007 to 8th September 2008 when the logger was swapped for maintenance and 16 cm for the period 22 September 2008 to 17th September 2010. The time series of stage heights were then converted to Q as described in Chapter 5.2.3.

3. Laboratory Methodology

3.1. Chapter Outline

This chapter outlines the methodology for the analysis of C, P, N and alkalinity in the water samples. The first part of the chapter describes the methodology used for C analysis. The second part outlines the P, N and alkalinity analyses. An overview of the analysis of each water sample is included in Figure 9. The choice of filter procedure and filter pore size is discussed and the impact of different sample storage procedures on return from the field on [C] is examined.

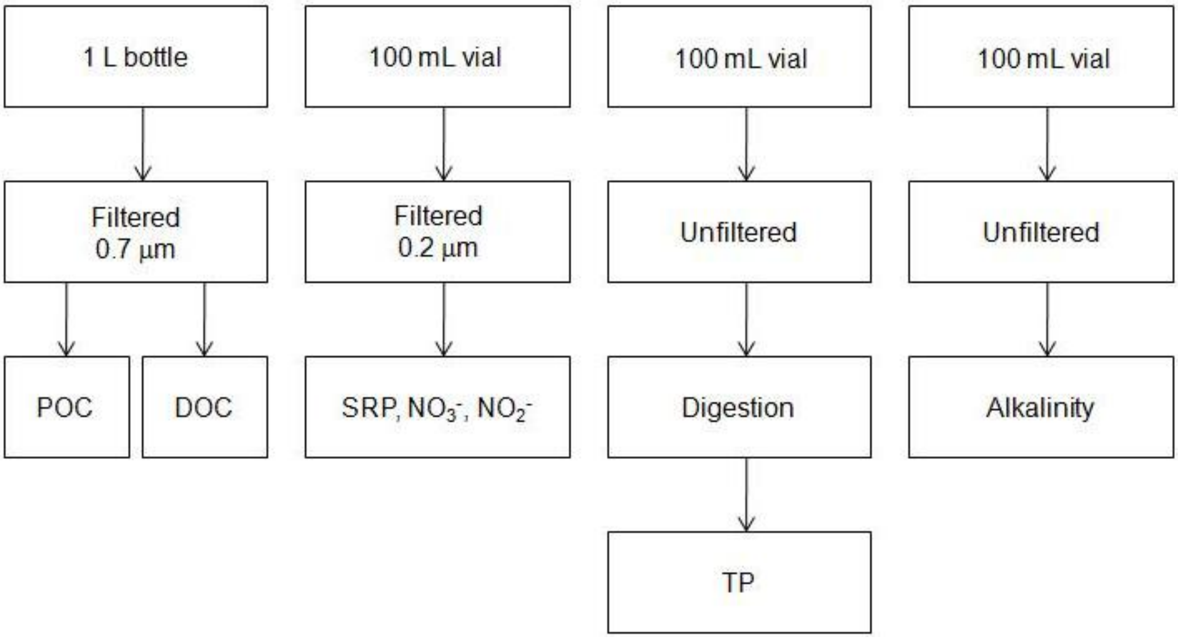


Figure 9. Overview of the analysis of each water sample.

3.2. Carbon Analysis

3.2.1. Particulate Organic Carbon

POC is defined in this research as the fraction of organic C retained on a 0.7 µm pore size glass fibre filter and was determined using a loss on ignition method. There is no standardised loss on ignition method for the determination of POC in water samples so the following procedure was employed using the method used on water samples from a peatland catchment outlined in Hope *et al.* (1997a) and used by others (e.g. Dawson *et al.,* 2002). The sample bottle was removed from the refrigerator and shaken prior to filtration to ensure that particulates were in suspension and not settled at the bottom of the bottle. A known volume, typically c.1 L, of sample was vacuum-filtered through a pre-combusted (450 °C for 8 hours) GF/F (0.7 μm) filter. To minimise contamination the filter assembly was rinsed thoroughly between samples with some of the next sample and between bi-monthly sampling occasions the filter assembly was soaked in 5 % nitric acid solution overnight and then rinsed thoroughly with de-ionised water.

Next the filter was oven-dried (105 °C for 3 hours), weighed after cooling in a desiccator for 5 minutes and a reading to 0.01 mg was taken. Failure to dry the sample adequately at low temperature before removing the organic matter at high temperature can inflate the estimate of organic matter in the sample since the weight loss associated with removal of hydration water is assumed to be organic matter (Pribyl, 2010). The filter was then ashed at 375 °C for 16 hours (Hope *et al.,* 1997a). This ignition temperature and time was chosen because more than 90 % of carbonaceous material has been shown to be removed under such conditions (Keeling, 1962). Organic matter oxidises at ~500 °C thus ashing at lower temperatures for a longer period avoids structural water loss from clay minerals and reduces the potential loss of CO_2 from inorganic matter and carbonates, which would result in an overestimate of POC (Ball, 1964). The filter was re-weighed after cooling in a desiccator for 5 minutes and the readings to 0.01 mg on the balance were stable almost immediately. Finally [POC] was calculated using the standard van Bemmelen conversion factor of 0.58 (van Bemmelen, 1891; *c.f* Pribyl, 2010), that is assuming that 58 % of organic matter comprises C. Although this is a figure for loss on ignition of soils, it was deemed more appropriate for the water samples in this research which drain from organic-rich soils compared to another common conversion factor of 0.33 derived for coastal surface sediment (Hunt, 1981).

From June 2006 to September 2007 the majority of the analysis of POC was carried out on samples that were frozen on return from the field, and, at a later date, usually within a week, de-frosted overnight and filtered. From October 2007 onwards samples for POC analysis were refrigerated and filtered immediately on return from the field, usually within 3 hours (see Chapter 2.4.2).

3.2.2. Dissolved Organic Carbon

Two methods have been used to determine DOC in water samples from the Whitelee catchments. From June 2006 to September 2007, prior to this research, the methodology outlined in Waldron *et al.* (2009) used a 100 mL aliquot of a 1 L sample which had been frozen on return from the field, de-frosted overnight and filtered for POC analysis. Where carbonate was likely to be present in the sample, the filtrate was acidified to pH 4 with 0.1 M H_2SO_4. It was then filtered through a GF/F filter, and reduced to a concentrate by rotary evaporation (at 50 °C and 50 mbar). The concentrate was subsequently freeze-dried to a powder. wt % C was assayed by analysis of c. 2 mg of dried powder on a Costech C/N/S analyser, linked to a ThermoFinnigan continuous flow mass spectrometer (at the Scottish Universities Environmental Research Centre). From the volume of sample filtered, mass of solid residue and the wt % C [DOC] was calculated.

From October 2007 to June 2010 DOC analysis was carried out on a 100 mL aliquot of the 1 L sample used for POC analysis which had been filtered through a GF/F filter on return from the field. The filtered 100 mL aliquot was frozen, for up to a year in some cases, prior to DOC analysis to minimise bacterial decomposition. After defrosting overnight, to convert inorganic C to dissolved CO_2, 50 mL was acidified with 0.01 M H_2SO_4 to pH 3.9 using a Mettler DL 20 Autotitrator and de-gassed for 20 minutes in an ultrasonic bath with the sample container lid loosened. The degassed samples were analysed on a Thermolux TOC analyser which oxidises organic C at high temperature (680 °C) in a stream of O_2 to CO_2, subsequently detected by a non-dispersive infra-red sensor.

Prior to each analysis run, linearity of the response to the standards was checked by calibration with standards prepared by the instrument, in the range of 10 – 60 mg L^{-1} (dilution of a stabilised 1000 mg L^{-1} total organic C standard solution of potassium hydrogen phthalate in water with acidified de-ionised water). Zero standards were analysed as the first two and last two samples on a run, and also every 9 samples in order to check the background CO_2 levels in the system, which were typically negligible. A gravimetrically prepared check standard (typically 10 mg L^{-1}) was analysed after every ten samples to check for drift and the instrument-prepared standards used for the calibration were included as samples in every run to assess analyser performance. On all occasions the analyser performed satisfactorily, within 1 % of standard concentration therefore drift correction was not necessary. The limit of detection of the DOC analyser is 1 mg L^{-1}. Reproducibility studies on 5 samples collected simultaneously on 20th October 2008 at sampling point 456 produced a mean [DOC] of 23 ± 0.6 mg L^{-1}, showing there is little intra-sample variation and that any contamination effects from sample containers are minimal and also that it is not necessary to run samples in duplicate.

3.3. Phosphorus and Nitrogen Analysis

Phosphorus and nitrogen analysis were primarily carried out by Helen Murray, however, some of the analysis was conducted by other analysts (Table 10) following identical protocols. The following methods used for the phosphorus and nitrogen analysis were taken from the Technicon Methods Handbook and were developed for low level analysis. It was decided to carry out the analysis for the same phosphorus and nitrogen species as the June 2006 to September 2007 pre-disturbance time series collected by Waldron *et al.* (2009), a decision based on time and cost constraints. The phosphorus and nitrogen species measured are the most important in terms of the sustainability of habitat downstream and the safe provision of drinking water for domestic use.

Table 10. Analysis carried out by other analysts.

Analyst	Parameters	Section of Time Series
Waldron *et al.* (2009)	DOC, POC, TP, SRP, NO_3^-, NO_2^-	Jun 2006 – Sep 2007
Nigel Andrews	SRP, NO_3^-, NO_2^-	Oct 2007 – Jan 2008
Steven Adam	SRP, NO_3^-, NO_2^-	Oct 2008 – Jan 2009
Paul Gaffney	SRP, NO_3^-, NO_2^-	Oct 2009 – Jan 2010

All glassware for the preparation of reagents and plastic filtration apparatus was soaked overnight in a 2 % solution of phosphate-free Decon® detergent before being rinsed with copious volumes of warm tap water followed by rinsing twice in de-ionised water and drying thoroughly. To reduce variability between analysts the stock standard solutions were kept consistent between analysts where possible.

3.3.1. Sample Filtration for SRP, NO_3^- and NO_2^-

On return from the field, the 100 mL aliquot for SRP, NO_3^- and NO_2^- analysis was briefly stored below 4 °C before filtration which was typically carried out within 3 hours of collection. The aliquot was shaken by hand prior to filtration to re-suspend any material which had settled during storage and 50 mL was vacuum-filtered through a Whatman 47 mm diameter 0.2 μm nylon membrane filter into a 50 mL centrifuge tube. Three blanks of de-ionised water were treated in the same way as the samples. The filter assembly was rinsed thoroughly with de-ionised water between samples and also with some of the next sample to avoid cross-contamination. These filtered samples and blanks were then stored overnight below 4 °C until analysis which was carried out typically within the following two days.

3.3.2. Analysis for SRP, TP, NO_3^- and NO_2^-

The nutrient concentrations were determined colorimetrically using a Technicon Autoanalyser II, a segmented flow system, which uses an air bubble to separate samples within the system and splits each sample into several segments. It consisted of an autosampler, peristaltic pump, water bath at 20 °C for reagents, water bath at 37 °C for reactions and mixing, manifold, colorimeter, chart recorder and computer (Figure 10). To minimise cross-contamination between samples wash water was injected through the system between samples. For NO_3^- and NO_2^- analysis the wash solution was 0.2 mL L^{-1} 15 % Brij-35 solution in de-ionised water, and de-ionised water only was used for SRP analysis system because the wetting agent Brij-35 interferes with the TP and SRP system. Each nutrient analysis was carried out using the same apparatus except for the manifold which consists of the appropriate tubing and mixing coils for the specific colorimetric reaction.

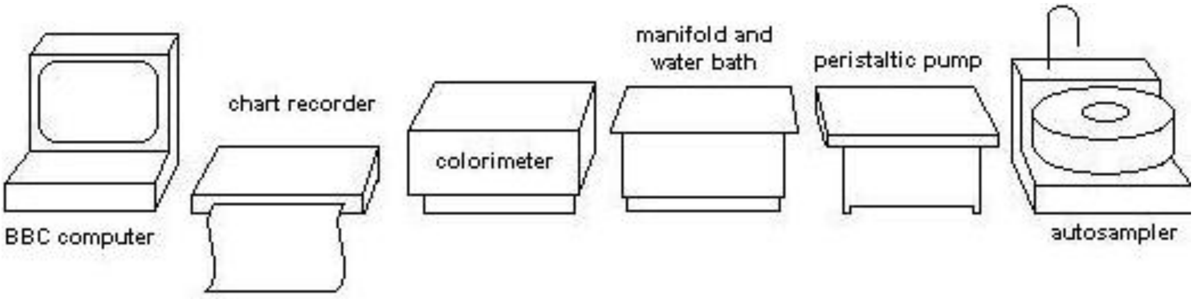


Figure 10. Diagram showing the main components of Technicon Autoanalyser II.

After the colour development, reaction in the manifold the sample passes through the colorimeter. In the colorimeter light of the appropriate wavelength is selected using a coloured filter. This light passes through the solution in the flow cell and the absorbance is proportional to colour intensity which is plotted as a peak on the chart and the peak height is recorded by the computer. The colour intensity of the samples was compared to that of a previously analysed known concentration standard and the peak height used to calculate concentration. Since concentration is calculated from peak height, the smoother the peak shape, the more precise the concentration value.

The manifold and tubing of the Technicon were cleaned when switching between determinants by rinsing for 15 minutes with either 5 % H_2SO_4 solution or a 1 M NaOH solution if the reagent mix had been alkaline or acidic respectively, followed by flushing with de-ionised water for 20 minutes.

A steady baseline signal and a regular bubble pattern were required on the Technicon Autoanalyser before any analysis was conducted. During a sample run, drift occurred due to electronic drift and changes in room temperature. To quantify drift, two standards followed by a wash and two zero standards were analysed after every 12 samples. The drift during the twelve samples was then calculated by the computer from the two adjacent sets of standards and used by the software to adjust the sample concentrations. In every run three blanks were analysed and subtracted by the software from the measured sample concentrations. Duplicate samples were analysed and a mean concentration calculated by the analyst.

3.3.2.1. SRP Analysis

To avoid changes caused by processes in solution and interactions of soluble compounds with suspended material of less than 0.2 μm during storage (House *et al.,* 1998), SRP was the priority analyte on return from the field, with analysis usually carried out within 24 hours of sample filtration (Kotlash and Chessman, 1998; Eaton *et al.,* 2005). SRP was measured using an ammonium molybdate-ascorbic acid method (Murphy and Riley, 1962) adapted for low level analysis. The method is based upon the orthophosphate ion reacting with ammonium molybdate in an acid solution to form phosphomolybdic acid, a faintly yellow coloured product. This is then reduced by ascorbic acid to give an intense blue colour. Antimony potassium tartrate is added to increase the rate of the reaction. This reaction is preferred over other methods as it is less temperature sensitive and the chromophore is more stable (Robards *et al.,* 1994). Figure 11 shows the manifold set up for SRP analysis. The method had a limit of quantification of 1 μg P L^{-1}. See Appendix 3 for the reagents required for P analysis on the Technicon Autoanalyser.

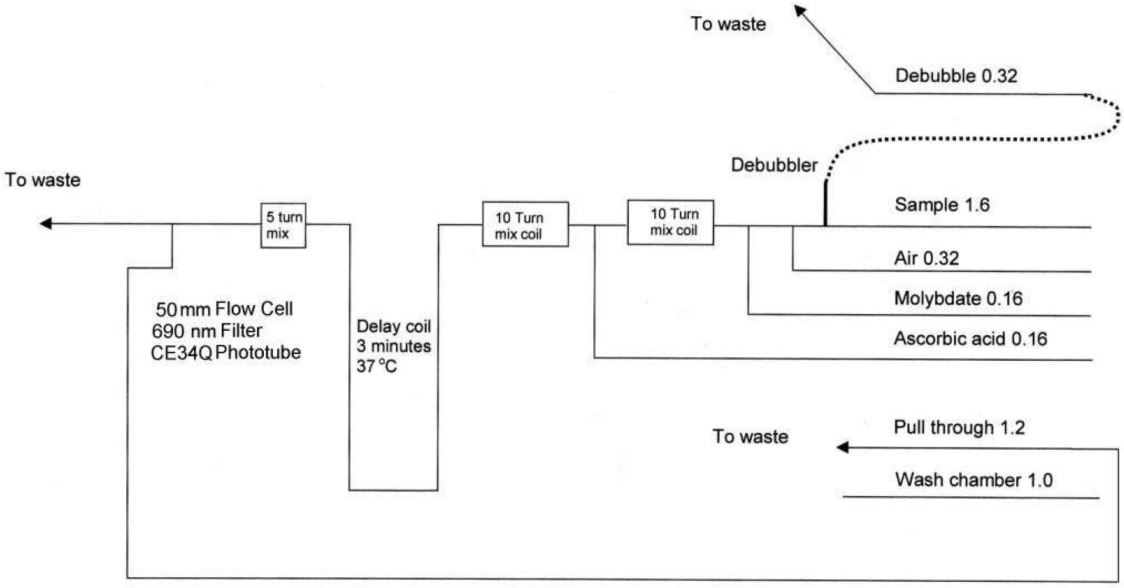


Figure 11. Manifold for SRP and TP analysis set up with a sampling rate of 40 per hour.

3.3.2.2. TP Analysis

TP analysis required the digestion of an unfiltered sample. As vapour losses were not an issue during refrigerated storage, analysis was carried out at a convenient time after sample collection; for some samples up to one year after collection. All glassware for the digestion of samples was soaked in phosphate-free 2 % Decon® solution overnight, rinsed thoroughly, soaked in 10 % hydrochloric acid for at least 30 minutes, then rinsed thoroughly with de-ionised water and dried.

The 100 mL unfiltered sample for TP analysis was removed from refrigeration, allowed to come to room temperature, shaken well and 25 mL pipetted into a small glass bottle. 0.5 mL of 30 % H_2SO_4 and 0.25 g of $K_2S_2O_8$ were added to each sample. The bottles were then capped loosely with aluminium foil and digested in an autoclave at 121 °C for 30 minutes (Eaton *et al.,* 2005). Once cooled the digests were transferred quantitatively to 50 mL volumetric flasks and made up to volume with de-ionised water. The same procedure was carried out on three blanks, using 25 mL de-ionised water, per batch of 20 digested samples. [TP] in the samples was determined by colorimetric analysis by the method used for SRP (see Chapter 3.3.2.1 and Appendix 3) using the same manifold set up as SRP (Figure 11).

3.3.2.3. NO_3^- Analysis

The water sample remaining after SRP analysis was kept refrigerated and N species were measured, usually two days after filtration, in order to minimise the loss of nutrients through assimilation by micro-organisms present in the water and, in the case of NO_2^-, bacterial conversion to NH_4^+ and NO_3^- (Kotlash and Chessman, 1998). [NO_3^-] was determined using a method based on the reaction in Mullin and Riley (1955) and the automated methods of Henriksen (1965) and Best (1976). NO_3^- is quantitatively reduced to NO_2^- by hydrazine under alkaline conditions using the copper (II) ion as the catalyst. The total NO_2^- is subsequently treated with sulphanilamide and N-1-napthylenediamine dihydrochloride under acidic conditions to form a pink azo dye. This method therefore measures TON, both NO_3^- and NO_2^- in the sample. In order to determine the [NO_3^-] in the sample, NO_2^- is measured separately (see Chapter 3.3.2.4) and subtracted from the [TON]. Figure 12 shows the manifold set up for TON analysis. The limit of quantification was 10 µg N L^{-1}. See Appendix 3 for the reagents required for TON analysis on the Technicon Autoanalyser.

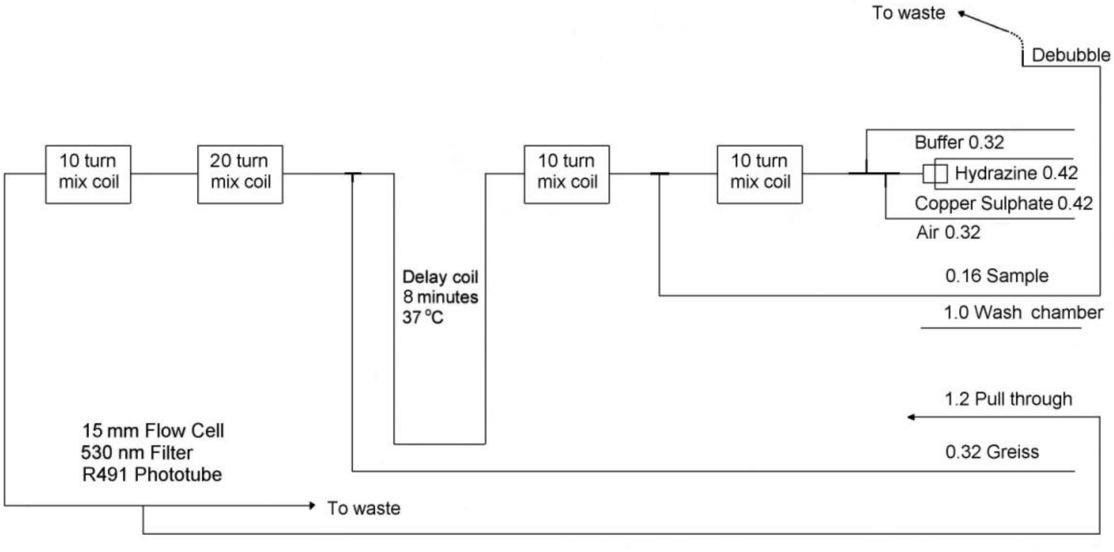


Figure 12. Manifold for TON analysis set up with a sampling rate of 50 per hour.

3.3.2.4. NO_2^- Analysis

[NO_2^-] was determined using an automated method based on Henriksen (1965) and Best (1976) which involves the diazotisation of sulphanilic acid by nitrites to form nitrous acid under acid conditions. The resultant diazonium salt then couples with the N-1-napthylenediamine dihydrochloride to form a deep pink coloured azo compound. This method used a large sample:reagent ratio and had a limit of quantification of 1 µg N L^{-1}. Figure 13 shows the manifold set up for NO_2^- analysis and the reagents required are included in Appendix 3.

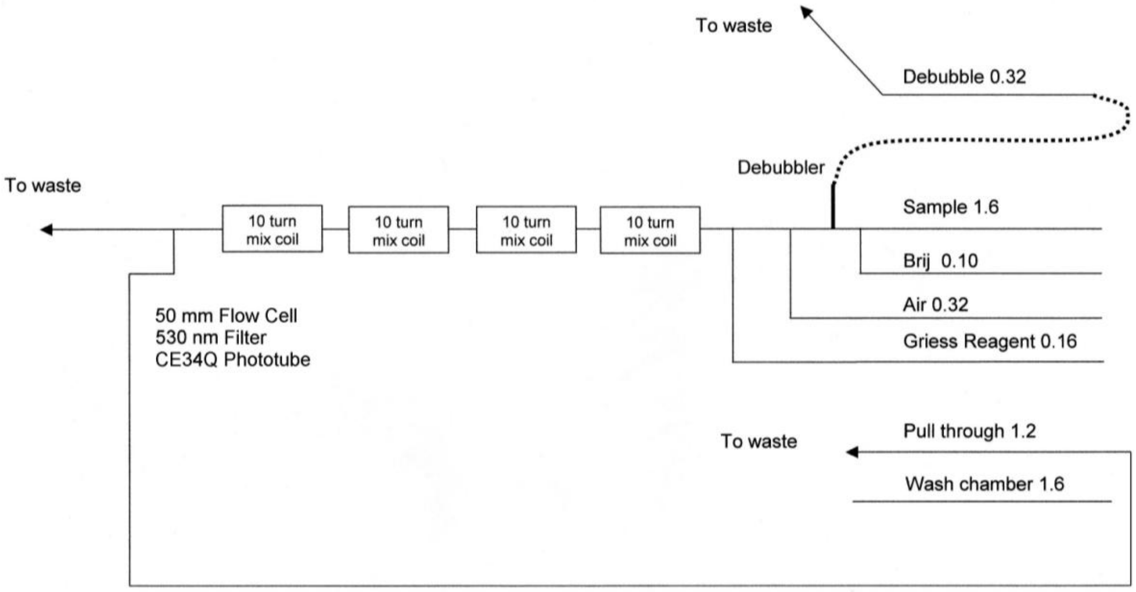


Figure 13. Manifold for NO_2^- analysis set up with a sampling rate of 40 per hour.

3.3.3. SRP and NO_2^- Analysis Colour Correction

The analysis of nutrient concentration by colorimetry is where reagents react with the analyte to produce a colour of a certain wavelength whose absorbance is then measured by a colorimeter. A problem can occur when this method is used to analyse naturally highly-coloured samples and where the ratio of colour to analyte required for very low level analysis is high, such as in this research. Here, the background colour of the sample may interfere in the measurement of concentration at the same wavelength and lead to an increased measure of absorbance and thus an over-estimation of concentration in the sample. Correction for the background colour of the sample is therefore required.

The need for colour correction only became apparent in October 2008 when the filter pore size comparison experiment was carried out (see Chapter 3.7). Spiky peaks on the Technicon chart output were generated by the samples filtered through 0.7 μm filters. To investigate the cause of these irregular peak shapes, samples were run with the non-reacting reagents only. For these samples, if the peak shape was caused by the chemical reaction between the sample and reagents it was predicted that no noise and no peaks would be seen. If it was caused by particulate matter then a noisy baseline and no peaks were expected. The results showed that when the samples were run with the non-reacting reagents there was a noisy baseline but also peaks. Thus something else in the samples, e.g. background colour from humic compounds in the dissolved aqueous phase, was also absorbing light at the same wavelength and contributing to the [SRP] calculated for the sample.

Running the same test with samples using the method for NO_2^- determination showed that background colour was also influencing the measured [NO_2^-]. Consequently the methods for SRP and NO_2^- determination were altered to take account of background colour in future sample analyses and the results of previous analyses were corrected as explained below. Background colour correction is not necessary for NO_3^- analysis as it is already accounted for in the subtraction of NO_2^- from TON. Establishing the procedure was largely the work of Adam (2009) but is discussed here as it is required as part of the analytical protocol for this research and is currently unpublished.

3.3.3.1. Colour Correction Procedure

To correct for background colour in the SRP and NO_2^- analyses, the samples were first analysed using the standard procedure and reagents to obtain non-colour corrected concentrations (Figure 14A). The relevant reagents were then replaced by the modified colour correction reagents (see Appendix 4) and the baseline was re-established. All other settings were kept the same so that the peak heights could be related directly to the peak heights of the previous run and subsequently subtracted. The same series of standards, blanks and samples was run and, since no colour reaction was taking place, both standards and blanks gave the same low reading, and the peaks produced here can be attributed to the background colour of the samples (Figure 14B).

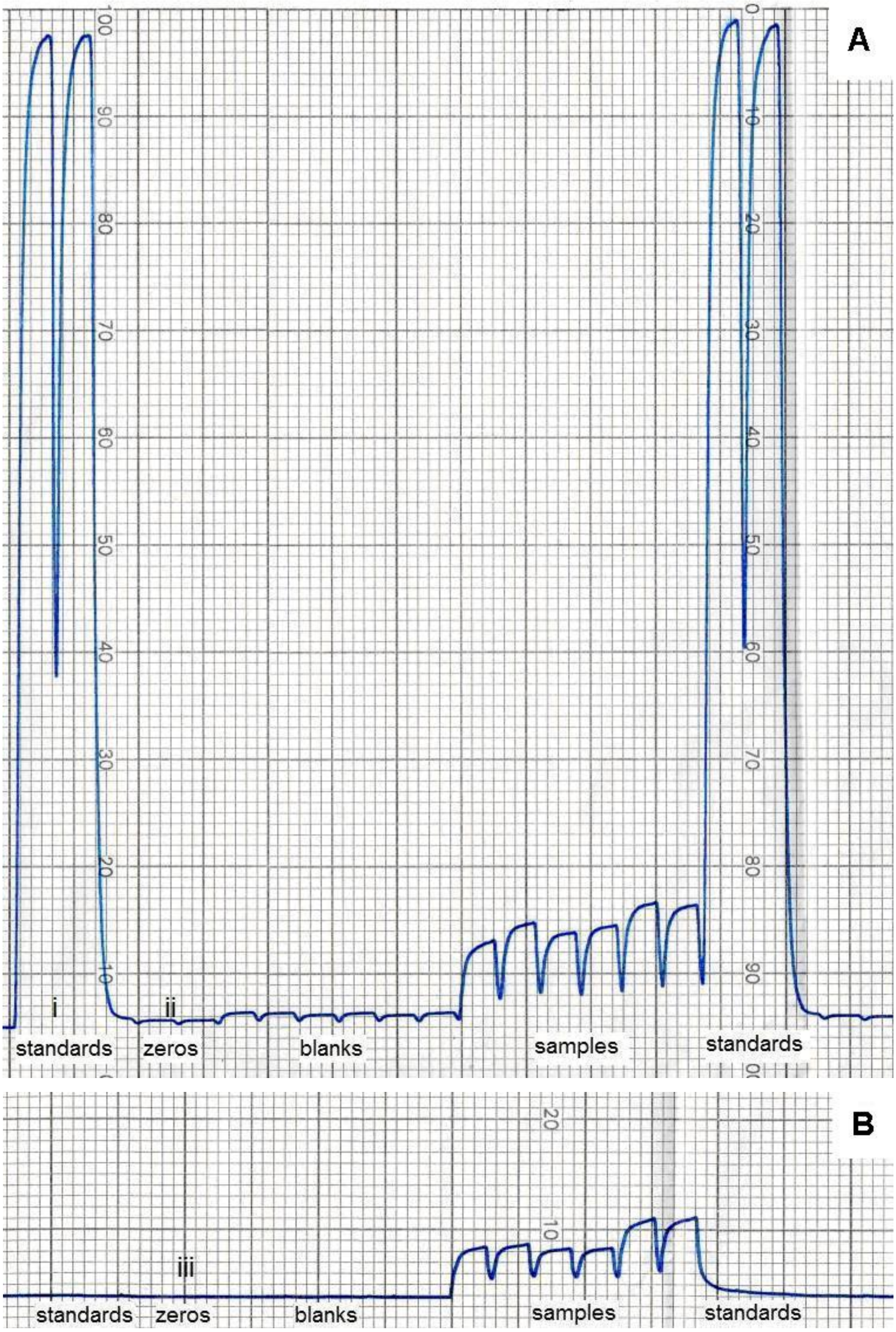


Figure 14. Panel A is an example Technicon chart of non-colour corrected data. Panel B shows the colour contribution peaks of the same samples. i indicates the non-colour corrected standard peaks. ii indicates the non-colour corrected zero. iii the colour correction zero.

3.3.3.2. Colour Correction Calculation

The method to correct for background colour is based on the assumption that the peaks produced by the reaction colour and the background colour are additive therefore the effect of the background colour can be quantified by subtracting the height of the peak produced by background colour in the absence of the colorimetric reagent from the sample peak height (Figure 14). The Technicon calculation software was run twice, once to determine uncorrected sample concentration and once to determine colour-corrected sample concentration. The colour corrected concentration for a sample was obtained by subtracting the concentration determined in the colour correction run from the concentration determined in the non-colour corrected run.

The contribution of colour to the sample peaks is summarised in Table 11 and was variable between catchments and between sampling occasions. The greatest contribution of colour to the sample peaks was found in the S-draining catchments which are more peatland-dominated (see Figure 7, Chapter 2.2 for soil types and Table 7, Chapter 2.4.1 for % of each catchment peat-based soils). Adam (2009) determined that, for water samples from all catchments on a number of sampling occasions, the absorbance was greater at 530 nm, the wavelength used to measure [NO_2^-], than at 690 nm, the wavelength used to measure [SRP]. This can explain why colour is a greater interference when analysing for [NO_2^-].

Table 11. Range of colour interference expressed as μg L^{-1} and as a % of peak height.

Parameter	S-draining Interference (μg L^{-1})	Average % contribution to peak height	N-draining Interference (μg L^{-1})	Average % contribution to peak height
[SRP]	1 - 14	15	0 - 4	9
[NO_2^-]	1 - 23	70	0 - 7	30

3.3.3.3. Retrospective Colour Correction

Direct colour correction, where two runs, one non-colour corrected, one colour correction, were carried out for all [SRP] and [NO_2^-] determinations from October 2008. Direct colour correction was not carried out prior to October 2008 and therefore this section of the time series was thought to over-estimate concentration. In order to retrospectively colour correct the [SRP] and [NO_2^-] time series from June 2006 to September 2008, the difference between the non-colour corrected concentration and the colour corrected concentration was regressed linearly with the [DOC], which is related to water colour, from the 34 sampling occasions between October 2008 and June 2010. From the relationships in Figure 15 and Figure 16, colour corrections were applied retrospectively to the non-colour corrected [SRP] and non-colour corrected [NO_2^-].

However, an individual colour correction for each catchment could not be justified due to the limited number of data points and variation around the regression line. Further to this, the variability between catchments meant that one correction relationship for all catchments would not be appropriate. A comparison of the regressions on the relationships of [SRP] and [NO_2^-] with [DOC] pooled N- and S-draining was carried out. The regressions for the pooled N- and S- draining catchments were found to be highly significantly different for both [SRP] and [NO_2^-] ($t = 6.66$, $p < 0.0001$, D.F. = 300 and $t = 6.01$, $p < 0.0001$, D.F. = 289 respectively), confirming that a single correction for all catchments regardless of soil type would not appropriately correct for water colour. Two colour corrections were therefore carried out for each parameter based on the dominance of different soil types at Whitelee because of the different contributions of water colour to peak height. The difference in soil types with the drainage divide of the Whitelee plateau, the peatland-dominated S-draining catchments and the more agricultural influenced N-draining catchments (Table 11) influences the colour of the water samples due to the differing types of organic matter and humic material mobilised in each catchment.

The two outlying high [DOC] values in the pooled N-draining samples were checked, found to be correct and therefore it was not justifiable to remove them from the regression used to determine the retrospective colour correction. For the few sampling occasions where [DOC] data were not available these concentrations were not reported. Data from 17U did not require correction since sampling here started after the colour-induced absorbance effect was noted.

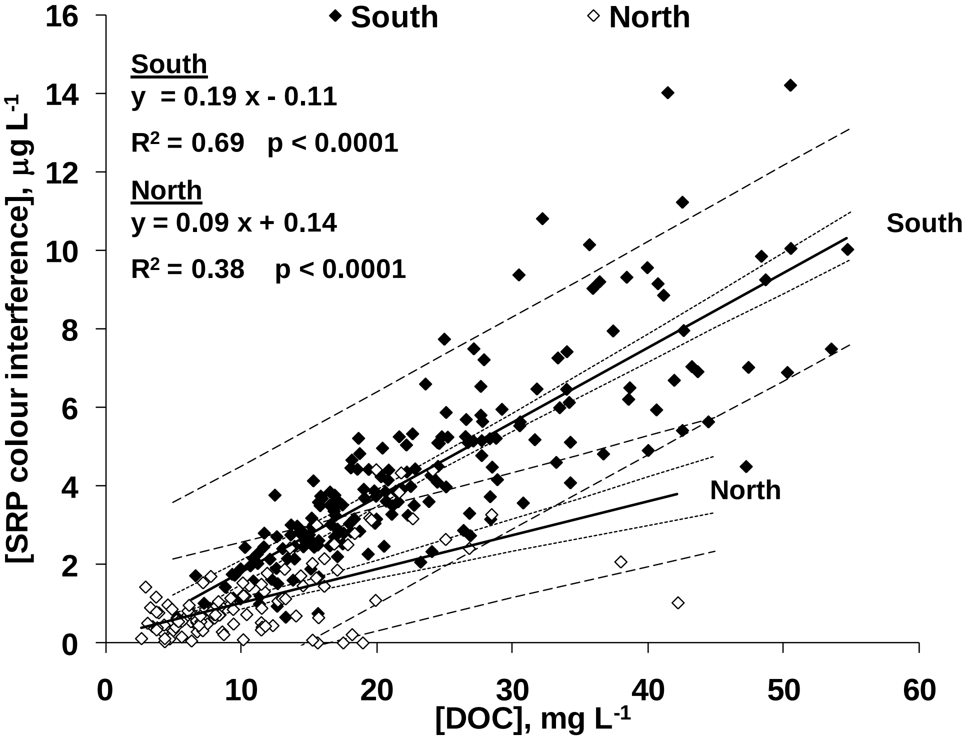


Figure 15. The relationships, solid black lines, applied for retrospective colour correction of [SRP] in the S- and N-draining catchments from June 2006 to September 2008. The short dash lines indicate the 95 % confidence intervals and the long dash lines the 95 % prediction intervals.

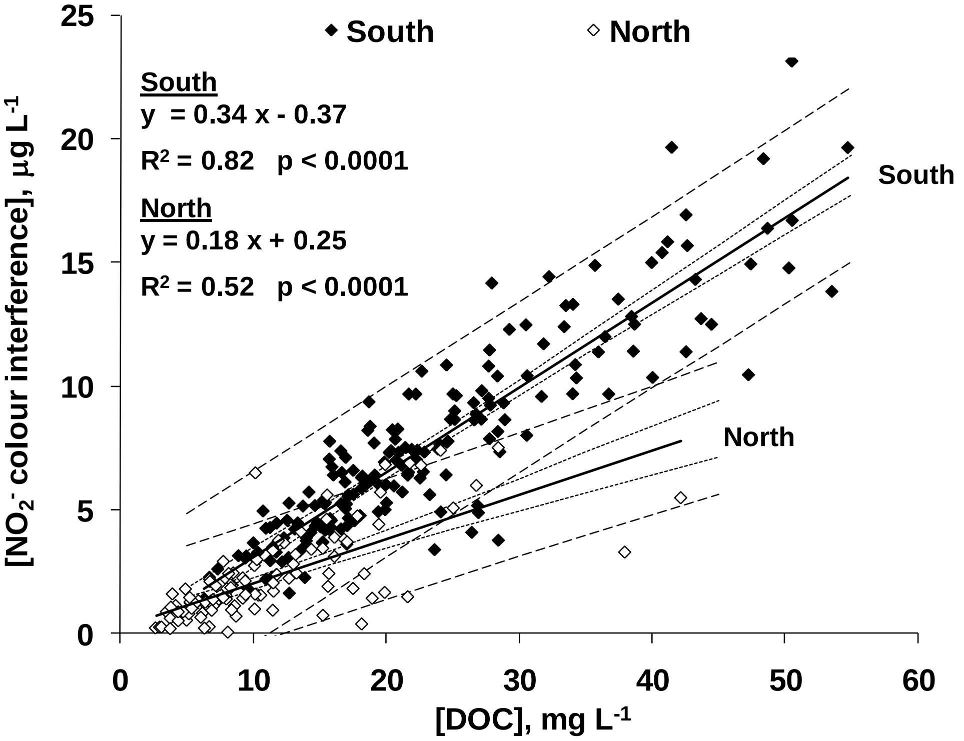


Figure 16. The relationships, solid black lines, applied for retrospective colour correction of [NO_2^-] in the S- and N-draining catchments from June 2006 to September 2008. The short dash lines indicate the 95 % confidence intervals and the long dash lines the 95 % prediction intervals.

3.4. Alkalinity Analysis

Water samples were analysed for alkalinity for one hydrologic year from October 2009 because alkalinity was required to determine the status of river water according to the Water Framework Directive (2000) UK Technical Advisory Group Environmental Standards for [SRP] (UKTAG, 2008) (see Chapter 1.3.2). Alkalinity was measured on an unfiltered sample immediately on return from the field using the method in MEWAM (1981a), as used by the Scottish Environment Protection Agency and the USA Environmental Protection Agency. A Metrohm DL20 auto-titrator was used which carries out acid-based titrations using a pH electrode to detect the endpoint and a micro-burette capable of measuring the titre to 0.1 μl. Prior to analysis the pH electrode was calibrated using pH 4.0 and 7.0 buffers. The alkalinity was determined by titrating 50 mL of sample to pH 4.5 with 0.01 M H_2SO_4. 1 mL of 0.01 M H_2SO_4 is equivalent to 1 mg of $CaCO_3$. The stirrer and pH electrode were rinsed with de-ionised water between samples, and between sampling occasions the electrode was conditioned in acidified 3 M KCl solution.

3.5. Uncertainties in Quantification of Concentration

A maximum uncertainty of ± 5.2 mg L^{-1} was calculated for [DOC]. This value is the maximum uncertainty on the lowest concentration standard measured on each calibration of the Thermolux TOC analyser calculated using the formulae for inverse confidence limits from Miller (2006) (see Appendix 6) as this was thought to be the greatest source of variation in [DOC].

Uncertainties in the determination of [POC], [SRP], [TP] and [NO_3^-] were not calculated as part of this research. The greatest source of uncertainty is thought to be from the representativeness of the sample collected. In terms of [POC], the experimental error associated with the loss on ignition method and in terms of [TP] there is potential for there to be errors associated with sample digestion (e.g. contamination as shown by variation in the blanks), however, these sources of variation are thought to be small compared to sample variability. The uncertainty due to instrument measurement variation in the Technicon Autoanalyser II will be small because using a high precision automated system reduces operator variability and any drift in the instrumentation is corrected by the software. In future multiple samples should be collected at the same time for analysis to quantify sample variability.

3.6. Sample Filtration Investigation

Since [SRP], [NO_3^-] and [NO_2^-] in a water sample can be decreased by microbial uptake and adsorption to particulate matter or, conversely, released into solution through microbial death, filtration is necessary to remove micro-organisms, such as bacteria and phytoplankton, and particulate matter. The length of time between sample collection and filtration is critical if measured concentrations are to be representative of field concentrations (MEWAM, 1981b). Nutrient concentrations can change (mostly losses) within 2 to 6 days if there is no attempt at preservation (Kotlash and Chessman, 1998).

To test if there was any loss or gain of SRP, NO_3^- and NO_2^- from the samples during the time period from collection to filtration, additional water samples were collected on all sampling occasions at all catchments from January to April 2009. These samples, hereafter named field-filtered, were filtered immediately at the time of collection using a new 0.2 µm Supor® membrane syringe filter and a 10 mL sterile syringe for each sample, rinsed with water from the sample point before use. The samples were filtered into the same type of 50 mL centrifuge tube as used in the laboratory and transported to the laboratory in cool boxes. [SRP], [NO_3^-] and [NO_2^-] in the field-filtered samples were determined at the same time and under the same conditions as the samples collected and filtered following the standard procedure, hereafter named the laboratory-filtered samples. Blanks for the field-filtered samples were prepared in the laboratory by filtering de-ionised water through the 0.2 µm syringe filters using fresh 10 mL sterile syringes. The two sets of samples were analysed using the standard SRP, NO_3^- and NO_2^- protocols and a paired t-test used to determine whether the sample populations have different means. This was done to determine whether there was a statistically significant difference due to the time of filtration or whether any difference was a coincidence of random sampling (Table 12).

There were significant differences for [SRP] and [NO_2^-] but not [NO_3^-] ($p = 0.54$, Table 12). The field-filtered samples had a higher [SRP] than the laboratory-filtered samples. The p value from the t-test (Table 12) of < 0.001 shows a highly significant mean difference of 2.78 µg L^{-1} between the two filtration methods. This difference was considered scientifically significant as well as statistically significant because a mean difference of 2.78 µg L^{-1} where the mean concentration values are less than 30 µg L^{-1} was approximately a 10 % difference. The laboratory-filtered samples contained greater [NO_2^-] than the field-filtered samples. The p value from the t-test ($p = 0.01$, Table 12) shows that this was a significant mean difference of 0.47 µg L^{-1} between the two filtration methods.

Table 12. Paired t-test results of [SRP], [NO_3^-] and [NO_2^-] in field-filtered and laboratory-filtered samples. N = 28.

	Mean [SRP], $\mu g\ L^{-1}$	Standard Deviation, $\mu g\ L^{-1}$
Laboratory	23.4	16.
Field	26.2	16.7
Difference	-2.78	3.48
95 % confidence intervals for mean difference: (-4.15, -1.40)		
t-test of mean difference = 0 (vs not = 0): t = -4.15 p < 0.001		

	Mean [NO_3^-], $mg\ L^{-1}$	Standard Deviation, $mg\ L^{-1}$
Laboratory	0.56	0.43
Field	0.56	0 43
Difference	-0.005	0.041
95 % confidence intervals for mean difference: (-0.02, 0.01)		
t-test of mean difference = 0 (vs not = 0): t = -0.62 p = 0.54		

	Mean [NO_2^-], $\mu g\ L^{-1}$	Standard Deviation, $\mu g\ L^{-1}$
Laboratory	5.9	4.7
Field	5.4	4.8
Difference	0.4	0.90
95 % Confidence Intervals for mean difference: (0.12, 0.82)		
T-Test of mean difference = 0 (vs not = 0): T = 2.76 P = 0.01		

To examine if it is the filter material which is affecting [SRP], [NO_3^-] and [NO_2^-], on one occasion the 100 mL aliquot was shaken well and split, with 50 mL filtered following the standard procedure and 50 mL filtered in the laboratory at the same time using the 0.2 µm Supor® membrane syringe filter and 10 mL syringe. The two sets of samples were analysed using the standard SRP, NO_3^- and NO_2^- protocols. A paired t-test (Table 13) was used to show whether the sample populations have statistically significant different means. These results were then compared with Table 12 to determine whether the difference was due to the time of filtration or the filtration material used.

Table 13 shows that the differences observed between [SRP] and [NO_2^-] Supor® membrane syringe filtered samples and the sample filtered through nylon membrane are consistent with the offset observed by comparison of field-filtered samples with laboratory filtered samples (Table 12). It seems likely that the greater [SRP] and lesser [NO_2^-] in Supor® membrane syringe filtered samples were due to the filter material rather than the timing of filtration as it was still obvious when the samples were filtered at the same time.

As immediate filtration in the field was a more expensive option, and would produce data not directly comparable with previous studies at this field site, samples for SRP, NO_3^- and NO_2^- analysis continued to be collected and stored in a cool box until return to the laboratory where filtration was performed immediately.

Table 13. Paired t-test of [SRP], [NO_3^-] and [NO_2^-] in 0.2 µm Supor® membrane syringe filtered and 0.2 µm nylon membrane filtered samples. N = 10.

	Mean [SRP], µg L^{-1}	Standard Deviation, µg L^{-1}
Nylon	25.0	28.7
Supor®	28.2	30.3
Difference	-3.21	3.07
95 % confidence intervals for mean difference: (1.01, 5.41)		
t-test of mean difference = 0 (vs not = 0): t = 3.31 p = 0.009		

	Mean [NO_3^-], mg L^{-1}	Standard Deviation, mg L^{-1}
Nylon	0.75	0.64
Supor®	0.75	0.65
Difference	-0.005	0.01
95 % confidence intervals for mean difference: (-0.02, 0.01)		
t-test of mean difference = 0 (vs not = 0): t = -0.62 p = 0.54		

	Mean [NO_2^-], µg L^{-1}	Standard Deviation, µg L^{-1}
Nylon	16.2	11.8
Supor®	14.8	12.0
Difference	1.45	1.22
95 % confidence intervals for mean difference: (-2.32, -0.58)		
t-test of mean difference = 0 (vs not = 0): t = -3.76 p = 0.004		

3.7. Filter Pore Size Investigation

Either 0.45 µm or 1 µm filters can be used to prepare a water sample for [SRP], [NO_3^-] and [NO_2^-] analysis (MEWAM, 1992) as long as the filter size used is stated, with the choice dependent on the loading of suspended material in the sample. Eaton *et al.* (2005), state that 0.45 µm filters should be used yet there is no evidence that this pore size is a true separation of the suspended and dissolved fractions. It is merely a convenient and replicable choice. For this research a 0.2 µm nylon membrane filter was used to prepare the samples for [SRP], [NO_3^-] and [NO_2^-] analysis. The main justification for the original choice was that it was thought that particles between 0.45 µm and 0.2 µm would interfere in the analysis giving spikes on the trace. Since there is ambiguity over filter pore size in the literature, a test was undertaken to assess the impact of filter pore size on [SRP], [NO_3^-] and [NO_2^-] in the Whitelee samples.

From July to September 2008 the samples for [SRP], [NO_3^-] and [NO_2^-] analysis were filtered through Whatman 0.2 µm nylon membrane filters as per the method described in Chapter 3.3.1. A further sample collected at the same time was filtered using a Whatman 0.7 µm GF/F filter. [SRP], [NO_3^-] and [NO_2^-] were determined using the same methods in the two different sets of pre-filtered samples. Examination of the NO_3^- and NO_2^- traces showed that pore size has no effect on peak shape. Figure 17 shows an example trace from the Technicon Autoanalyser II of peaks for samples analysed for SRP prepared with different filter pore sizes and shows the effect different pore sizes can have on SRP peak shape. The 0.2 µm filtered samples provide the desired conical peak shape for accurate calculation of the [SRP]. The 0.7 µm filtered samples however, in contrast, yield a poorly resolved peak shape with spiking at the top of the peak. This phenomenon occurs because, although the 0.7 µm filtration screens out a large proportion of particulates and micro-organisms from the water sample, the filtration process may neither remove bacteria completely nor colloidal particulate materials, and the light in the colorimeter bounces off these particulates, giving rise to interference in a particularly sensitive low range system. It is difficult for the Technicon software to determine accurately the height of spiky peaks, because the spikes can add 10 % on to the peak height and therefore result in unreliable [SRP]. Based on the effect of filter pore size on peak shape, the 0.2 µm filters were used for the analysis of the Whitelee samples as the peak shapes are clearer and thus more accurate. The use of this pore size is considered when comparing the Whitelee data to the results from other studies.

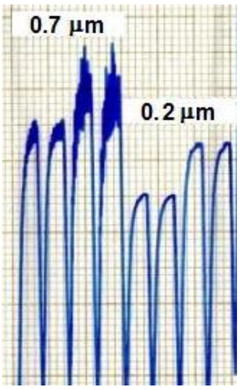


Figure 17. Peaks from SRP trace of two samples filtered through the different pore sizes. 0.7 µm filtered samples yield a spiky peak shape.

3.8. Carbon Analysis Investigation

A change in [POC] and temporal patterns was observed after October 2007, coincident with the analysis as part of this Ph.D research (Figure 18). After this date the mean [POC] in the S-draining catchments decreased from 6.13 mg C L^{-1} to 1.63 mg C L^{-1}, and in the N-draining catchments from 4.53 mg C L^{-1} to 2.07 mg C L^{-1}. The apparent seasonal variation before October 2007 was also no longer observed. Thus it was considered that differing protocols between analysts were influencing the C partitioning in samples. To compare C exports pre- and post-construction it was necessary to identify why this difference had arisen. The protocols used by each analyst to determine POC and DOC are shown in (Figure 19 and Figure 20).

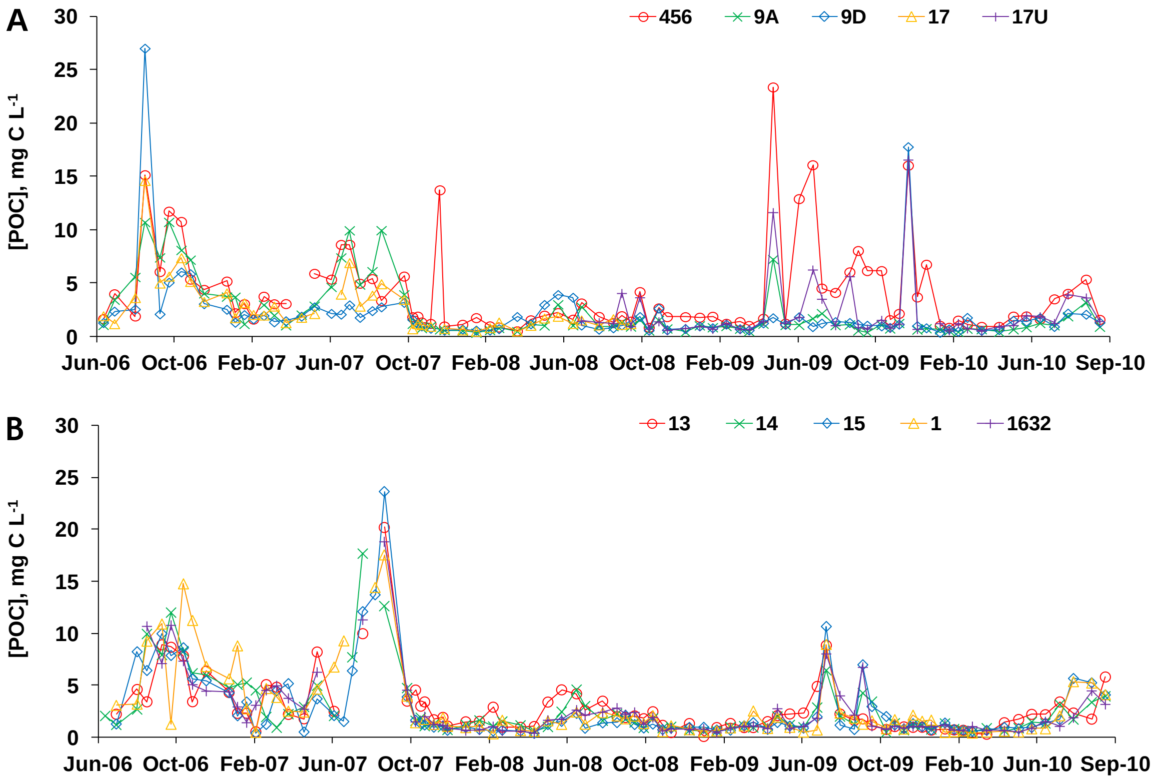


Figure 18. [POC] time series for all the Whitelee catchments with the N-draining catchments in Panel A, and the S-draining in Panel B. The change in analyst in October 2007 is shown by a drop in [POC] and a loss of seasonal signal.

3.8.1. Field Protocol

All analysts followed the same protocol for sample collection in the field as described in Chapter 2.4.2.

3.8.2. Loss on Ignition Measurement Protocol

Pre-ashed (450 °C for 8 hours) Whatman Microfibre GF/F grade (rapid flow rate and high retention, high loading capacity glass microfibre, 0.7 µm retention, 47 mm diameter) filters were used by all analysts. One difference in protocol between the analysts was the loss on ignition temperature. The lower concentration samples from October 2007 onwards were ignited at 350 °C whereas the previous samples had been ignited at 375 °C. Ignition at too low or too high a temperature may seriously under- or overestimate the quantity of organic matter resulting in [POC] that are too low or too high (Pribyl, 2010). To test the effect of differing ignition temperatures, duplicate water samples were collected on one occasion in July 2008 from all sampling points and a paired t-test used to determine whether ignition temperature was having an impact on [POC] (Table 14). There was a mean difference of 0.25 mg L^{-1} with the samples ignited at the higher temperature yielding a higher [POC], but this mean difference was not statistically significant (p = 0.68). From July 2008 the ignition temperature used was 375 °C.

Table 14. Paired t-test conducted for the filter tests of [POC] in mg C L^{-1} determined for ignition temperature of 350 °C v. 375 °C. N = 4.

	Mean [POC], mg L^{-1}	Standard Deviation, mg L^{-1}
350 °C	2.58	0.56
375 °C	2.83	0.78
Difference	-0.25	1.09
95 % confidence intervals for mean difference: (-1.98, 1.48)		
t-test of mean difference = 0 (vs not = 0): t = -0.46 p = 0.68		

Another inconsistency between analysts was that the filters were weighed either immediately upon removal from the furnace or after cooling to room temperature in a desiccator. Hot objects create convection currents which distort mass measurements, however, weighing the filters once at room temperature could allow absorption of moisture from the atmosphere which could be a potential source of the difference in [POC]. To ascertain if filter temperature affected mass determination, a comparison between weighing filters hot and cool was carried out from August to October 2008 on samples from all sampling points on 4 sampling occasions (Table 15). The temperature of the filters when weighed has a negligible impact on mean [POC] (Table 15), and this small difference of hot filters yielding 0.01 mg L^{-1} more than the cool ones is not statistically significant (p = 0.43).

Table 15. Paired t-test of [POC] in mg C L^{-1} determined when filters were weighed immediately after removal from the furnace (hot) and after cooling to room temperature (cool). N = 48.

	Mean [POC], mg L^{-1}	Standard Deviation, mg L^{-1}
Hot	1.71	0.93
Cool	1.70	0.90
Difference	0.01	0.14
95 % confidence intervals for mean difference: (-0.025, 0.058)		
t-test of mean difference = 0 (vs not = 0): t = 0.79 p = 0.43		

3.8.3. Sample Storage Comparison

Since the sample collection and loss on ignition protocols did not account for the decrease in [POC], a comparative study of the sample storage methods on return from the field was carried out, since these methods differed between analysts. The majority of samples collected between June 2006 and September 2007 were frozen on return from the field, de-frosted at a later date and filtered (Figure 19). From October 2007 onwards samples were refrigerated on return from the field and filtered within 3 hours (Figure 20). To assess the impact of different storage mechanisms on return from the field on [POC], two 1 L samples were collected at every sampling point on each sampling occasion from June 2009 until February 2010. One bottle, the refrigerated sample, was filtered immediately on return from the field as described (Figure 20), and the other, the frozen sample, was treated as outlined in Figure 21. Hereafter these samples subjected to differing storage methods are termed refrigerated and frozen respectively. [POC] and [DOC] were then determined on both sets of samples.

Freezing the samples prior to filtration yielded a statistically significant ($p < 0.01$) higher [POC] than refrigeration, with a mean difference of 8.53 mg L^{-1} (Figure 22 and Table 16), which is the same magnitude as the decrease observed from October 2007 (Figure 18). It is hypothesised that the difference is caused by the flocculation or aggregation of particles to greater than 0.7 μm during the freezing process. They are then removed during filtration and contribute to an increased POC fraction of the sample. Previous work on seawater has also postulated aggregation as the explanation for the determination of [POC], using a GF/F filter based method, of up to two orders of magnitude higher in water samples with temperatures < 0°C than in samples > 0°C (Turnewitsch *et al.,* 2007).

Table 16. Paired t-test results for [POC] determined from frozen and refrigerated samples. N = 103.

	Mean [POC], mg L^{-1}	Standard Deviation, mg L^{-1}
Refrigerated	2.1	2.2
Frozen	10.6	8.3
Difference	-8.53	7.37
95 % confidence intervals for mean difference: (-9.97, -7.09)		
t-test of mean difference = 0 (vs not = 0): t = -11.75 p < 0.01		

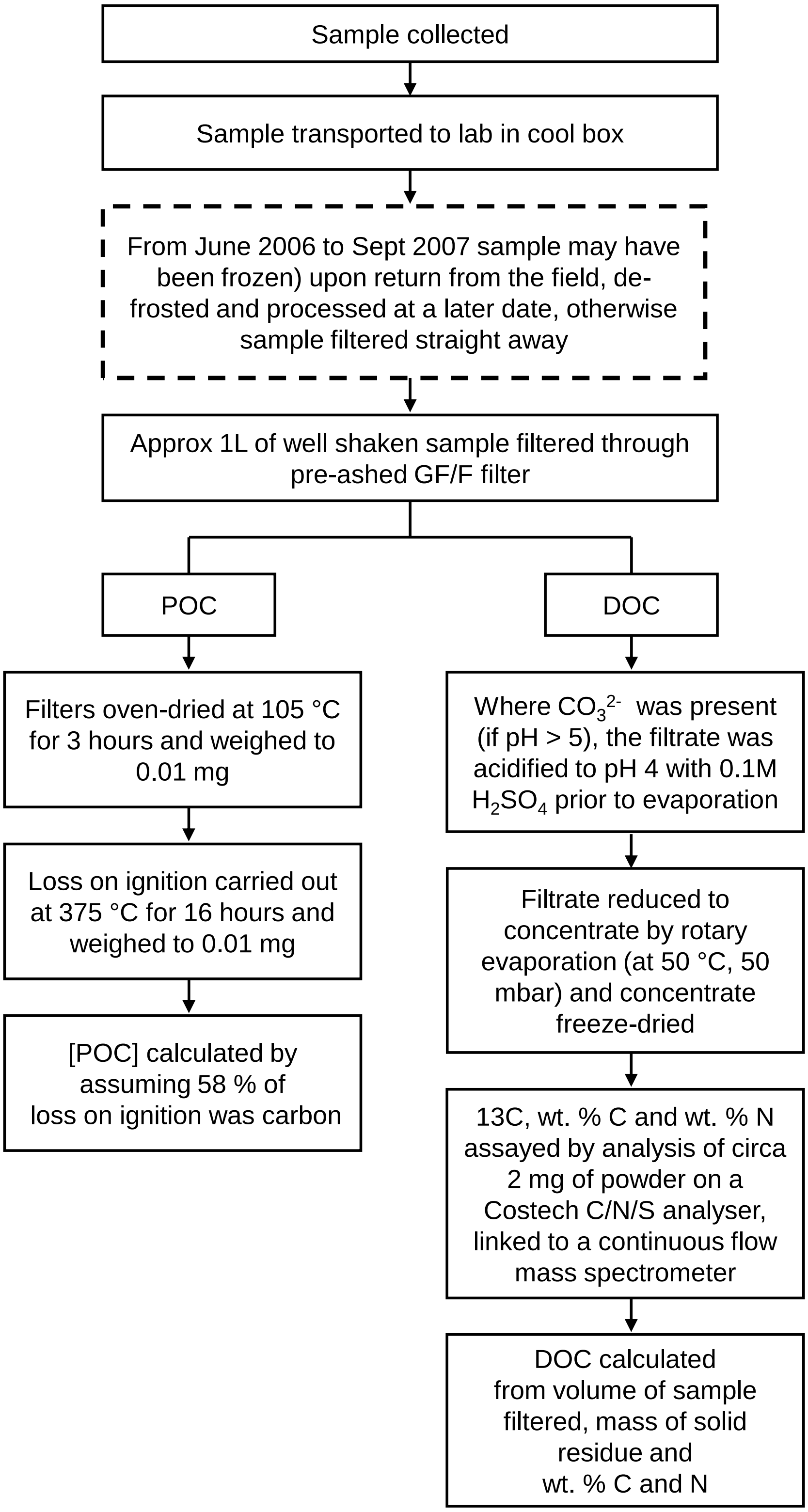


Figure 19. Methods used for C analysis until September 2007 with stage of protocol where flocculation may be occurring in a thick dashed line box.

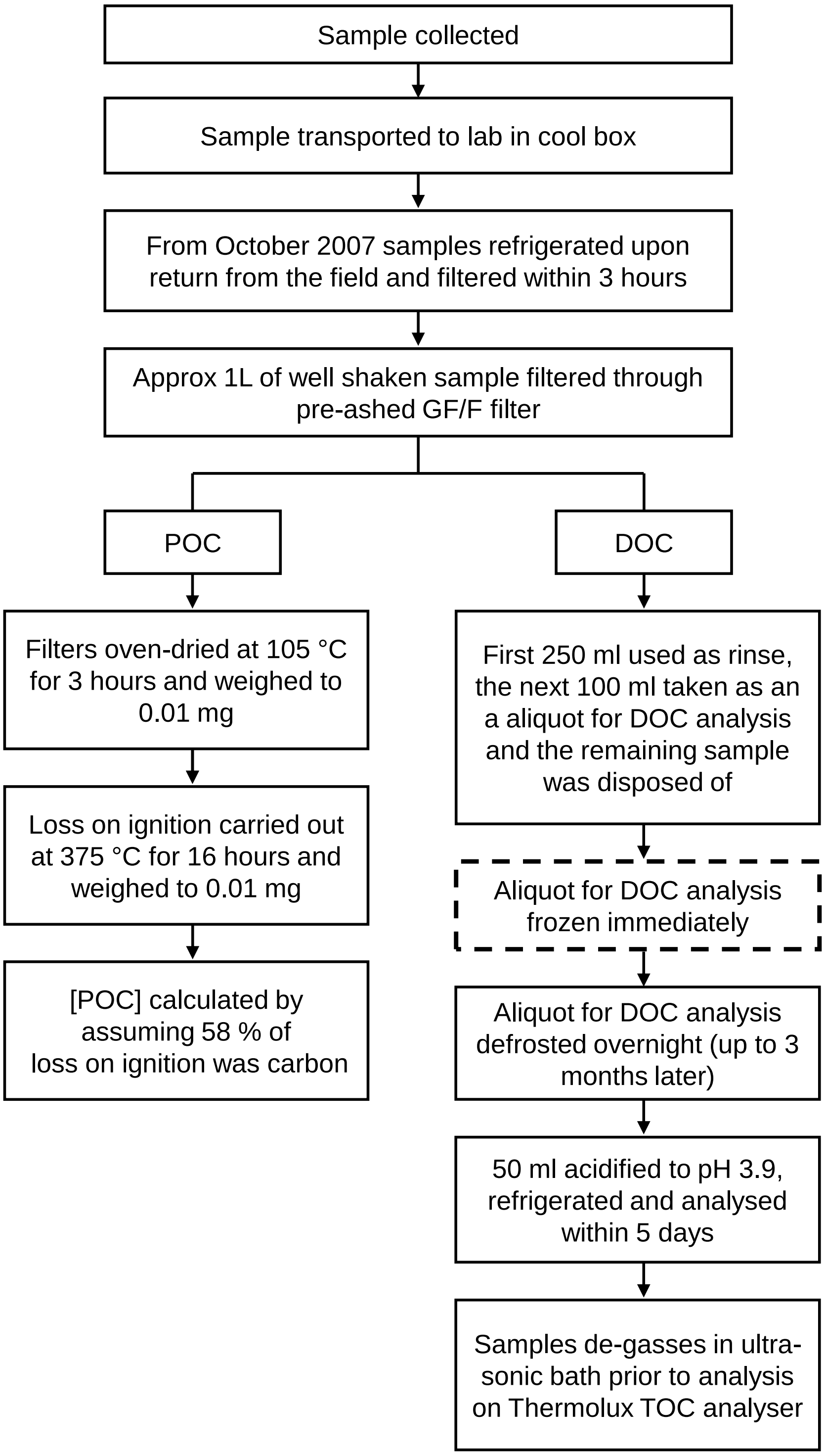


Figure 20. Methods used for C analysis from October 2007 with stage of protocol where flocculation may be occurring in a thick dashed line box.

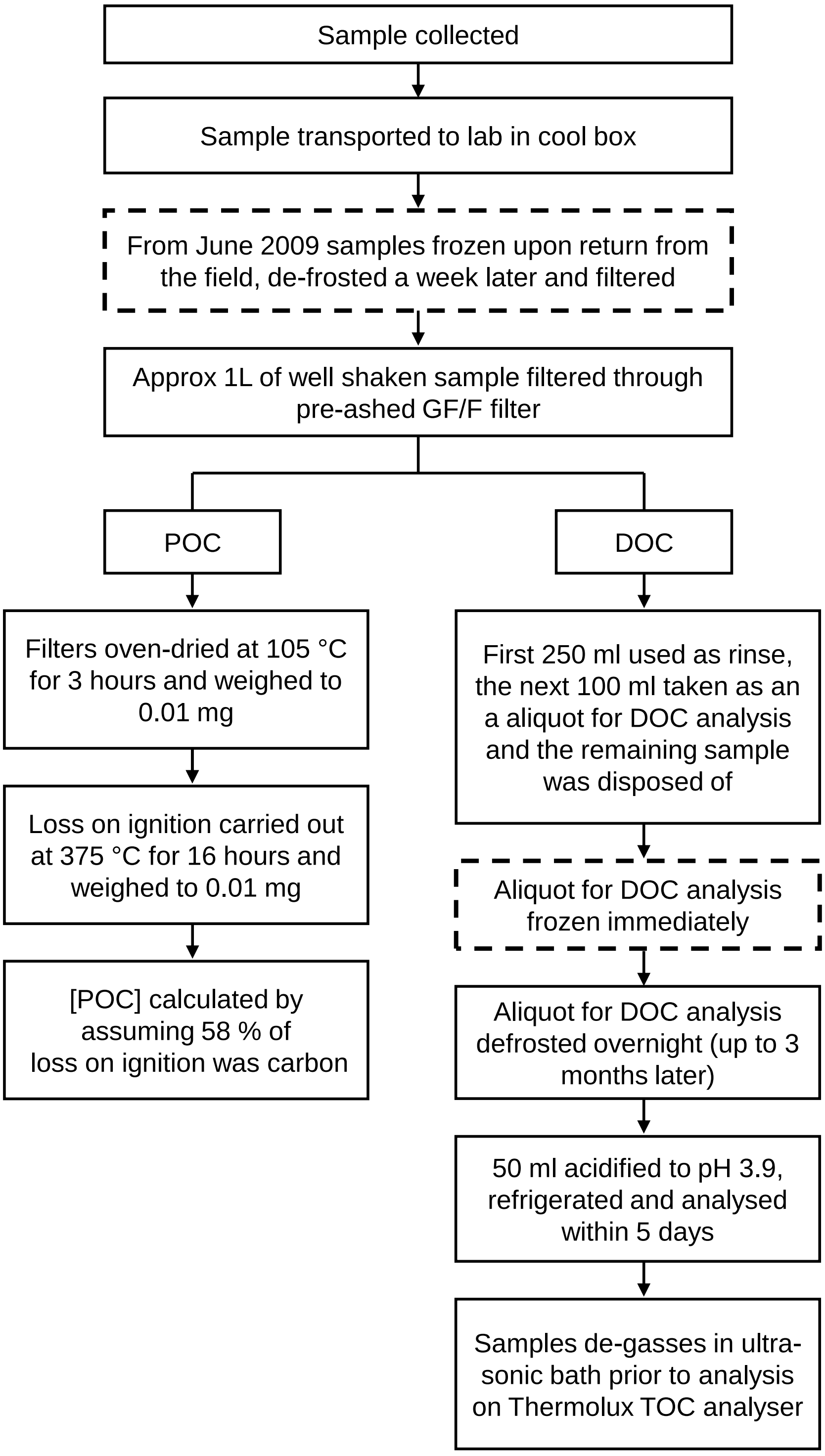


Figure 21. Methods used for C analysis of frozen test samples with stages of protocol where flocculation may be occurring in a thick dashed line box.

Figure 22 shows the effect of freezing on [POC] is variable between and within catchments, as there are wide prediction intervals and many points outwith the 95 % confidence intervals. The relationship between the two storage mechanisms was therefore considered insufficiently robust to apply a single correction factor for all catchments. Catchment specific correction factors could also not be applied because the R^2 values for each catchment ranged from 0.15 in catchment 9A to 0.55 in catchment 13 (Table 17). Relationships were only significant at three of the sampling points, but the higher R^2 values were influenced by outlying values.

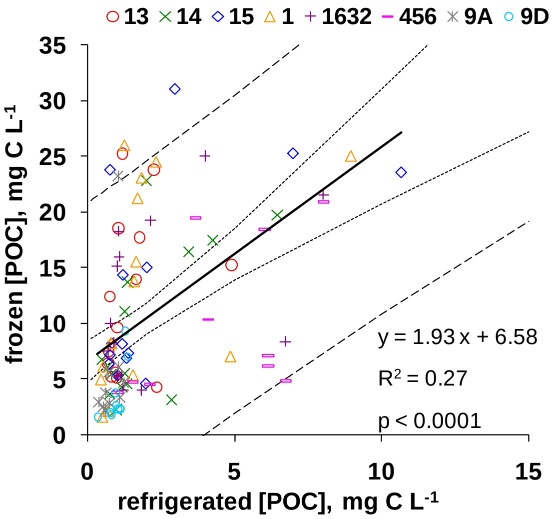


Figure 22. Comparison of [POC] in frozen samples vs. refrigerated for all sampling points, June 2009-February 2010. The solid line is the regression line. The short dashed lines indicate the 95 % confidence intervals and the long dashed lines the 95 % prediction intervals.

Table 17. Linear relationships between frozen and refrigerated samples for each sampling point.

Catchment	R^2	p	No. of samples
13	0.55	0.001	15
14	0.43	0.008	15
15	0.34	0.029	14
1	0.20	0.096	15
1632	0.17	0.148	14
456	0.22	0.167	10
9A	0.15	0.263	10
9D	0.45	0.034	10

Having established that freezing samples on return from the field until filtration increases [POC], it was assumed that [TOC] would be the same in paired refrigerated and frozen samples. This assumption was not true. There is a significant linear relationship between [TOC] for a sample refrigerated or stored frozen (R^2 = 0.77, p < 0.001, Figure 23). The mean difference of 6.76 mg L^{-1} (Table 18) shows that higher [TOC] were determined in frozen samples compared to refrigerated samples, but this difference is less than the combined mean difference for [POC] and [DOC] between the frozen and refrigerated samples. Therefore, from October 2007 onwards when samples were refrigerated, the organic C in samples may be under-estimated as loss of C appears to occur during processing, not during sample storage.

In summary, it appears that freezing samples before filtration promotes flocculation of a proportion of the < 0.7 μm DOC, such that, when filtered, [POC] increases and therefore [DOC] decreases. However, since the difference in [TOC] between refrigerated and frozen samples is less than the sum of the differences in [POC] and [DOC], C mass balance is not maintained and there is a second stage of C loss during sample processing.

Table 18. Paired t-test results for [TOC] determined from frozen and refrigerated samples. N = 80.

	Mean [TOC], mg L^{-1}	Standard Deviation, mg L^{-1}
Refrigerated	23.2	12.1
Frozen	30.0	15.8
Difference	-6.76	7.66
95 % confidence intervals for mean difference: (-8.46, -5.05)		
t-test of mean difference = 0 (vs not = 0): t = -7.89 p < 0.0001		

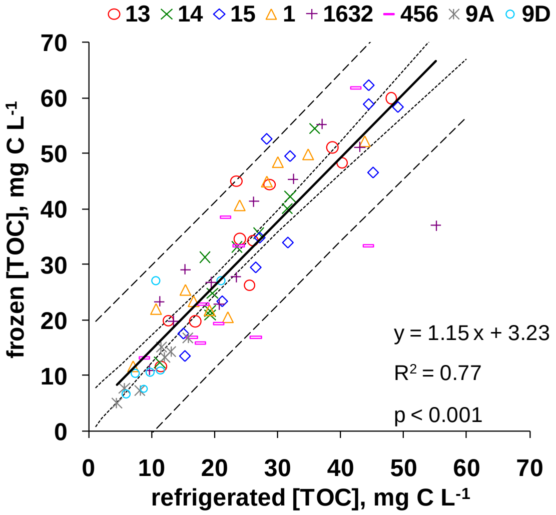


Figure 23. Comparison of [TOC] (POC + DOC) in frozen samples compared with refrigerated. The solid line shows the regression line. The short dashed lines indicate the 95 % confidence intervals and the long dashed lines the 95 % prediction intervals.

3.8.4. Correction for Under-Estimation in [DOC]

After filtration the aliquot for [DOC] analysis for samples collected from October 2007 onwards was frozen to be prepared for analysis at a later date. It was hypothesised that, in the samples refrigerated and filtered on the day of collection, loss of DOC to the POC pool due to flocculation is occurring after filtration during frozen storage prior to DOC analysis. In the samples frozen prior to filtering, flocculation of DOC should be minimal during frozen storage after filtration, as it has already occurred prior to filtration and will be retained on the filter during POC analysis. Thus organic C has not been lost from the TOC pool. To test this hypothesis the remaining 50 mL of acidified and sparged aliquot not used for DOC analysis was compared with the remaining 50 mL of untreated aliquot of both the refrigerated and frozen DOC aliquots to look for flocculation in the samples. A visual assessment was carried out as filtration and loss on ignition of such a small volume is not viable. Greater amounts of flocculation were observed in both the refrigerated 50 mL of acidified and sparged aliquot and the remaining 50 mL of untreated aliquot for DOC analysis compared to equivalent aliquots for the frozen samples (Figure 24) supporting the hypothesis of the cause of C loss in the refrigerated samples.

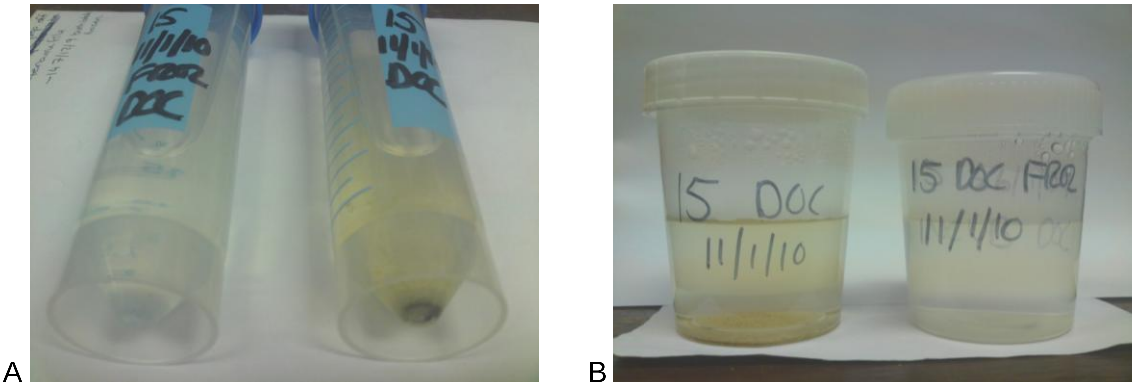


Figure 24. Examples of loss of C from dissolved to particulate fraction for samples from Catchment 15. Panel A - comparison of 50 mL of acidified and sparged aliquot for DOC analysis, with the frozen sample on the left and the refrigerated sample, with noticeably greater flocculation, on the right. Panel B - comparison of 50 mL of untreated aliquot for DOC analysis with the frozen sample on the right and the refrigerated sample, with greater flocculation, on the left.

Hence it is concluded that [TOC] determined in samples processed before September 2007 are accurate. However, [POC] and [DOC] before September 2007 are affected by the artefact of freezing and it was not possible to back-correct the data. Measurements of [TOC] and [DOC] from October 2007 are underestimates because a proportion of the DOC pool was lost during storage. In order to provide a correction for the underestimates of [DOC] from October 2007, all aliquots for DOC analysis collected between March 2010 and June 2010 were split after filtration into 50 mL which was frozen and 50 mL which was refrigerated before DOC analysis. The significant linear regression relationship between [DOC] determined in refrigerated and frozen aliquots of these samples (R^2 = 0.90, p < 0.001, Figure 25) was used to correct [DOC] and consequently [TOC] in samples between October 2007 and June 2010.

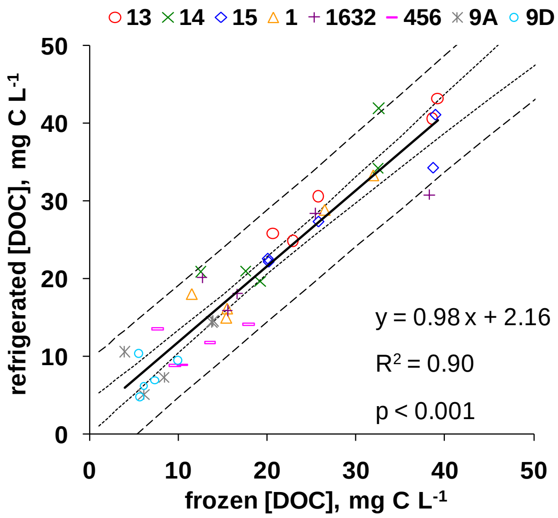


Figure 25. Retrospective correction of [DOC] to correct the data from October 2007 to June 2010 for losses due to storage mechanism. The solid line shows the regression line. The short dashed lines indicate the 95 % confidence intervals and the long dashed lines the 95 % prediction intervals.

4. Impacts of Disturbance on Streamwater Chemistry

4.1. Chapter Outline

Here, discharge for the study period and the flow duration curve of the nearest long-term SEPA gauged catchment are presented as well as data from the three SEPA rainfall gauges nearest to the Whitelee catchments. These data related to catchment hydrology are followed by the time series of the approximate bi-monthly sampling. TOC, TP, SRP and NO_3^- time series were constructed for October 2007 to September 2010, and are presented with data from Waldron *et al.* (2009) for June 2006 to September 2007. Due to the differing storage methods of samples on return to the laboratory between analysts rendering the dissolved and particulate C fractions for October 2007 to September 2010 not comparable with the earlier data (see Chapter 3.8), DOC and POC time series are only presented for three years, for the period from October 2007 to September 2010. For each parameter, whether windfarm-related disturbance impact is detectable at the sampling points outwith the immediate area of disturbance is assessed. This is done by performing harmonic regression analysis using Minitab® v16 on the TOC and NO_3^- data since there are no environmental standards available to assess for impact. As the DOC and POC time series were too short to compare before-and-after potential windfarm-related impact, harmonic regression analysis was not carried out on these two parameters. The Water Framework Directive (2000) UK Technical Advisory Group has produced Environmental Standards for SRP in river water (UKTAG, 2008). These were used on the SRP data to assess for disturbance impact. NO_2^- data were only collected to calculate $[NO_3^-]$ from [TON] and is therefore not presented. Inter-catchment and annual differences in streamwater chemistry were identified and from differences in the time series, the most likely controls on streamwater chemistry are discussed.

4.2. Catchment Hydrology

The hydrograph for the study period and the flow duration curve of the nearest long-term SEPA gauged catchment are presented. The In-situ Inc. multi-parameter Troll 9000 water quality logger time series follow along with data from the nearest SEPA rainfall gauges to the study catchments.

4.2.1. Discharge Data

In order to investigate concentration-flow relationships and to calculate C, P and N exports for the Whitelee catchments, the river flows had to be gauged. Due to resource limitations continuous discharge, hereafter named Q, monitoring could not be conducted at all of the sampling sites throughout the study period so Q data (Figure 26) were obtained from the nearest long-term river flow gauging station which is operated by the Scottish Environment Protection Agency, in the town of Newmilns on the River Irvine, 3 km west of sampling point 1 (see Figure 6, Chapter 2.2 for location). The volume of half-hourly Q from SEPA Newmilns was totalled for each hydrologic year in order to compare differences in hydrology between years (Table 19). 2006-2007 was the wettest year with a total volume of half-hourly Q of 48295 m^3, with 2009-2010 the driest year with a total of 34728 m^3 (Table 19).

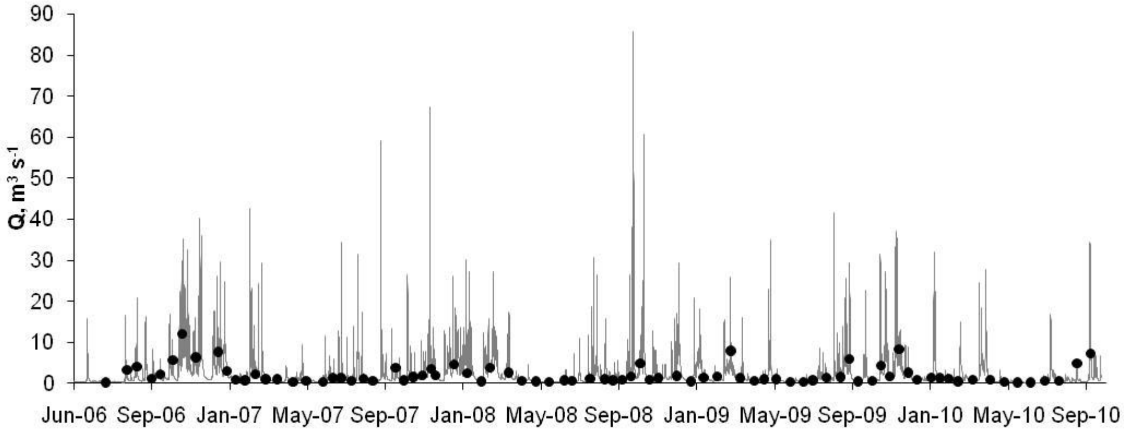


Figure 26. Hourly discharge (grey line) from the nearest long-term gauged catchment (River Irvine in Newmilns) for June 2006 to June 2010. Catchment area is 72.8 km^2. Discharge at approximate time of water sampling (time when catchment 1, the nearest sampling point, was sampled) indicated by black dots.

Table 19. Total volume of half-hourly Q from SEPA Newmilns per hydrologic year.

Hydrologic Year	Total volume of half-hourly Q from SEPA Newmilns (m^3)
2006-2007	48295
2007-2008	44547
2008-2009	45136
2009-2010	34728

The flow duration curve produced by SEPA for the River Irvine in Newmilns (derived from mean daily Q from October 1976 to September 2009, Figure 27) was used to assess how representative of long-term flow conditions the sampled flows were. Comparison with the flow duration curve showed that on the occasions sampled the probability of occurrence of flows ranged from 3 to 97 %, therefore the sampling regime employed sampled a representative range of flow conditions. The median Q of the River Irvine at Newmilns during the study period was 1.18 m^3 s^{-1}, with a probability of occurrence of 47 %.

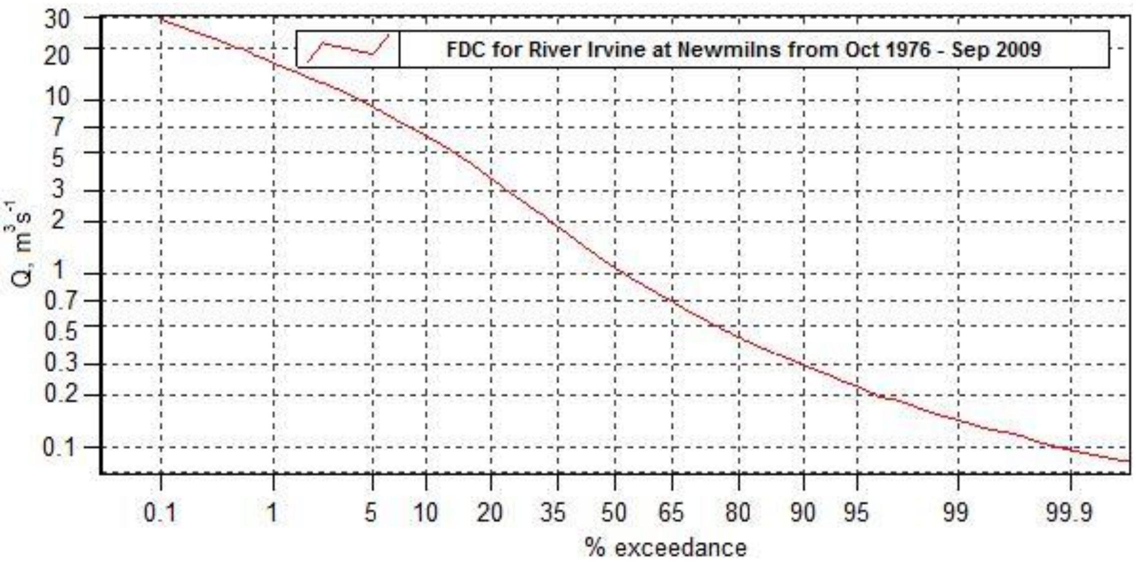


Figure 27. Flow duration curve for the River Irvine at Newmilns with axes on a cyclical log scale. Figure courtesy of SEPA.

4.2.2. Water Quality Logger Time Series

The water quality data are presented here and discussed with reference to what can be inferred from it regarding terrestrial and in-stream biological activity and water source.

4.2.2.1. Water Temperature

Water temperature reflects soil temperature and increased soil temperature increases soil microbial activity and therefore C, P and N cycling. Higher water temperatures also indicate surface/near-surface water flow with shorter residence compared to deeper soil water and groundwater which tends to be cooler. Thus water temperatures is an indicator of both the production and transport of C, P and N. Water temperature in catchment 13 varied between -0.13 °C (January 2010) to 25.8 °C (June 2009) showing that there is a wide range in temperature with the seasons (Figure 28A). As well as the expected seasonal response there is also clear diurnal variation in water temperature, which has also been observed at peatland streams in north-east of Scotland (Dawson *et al.*, 2001b). At Whitelee the greatest diurnal variation in temperature occurred over May and June, where the temperature difference can be as great as 11.3 °C (29th May 2009) with the minimum temperature occurring approximately 6 am, and the maximum temperature around 4pm. The diurnal variation is much smaller over the winter months.

4.2.2.2. Conductivity

Specific conductivity measures the ability of a solution to conduct an electrical current. A greater amount of charged ionic species present in solution will register a greater specific conductivity. In catchment 13 at Whitelee specific conductivity ranged from 2.73 µS cm^{-1} (January 2010) to 302.66 µS cm^{-1} (June 2008) (Figure 28B). The conductivity of rivers is affected by the geology of the area through which the water flows and at Whitelee where the underlying geology is Carboniferous sandstone (see Chapter 2.2) a low to medium range of conductivity was observed. A sudden change in conductivity often shows a pollution event as it indicates there is a greater amount and mobility of ions in the river but changes in conductivity can also indicate whether river flow is low or high. During May 2008, June 2009 and June 2010 the stage height readings (Figure 28D) show there were prolonged periods of low flow in catchment 13. Specific conductivity was greater during these low flow periods (Figure 28B). This is because the flow is likely to be composed mainly of baseflow which has high conductivity as it has acquired ions from the rocks through which it moved before it reached the river network. The longer water residence time in the soil, the greater the influence on specific conductivity from products of soil and parent material weathering (Kobayashi *et al.,* 1990). During higher stage heights (Figure 28D) the conductivity is lower (Figure 28C). This is likely to be the result of surface runoff from rainfall entering the river. Surface runoff has a lower conductivity and the increased volume of water now in the river dilutes the concentration of the in-stream ions leading to a lower conductivity (Austnes *et al.,* 2010).

4.2.2.3. pH

pH in catchment 13 at Whitelee ranged from 4.74 (January 2008) to 8.99 (June 2009) (Figure 28C), a wide range for a peatland catchment. Much of this variation is likely to be caused by changes in flow. During periods of low flow (Figure 28D) e.g. May 2008, June 2009 and June 2010, there are prolonged periods of time where there is greater pH. At

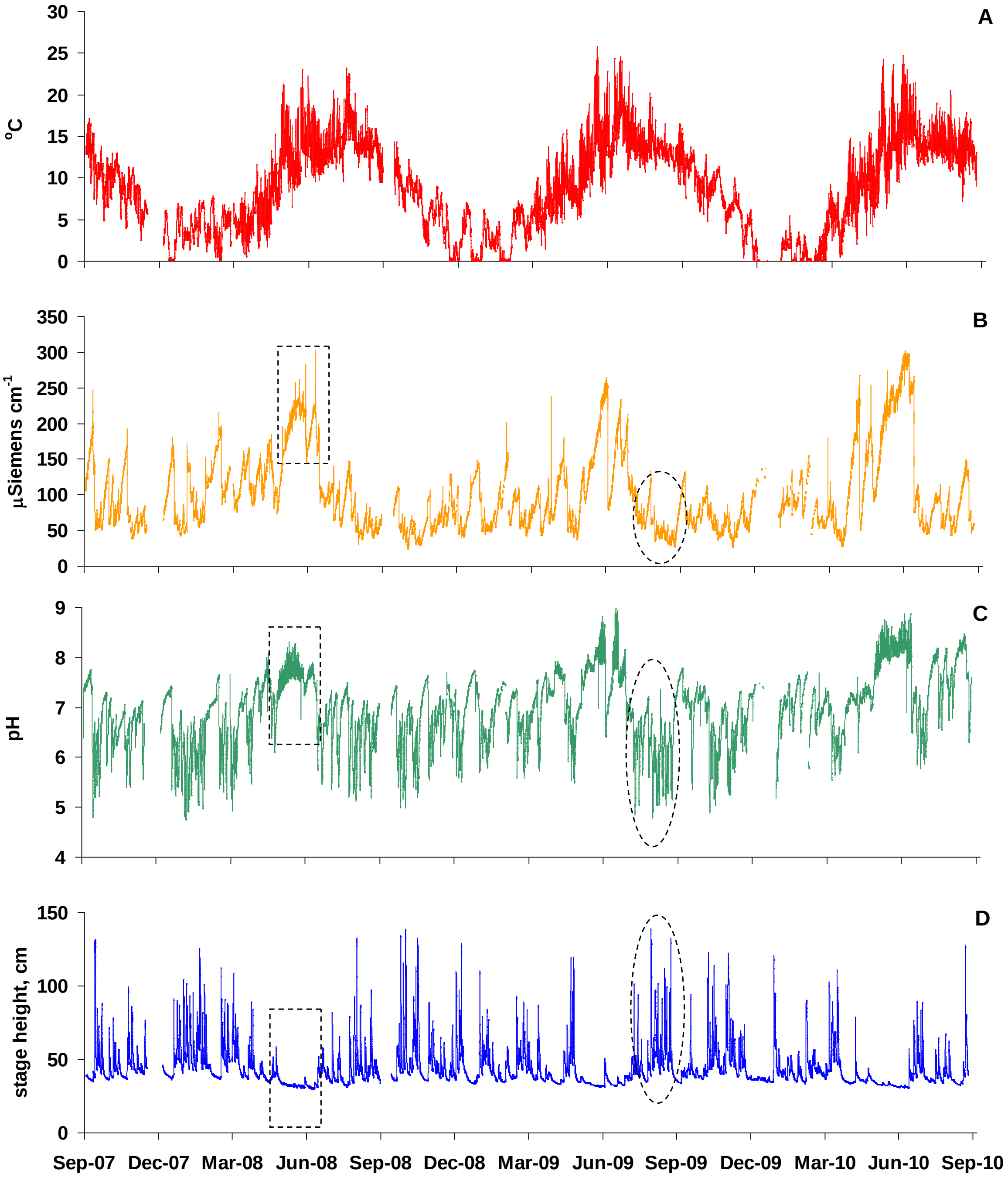


Figure 28. Half-hourly time series of temperature (Panel A), conductivity (Panel B), pH (Panel C) and stage height (Panel D) for catchment 13 from In-situ Troll 9000 water quality logger. Dash line boxes indicate an example of low flow. Dash line ovals show an example of high flow.

these times over the summer the flow is likely to be largely made up of the baseflow component (Neal *et al.,* 1992; Tetzlaff *et al.,* 2007). Since the origin of baseflow is groundwater, the water prior to reaching the stream has acquired ions from the rocks through which it moves, which means that there are few H^+ ions in solution. During higher flows the pH lowers suddenly as more dissolved H^+ ions enter the river in runoff and overland flow. At Whitelee after this drop in pH related to high flow, there is a gradual recovery back to a higher pH seen as an arc shaped response in the time series (Figure 28C).

4.2.2.4. Stage Height

Stage height ranges from 29.2 cm (June 2008) to 139.2 cm (October 2009) in catchment 13 (Figure 28D).

4.2.3. SEPA Rainfall Data

Data from the three SEPA tipping bucket rainfall gauges nearest to the Whitelee catchments were obtained. The monthly rainfall totals for the four hydrologic years are presented in Figure 29 and the annual rainfall totals in Table 20. Picketlaw, to the north of the Whitelee plateau, receives the greatest amount of rainfall throughout the period of research, with Amlaird, to the west, receiving the least. Mean annual rainfall at Saughall from 1975 to 2005 was 1342 mm (data courtesy of Michael Chalton, Saughall Meteorological Station) so Table 20 shows 2006-2007 and 2008-2009 had above average rainfall, and 2009-2010 had below average rainfall.

Table 20. Annual rainfall totals for the three SEPA tipping bucket rainfall gauges nearest to the Whitelee catchments, Picketlaw, to the north, Amlaird, to the west, and Saughall, to the south (locations in Figure 6, Chapter 2.2).

Hydrologic Year	Picketlaw (mm)	Amlaird (mm)	Saughall (mm)
2006-2007	1865	1565	1657
2007-2008	1579	1099	1350
2008-2009	1626	1350	1462
2009-2010	1270	1250	1180

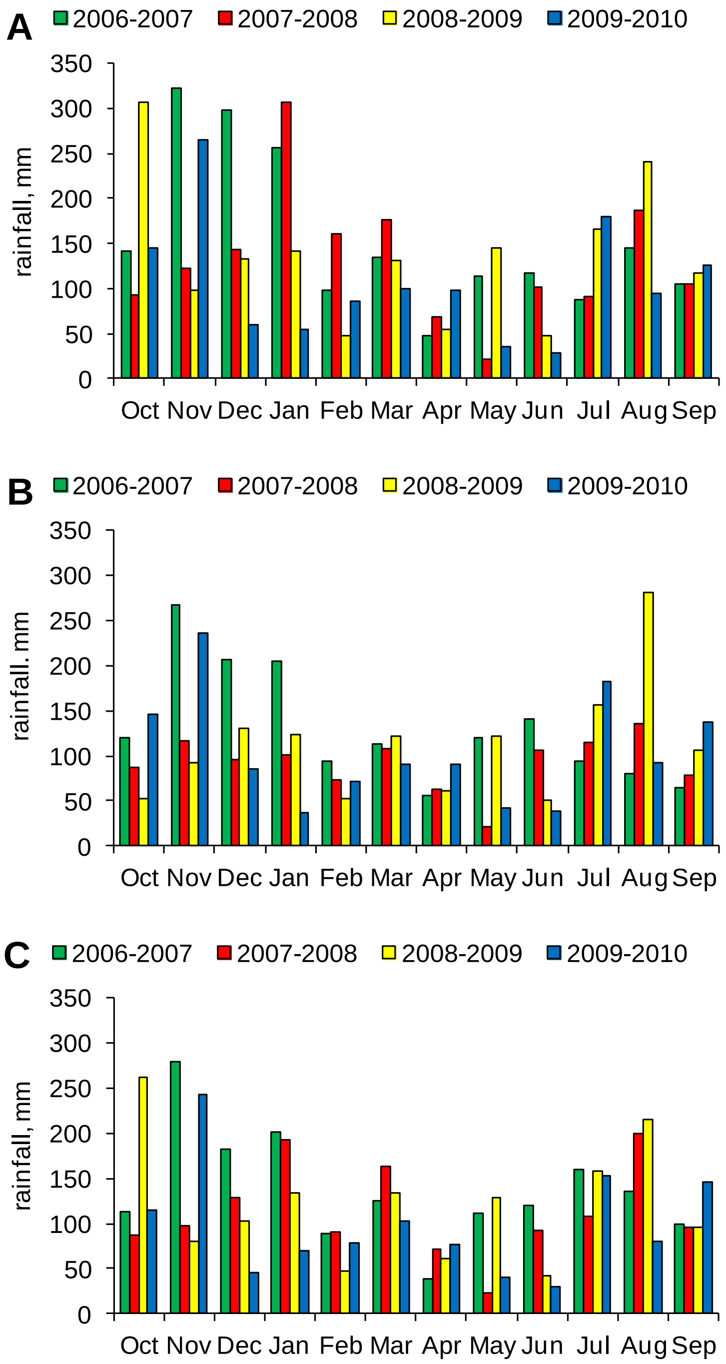


Figure 29. Monthly rainfall totals for four hydrologic years from the three SEPA tipping bucket rainfall gauges nearest to the Whitelee area. Panel A, Picketlaw, to the north of the Whitelee plateau, panel B, Amlaird to the west and panel C, Saughall, to the south (locations in Figure 6, Chapter 2.2).

4.3. Bi-monthly Time Series

Chapters 2 and 3 outlined the field and laboratory methodologies for generating the time series. Gaps exist in the [SRP] and [NO_3^-] datasets from Waldron *et al.* (2009), < 10 % of the overall time series length, due to logistical difficulties in analyzing the samples quickly enough on return from the field to be confident that the measured concentration represented field concentrations accurately. Summary tables of the mean, median and range of concentrations in each catchment are provided in Appendix 5. The time series are presented in this section of the chapter with a brief description and are discussed in greater detail and compared with results from other catchments later in the chapter.

4.3.1. Carbon

[DOC] in the N-draining catchments ranged from 2.9 mg L^{-1} (9D, February 2007) to 41.4 mg L^{-1} (456, October 2009) (Figure 30). [DOC] in the S-draining catchments is higher than that of the N-draining catchments, with [DOC] ranging from 5.2 mg L^{-1} (1, February 2007) to 57.1 mg L^{-1} (13, August 2008) (Figure 30). All catchment [DOC] exhibited seasonality with maximum concentrations towards the end of each summer and lowest concentrations in winter (Figure 30).

[POC] in the N-draining catchments ranged from 0.31 mg L^{-1} (9A, January 2008) to 23.4 mg L^{-1} (456, April 2009) (Figure 31). [POC] in the S-draining catchments was lower than in the N-draining catchments, ranging from 0.09 mg L^{-1} (13, January 2009) to 10.7 mg L^{-1} (15, July 2009) (Figure 31). [POC] shows less seasonality than [DOC] (Figure 31). N-draining catchment 456 has a spiky pattern in [POC] often having the highest [POC] of all the catchments from April 2009 to December 2009 (Figure 31).

[TOC] in the N-draining catchments ranged from 4.2 mg L^{-1} (9D, January 2008) to 47.5 mg L^{-1} (456, October 2009) (Figure 32) with [POC] on average 14.1 ± 15.2 % of the [TOC]. [TOC] in the S-draining catchments was higher than that of the N-draining catchments, with [TOC] ranging from 5.6 mg L^{-1} (1, February 2007) to 59.1 mg L^{-1} (13, August, 2008) (Figure 32). In the S-draining catchments, [POC] was on average 6.5 ± 4.4 % of the [TOC]. The strong seasonal signal in [TOC] is driven by [DOC] rather than [POC] (Figure 32).

4.3.2. Phosphorus

In the N-draining catchments [SRP] ranged from the limit of quantification of 1 μg L^{-1} (9A, May 2010) to 149 μg L^{-1} (456, December 2009) (Figure 33) with [SRP] in the S-draining catchments ranging from as low as the limit of quantification of 1 μg L^{-1} (15, March 2007) to 289 μg L^{-1} (14, June 2010) (Figure 33). In both N- and S-draining catchments [SRP] was higher in the summer months. The greatest [SRP] over the period of research was generally observed in S-draining catchments 13 and 14 from October 2007 right through until September 2010. Catchments 456 and 14 have occasional spikes in [SRP] (Figure 33).

In the N-draining catchments [TP] ranged from 2 μg L^{-1} (9D, March 2008) to 255 μg L^{-1} (456, October 2007) (Figure 34). In these catchments [SRP] was on average 43.7 ± 37.5 % of the [TP]. [TP] in the S-draining catchments ranged from 3 μg L^{-1} (15, January 2007) to 328 μg L^{-1} (13, May 2008) (Figure 34), with [SRP] on average 59.5 ± 37.7 % of the [TP]. [TP] showed a seasonal pattern with the highest concentrations in the summer months. The greatest [TP] was generally in S-draining catchments 13 and 14 from October 2007 until September 2010.

4.3.3. Nitrogen

[NO_3^-] in the N-draining catchments ranged from 0.13 mg L^{-1} (9D, September 2009) to 2.44 mg L^{-1} (456, April 2010) (Figure 35). In the S-draining catchments [NO_3^-] was lower than the N-draining catchments and ranged from 0.001 mg L^{-1} (1632, May 2010) to 0.88 mg L^{-1} (1632, August 2008) (Figure 35). [NO_3^-] showed the opposite seasonality to C and P, with greater concentrations over winter and spring, and lower concentrations in summer and autumn.

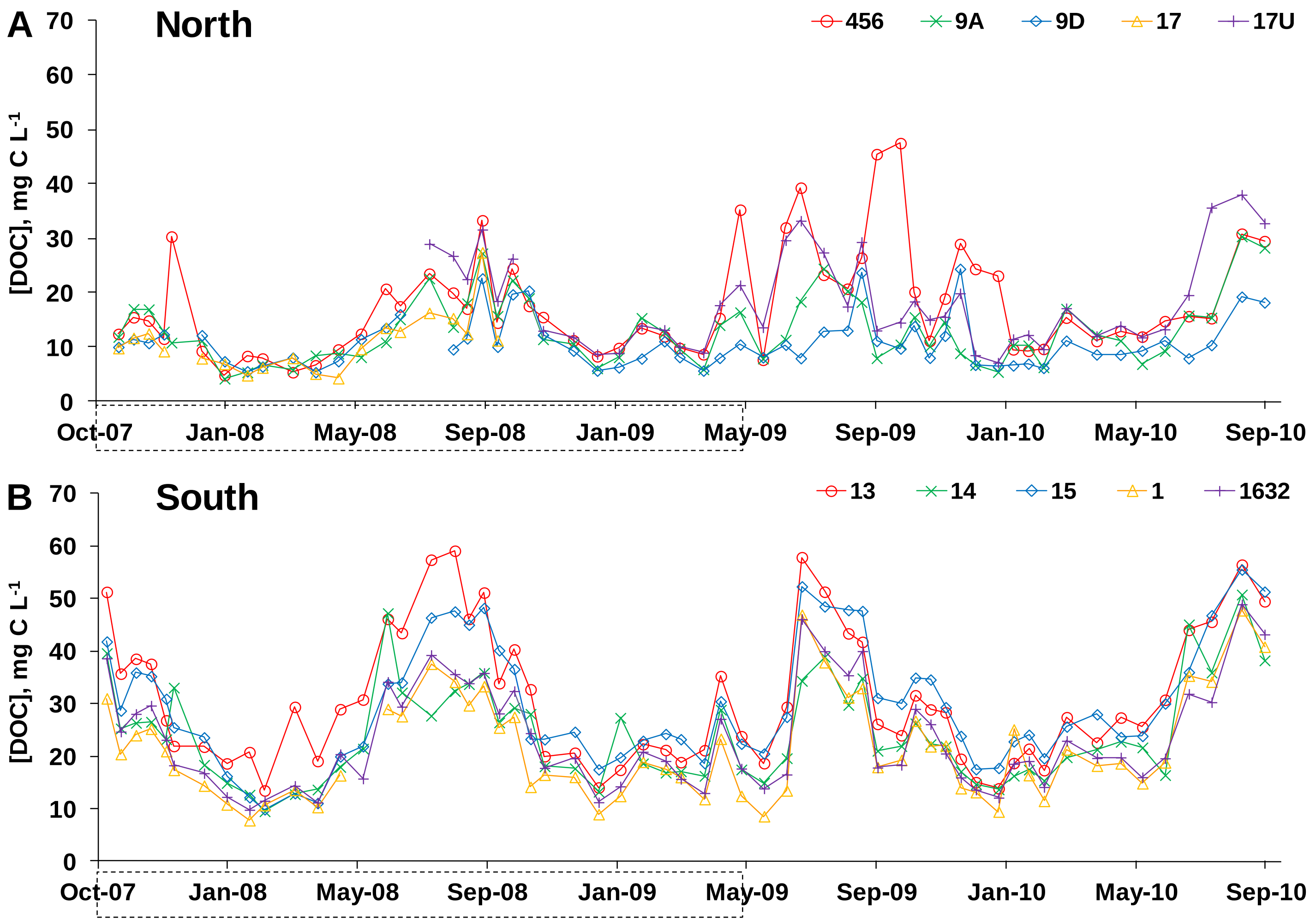


Figure 30. DOC time series. Panel A shows the N-draining catchments; panel B the S-draining. The period of the time series subject to windfarm-related disturbance is shown in the dashed box. Due to the differing storage methods of samples on return to the laboratory, the DOC time series was constructed for three years only from October 2007. The maximum uncertainty on [DOC] is ± 5.2 mg L^{-1} (see Appendix 6).

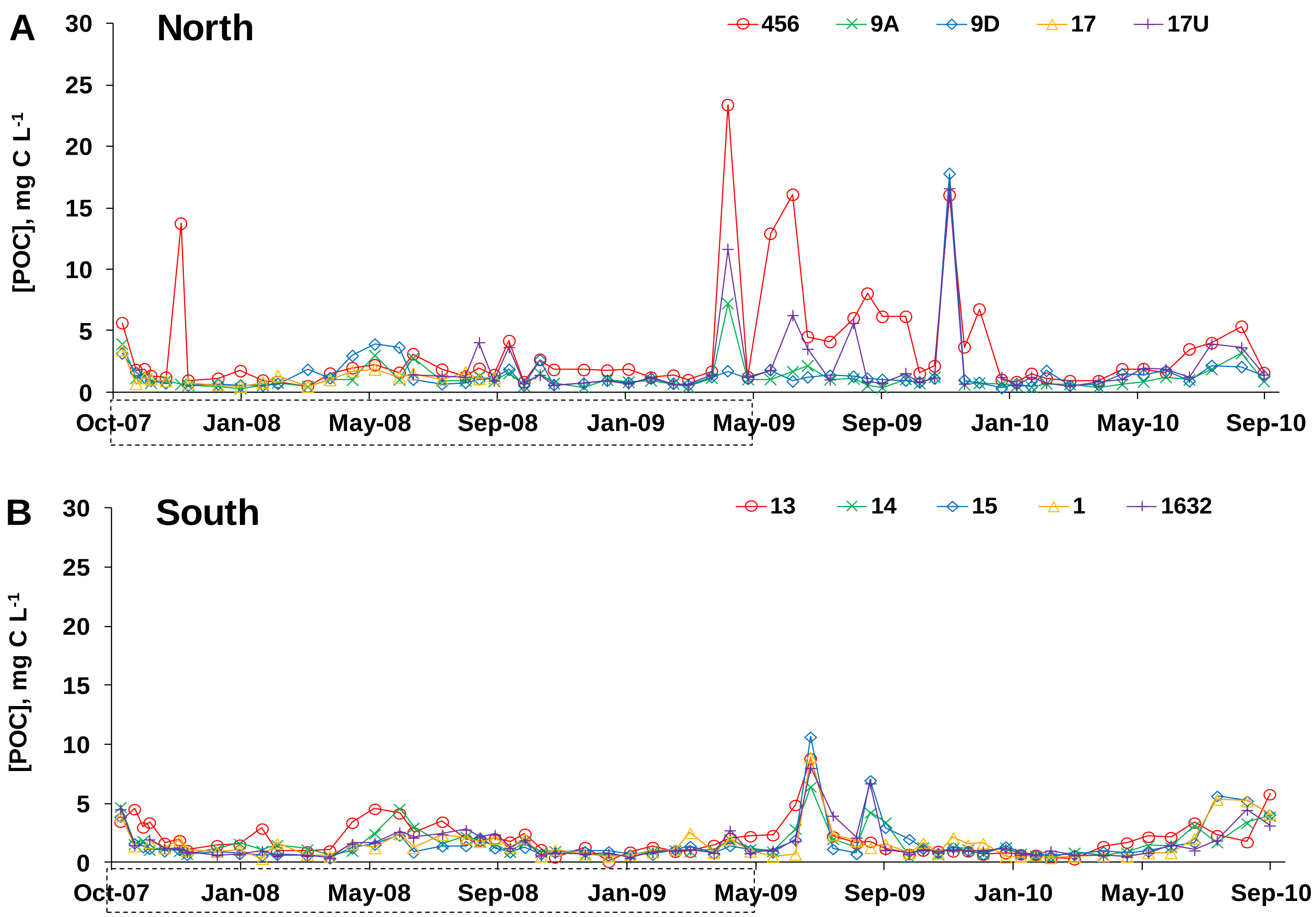


Figure 31. POC time series. Panel A shows the N-draining catchments; panel B the S-draining. The period of the time series subject to windfarm-related disturbance is shown in the dashed box. Due to the differing storage methods of samples on return to the laboratory, the POC time series was constructed for three years only from October 2007.

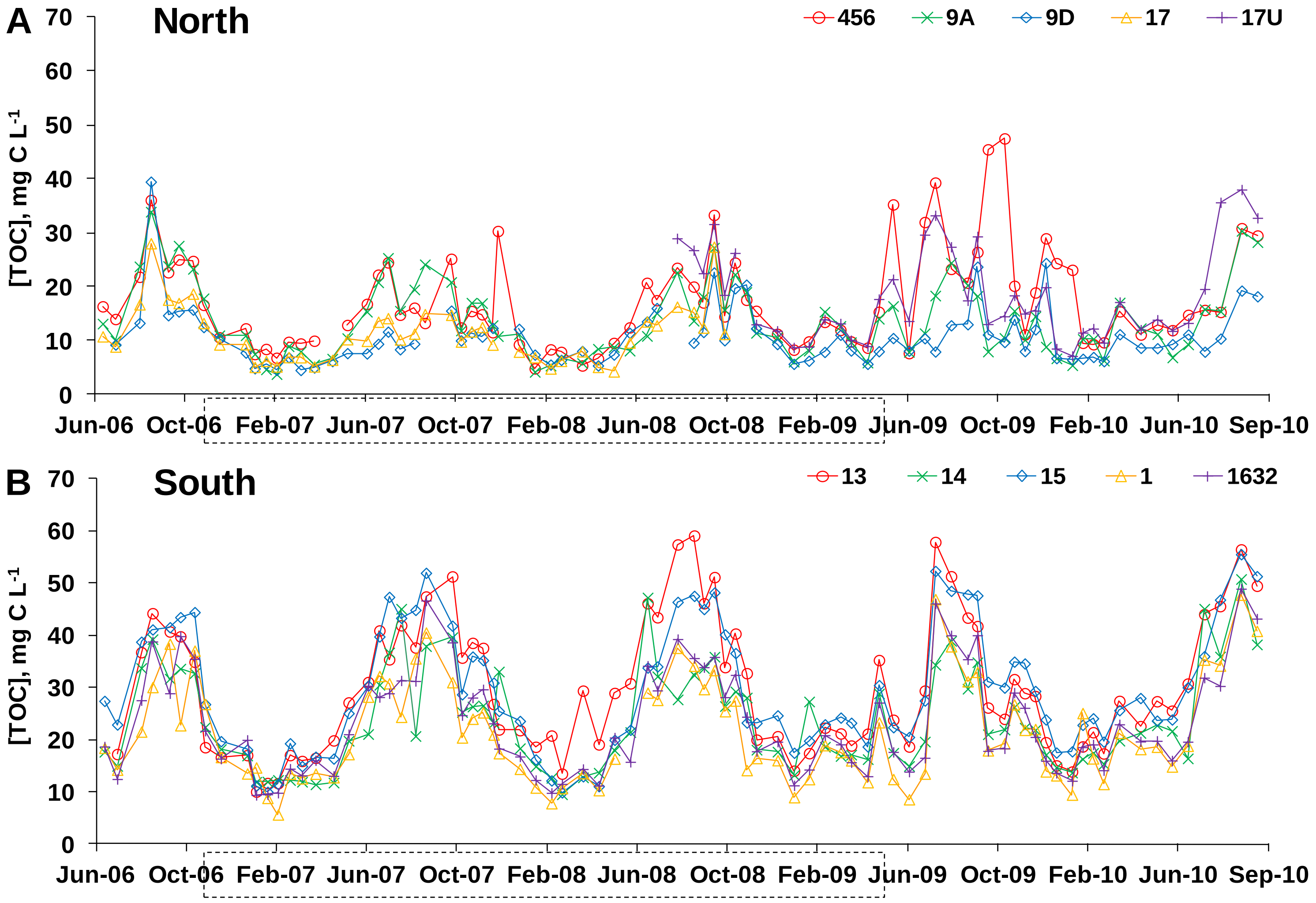


Figure 32. TOC time series. Panel A shows the N-draining catchments; panel B the S-draining. The period of the time series subject to windfarm-related disturbance is shown in the dashed box. Data for June 2006 to September 2007 from Waldron *et al.* (2009).

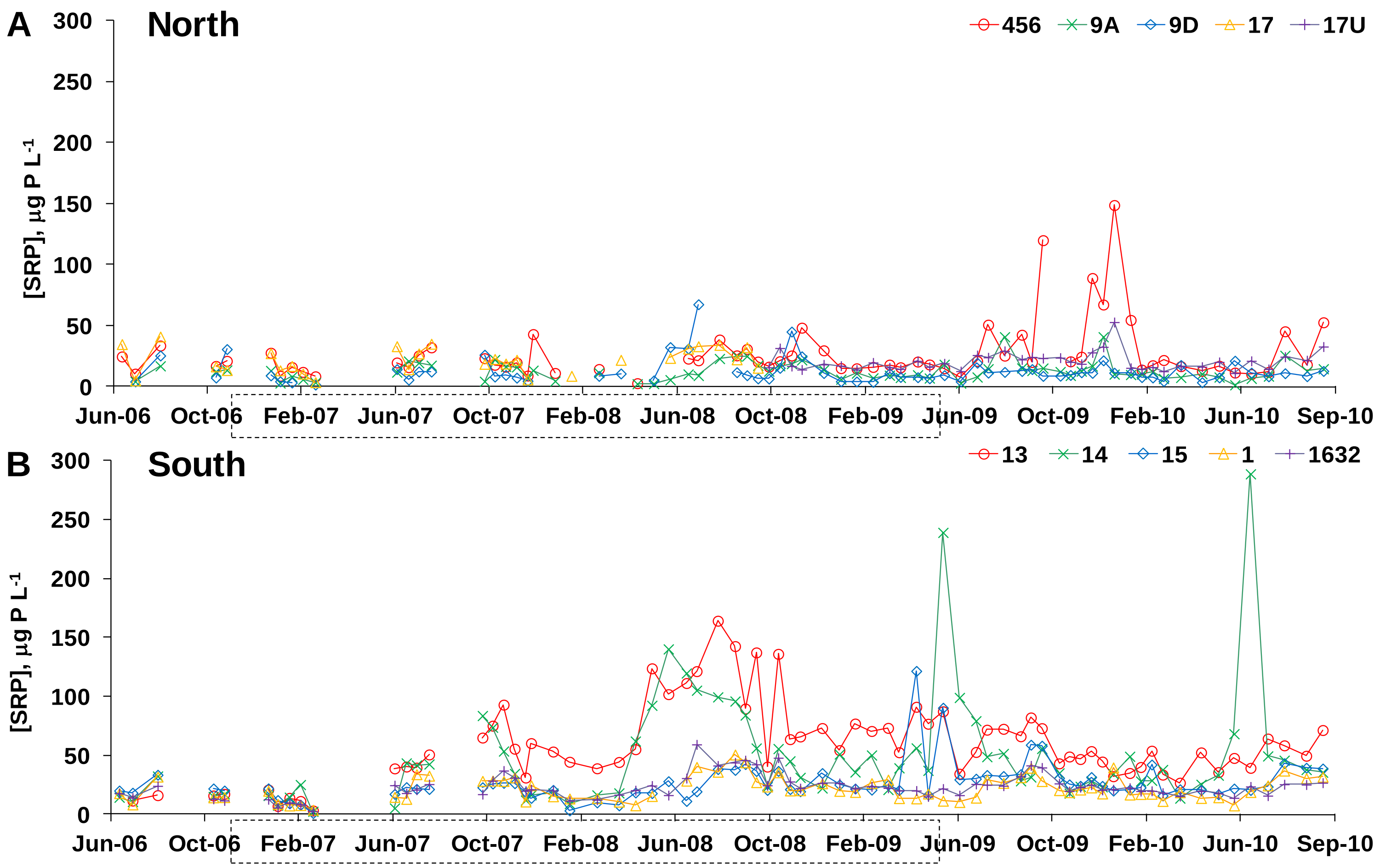


Figure 33. SRP time series. Panel A shows the N-draining catchments; panel B the S-draining. The period of the time series subject to windfarm-related disturbance is shown in the dashed box. Data for June 2006 to September 2007 from Waldron *et al.* (2009). All data have been colour corrected for interferences in the analytical method, using a back-correction from June 2006 to September 2008, and directly from October 2008 (see Chapter 3.3.3).

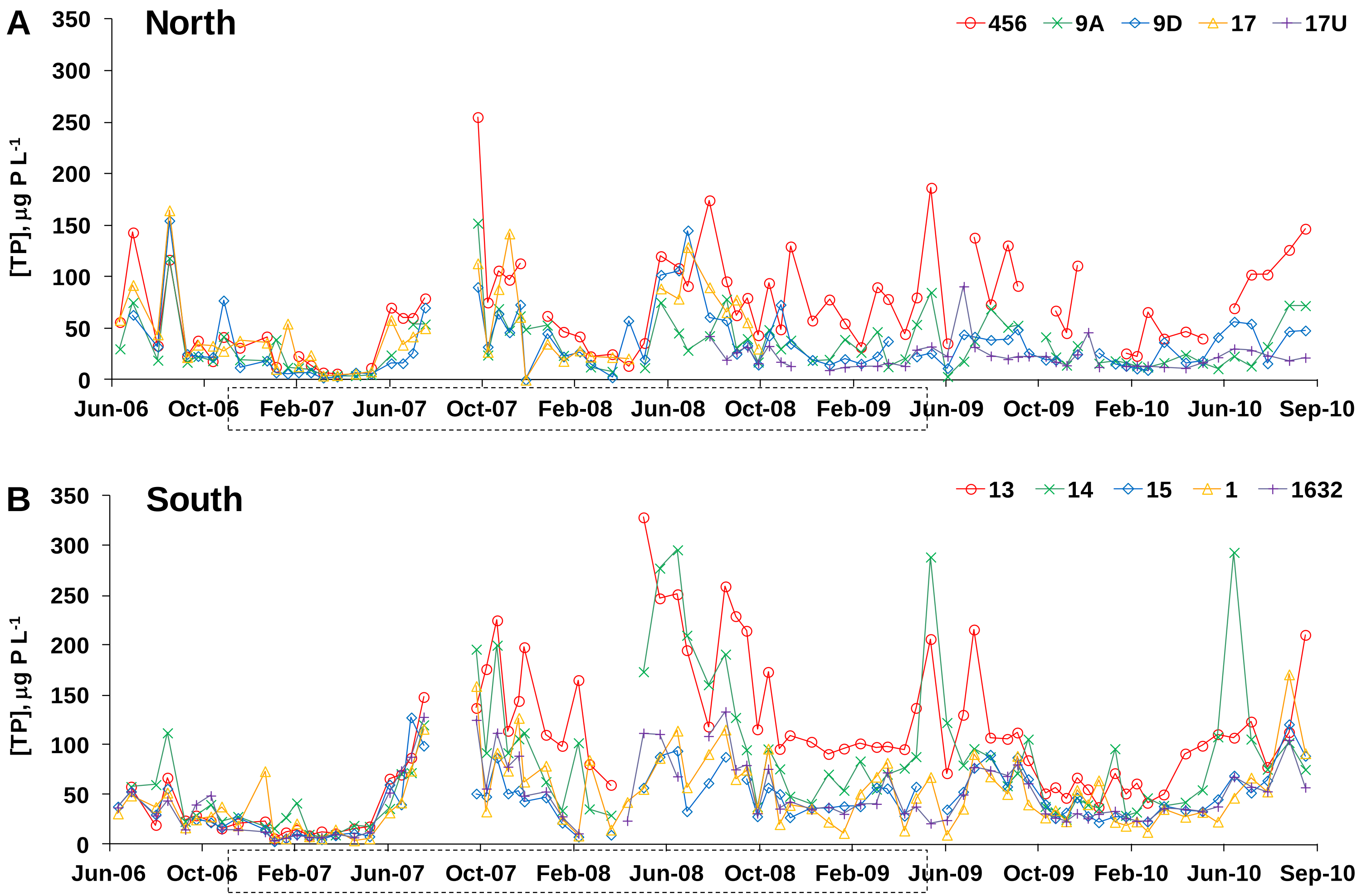


Figure 34. TP time series. Panel A shows the N-draining catchments; panel B the S-draining. The period of the time series subject to windfarm-related disturbance is shown in the dashed box. Data for June 2006 to September 2007 from Waldron *et al.* (2009).

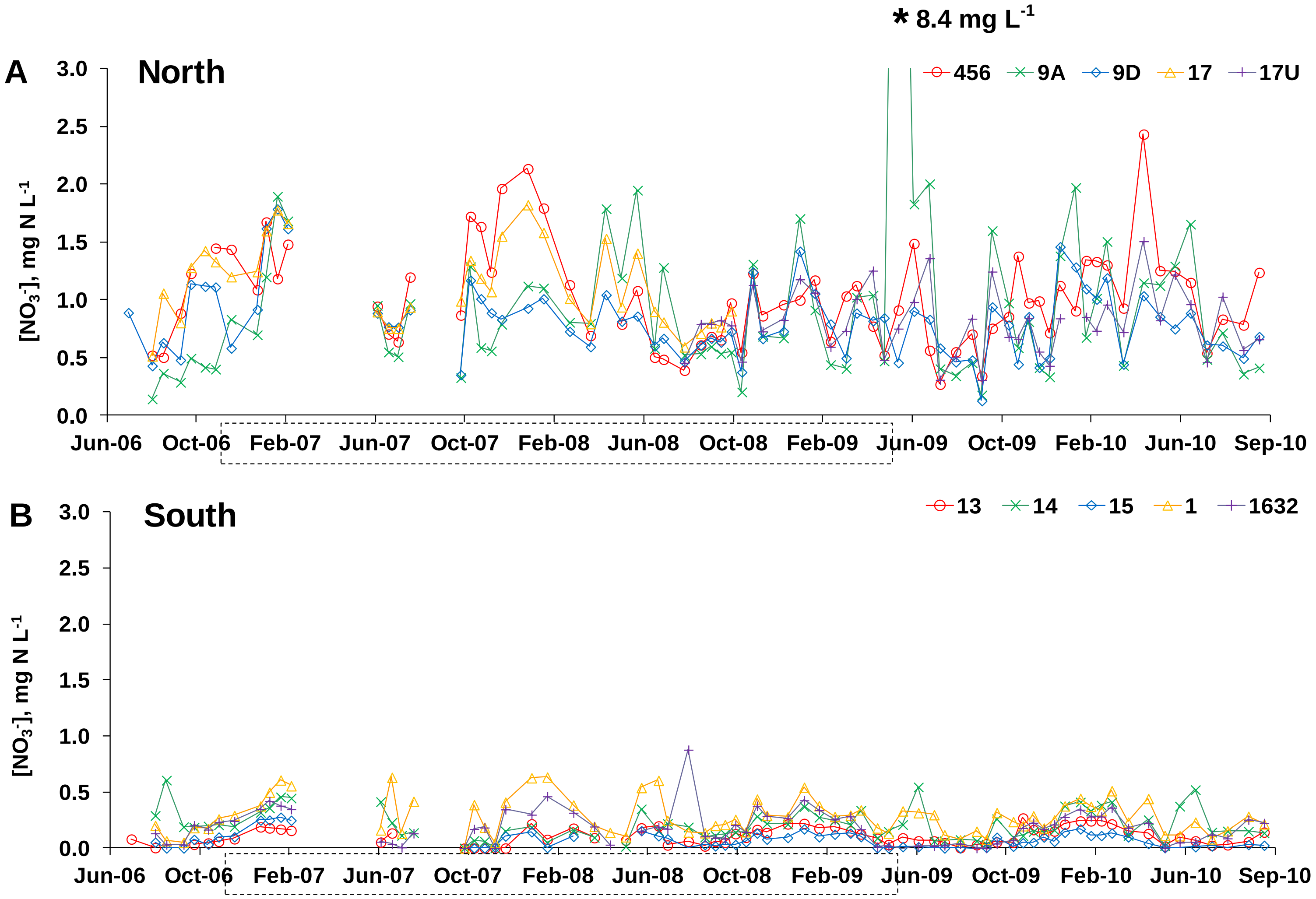


Figure 35. NO$_3^-$ time series. Panel A shows the N-draining catchments; panel B the S-draining. The period of the time series subject to windfarm-related disturbance is shown in the dashed box. Data for June 2006 to September 2007 from Waldron *et al.* (2009). High value during May 2009 for catchment 9A marked with asterisk.

4.4. Inter-Catchment and Annual Trends in Time Series

4.4.1. Carbon

4.4.1.1. Dissolved Organic Carbon

[DOC] in Scottish peat-dominated catchment streamwaters have been reported to range between 0.8 and 56.6 mg L^{-1} (e.g. Dawson *et al.,* 1995; Hope *et al.,* 1997a,b; Dawson *et al.,* 2002; Billett *et al.,* 2004; Dawson *et al.,* 2004; Tetzlaff *et al.,* 2007; Dawson *et al.,* 2008; Grieve and Gilvear, 2008; Dinsmore *et al.,* 2010). The [DOC] for 2007-2010 for the Whitelee catchments, ranging from 2.9 to 57.1 mg L^{-1}, is comparable to these observations from other catchments.

The wide range of [DOC] at Whitelee is caused by the seasonality in [DOC] (Figure 30). In the Whitelee catchments the greatest [DOC] occurs between July and October with correspondingly lower [DOC] from December to May. This marked autumnal flush in [DOC] was also observed by Waldron *et al.* (2009) and the continuation of the bi-monthly time series showed a similar seasonal amplitude to the earlier data. Streamwater in other UK upland peat catchments have been shown to have a seasonal periodicity in [DOC] (e.g. Naden and McDonald, 1989; Cummins and Farrell, 2003b; Billett *et al.*, 2004; Worrall *et al.*, 2006; Clark *et al.*, 2007; Dawson *et al.*, 2008; Dawson *et al.*, 2011).

The pattern of [DOC] at Whitelee is similar to that of water temperature in catchment 13 (see Figure 28, Chapter 2.5). Rather than being dependent on water temperature as this comparison may suggest, and although in-stream fluvial processes can increase [DOC] (Dawson *et al.*, 2001a,b), [DOC] is likely to be driven by soil temperature (Grieve, 1991). The timing of the maxima of [DOC] is likely to be controlled by peak terrestrial productivity, which influences the supply of organic matter for transport. Higher temperatures during the summer drive biological activity, increasing the decomposition of organic matter and solubility of C (Grieve, 1990; Miller *et al.*, 2001; Billett *et al.*, 2006; Clark *et al.*, 2007; Dawson *et al.,* 2008, Dawson *et al.,* 2011) generating a store of DOC in the peat. The increased quantity of available DOC in terrestrial stores is flushed out in the transition from lower water tables as the catchment wets up during the autumn (Worrall *et al.*, 2006; Tipping *et al.,* 2007; Dawson *et al.,* 2008). [DOC] are likely to be lower in the winter with decreasing temperature because of a decrease in fermentative processes which break down organic matter and in phenol oxidase activity (Freeman *et al.*, 2001b). The latter enzyme is associated with C cycling in soil and its presence in soil environments is important to the formation of humic substances. Therefore, because less DOC is produced in the soil during colder conditions, and less is available to be flushed out during winter/spring as the DOC store has become depleted (Brooks *et al.,* 1999), a decrease in [DOC] is observed. The distinct annual signal in [DOC] at Whitelee reflects these changes in seasonal productivity.

The occurrence of higher [DOC] in the S-draining compared to the N-draining catchments concurs with the earlier study of Whitelee by Waldron *et al.* (2009). This spatial variation in [DOC], which will be examined in greater detail in Chapter 6, is hypothesised to be caused by differing soil types and associated land use on either side of the drainage divide. Higher [DOC] in S-draining catchments could be due to greater extent of commercial forestry plantations in these catchments. Higher [C] have been reported in streams draining forested catchments in studies in other parts of Scotland. At Loch Fleet in southwest Scotland, discharge-weighted mean streamwater [DOC] showed only small differences between two catchments of a similar size draining afforested versus moorland catchments, although during storm events [DOC] in the forest stream were twice those in the moorland stream (Grieve, 1990). Large significant differences in soil solution [TOC] have been observed in a paired catchment study in Loch Dee, southwest Scotland, between forest and moorland sites with comparable slope angles and elevations. The forested sites are characterised by soil solution [TOC] up to 50 % greater than the moorland sites (Grieve and Marsden, 2001). This means that in catchments where there are large areas of forestry there is a greater pool of TOC available to reach the stream network (Grieve and Marsden, 2001).

As well as afforestation, deforestation can impact on streamwater chemistry; although results from a number of studies provide conflicting evidence of the effects of clear-felling on [DOC] (*c.f.* Hope *et al.,* 1994). Clear-felling has been reported to result in little change in [DOC] (McDowell and Likens, 1988), whereas in other catchments a slight increase in [DOC] was observed (Hobbie and Likens, 1973; Neal *et al.,* 2004) and in some cases decreased [DOC] was identified (Meyer and Tate, 1983). This variation in the response of different catchments to deforestation is probably because [DOC] is also influenced by factors such as hydrology, season, slope, antecedent temperature and rainfall conditions, catchment size (Eckhardt and Moore, 1990; Grieve, 1994; Dawson *et al.,* 2002, Dawson *et al.,* 2011) and the spatial extent of peatlands within the catchment in addition to forest management (Grieve and Marsden, 2001). Statistically significant increases in streamwater [DOC] were observed compared to a control catchment after clear-felling on blanket peat in Ireland (Cummins and Farrell (2003a). This impact was superimposed on the strong seasonal cycle for up to three years after the start of disturbance with the increases observed during the maximum phase of the seasonal cycle only. Deforestation enhanced [DOC] superimposed on [DOC] which varied seasonally following the commencement of felling and attributed this to increased organic matter decomposition at the soil surface where fresh litter material was provided due to the felling (Tetzlaff *et al.,* 2007).

It has been consistently found that peatland streamwaters have the highest [DOC] compared to rivers draining other soil types (Thurman, 1985). For example, in north-east England the North Tyne river, which has a catchment dominated by upland peats that reach up to 10 m deep, was characterised by higher [DOC] than the South Tyne river, which drains a catchment containing a greater proportion of brown earth soils (Baker *et al.,* 2008). Broad statistically positive relationships exist between both peat coverage, and more specifically the soil C pool, and streamwater [DOC] have been observed at catchment scales ranging from < 1 to 1800 km^2 (Hope *et al.,* 1994, 1997a,b; Aitkenhead *et al.,* 1999; Dawson *et al.,* 2002; Kortelainen *et al.,* 2006, Dawson *et al.,* 2011). As peatlands represent a large pool of organic C, peatland streams are characterised by high allochthonous [DOC] (Fiebig *et al.,* 1990; Grieve, 1991, Hope *et al.,* 1997a; Dinsmore *et al.,* 2010), especially in catchments where soils are consistently saturated and throughflow primarily occurs in the near-surface peat layers (Aitkenhead *et al.,* 1999; Billett *et al.,* 2004).

However, the relationship between streamwater [DOC] and percentage peat coverage may occur in the upper part of the catchment only and becomes weaker downstream as the soil C pool becomes proportionally smaller (Dawson *et al.*, 2001a; Dawson *et al.*, 2004; Billett *et al.*, 2006; Dawson *et al.*, 2008, Dawson *et al.*, 2011). As stream order increases, terrestrial organic C inputs become less significant since further downstream freer draining mineral soils become spatially more important, therefore percentage peat cover as an approximation of the soil C pool can explain only the variation in [DOC] between small catchments. The main control on small-scale spatial changes in streamwater [DOC] in upland headwater catchments is the difference between soil water inputs from different parts of the catchment as the stream flows through different soil types (Grieve, 1990). It is hypothesised that the difference in soil types explains the differences in [DOC] with the topographic divide. The S-draining catchments have more peatland than the N-draining catchments (see Table 7, Chapter 2.4.1), which contain soils of substantially lower organic matter (e.g. non-calcareous gleys) and better drained soils (e.g. brown forest soils) and consequently the streamwaters have lower [DOC].

The seasonal variation and differences between catchments in [DOC] make the assessment of the effects of disturbance on [DOC] in the Whitelee catchments difficult. Pronounced temporal variations in [DOC] complicate the interpretation of before-and-after comparisons, and within-catchment spatial variations obscure the results of paired catchment studies (Grieve, 1994). It is hypothesised that the disturbance of peat through the construction of a windfarm may increase the loss of C from the terrestrial stores to the aquatic system. In addition to the hypothesized impact which hosting the windfarm access tracks and turbine foundations may have on streamwater chemistry (Grieve and Gilvear, 2008) (see Chapter 1.4.1), forest management can impact on streamwater chemistry, and in particular on [DOC].

Figure 30, Figure 31 and Figure 32 show that for most of the Whitelee catchments there was no obvious increase in streamwater [C] during the time series using a bi-monthly sampling frequency, although there is a suggestion in the data that [DOC] increased slightly in catchment 13 during summer/autumn 2008, after a period of large scale deforestation, compared to the other catchments. This potential impact is examined in Chapter 6, although it is hypothesised that the percentage of the catchment covered with peat-based soils plays a more significant role in determining streamwater [DOC] than windfarm-related disturbance.

4.4.1.2. Particulate Organic Carbon

[POC] in the Whitelee catchments ranged from 0.09 mg L^{-1} to 23.4 mg L^{-1} (Figure 31), which is similar to the range in [POC] of 0.00 mg L^{-1} to 22.9 mg L^{-1} observed in peat-dominated catchments in northeast of Scotland (Dawson *et al.,* 2004). Mean [POC] over the three years for all the Whitelee catchments was 1.8 mg L^{-1}, similar to mean [POC] over 2 years at Auchencorth of 1.6 mg L^{-1} (Dinsmore *et al.,* 2010). Catchment [POC] had little seasonal variation compared to the variation seen in [DOC], similar to observations in peatland catchments in northeast Scotland (Dawson *et al.*, 2004).

The most apparent trend in the [POC] time series is that the concentrations are lower in the S-draining catchments than in the N-draining catchments (Figure 31), with catchment

456 often having the highest [POC] of all the catchments, especially from April to December 2009. The spikes in [POC] in catchment 456 are an indication of point-source pollution and are thought to be due to a nearby dairy cattle farm which is a known source of contamination (Edwards and Withers, 2008). Hardstanding areas on dairy farms, such as in catchment 456, receive fresh faecal material daily, and they are cleaned more frequently than in other types of livestock farms (Edwards and Withers, 2008). This larger volume of water and available organic matter increases the likelihood of POC reaching the stream network at 456. As the farm is <1 km upstream of the sampling point, there is a limited dilution potential available by this point downstream which means that it is strongly impacted by agricultural C loss.

There are other peaks in the [POC] time series which cannot be attributed to point source pollution. For example, a peak occurred in all the S-draining catchments during July 2009. The occurrence of this peak in all these catchments suggests it was not caused by windfarm-related construction or deforestation because disturbances such as these would not extend across all catchments at the same time. It is likely that this spike in particular is due to an extended drier period during June 2009. The drier conditions and higher temperatures during this period are likely to have increased the drying and cracking of peat, making it more susceptible to erosion, generating a store of POC in the terrestrial ecosystem which was flushed out in the first rainfall after the dry period.

Based on increased suspended solid loads observed by Grieve and Gilvear (2008) it was presumed that a clear increase in [POC] would be observed in the Whitelee catchments, with the timings coinciding with windfarm-related disturbance such as borrow pit creation, the construction of access tracks and installation of turbine bases in each of the catchments. Significant increases in streamwater [POC] have also been documented following deforestation (Hobbie and Likens, 1973; Gurtz *et al.,* 1980) and known to cause increases in soil C losses by erosion and sedimentation to upland streams (Farmer and Nisbet, 2004), but it has also been reported that harvesting of upland blanket peat forest does not necessarily lead to significantly increased suspended solid concentrations in receiving waters if the Forests and Water Guidelines (2003) are adhered to (Rodgers *et al.,* 2011). No sudden increase or pulse in [POC] was observed at Whitelee (Figure 31).

Four possible explanations for this are:

1. There was no erosion of peat during windfarm construction and therefore no impact on streamwater chemistry. This is unlikely due to the large volume of peat disturbed, around 300,000 m^3, exposed due to the excavation of borrow pits, insertion of turbine foundations, construction of access roads and associated forestry operations.

2. More plausibly, there is an impact of windfarm construction on [POC] but it is not observed outwith the immediate area of disturbance. Dilution between the area of disturbance and the sampling point may lessen impact or any increased [POC] may be buffered through the cycling of POC within the river system upstream of the sampling point by bacteria and aquatic organisms respiring POC, and also DOC, which are removed from the streamwater through evasion.

3. Measures in place to mitigate impact on streamwater chemistry have been effective so no impact is observed outwith the immediate zone of disturbance. At Whitelee, settling ponds (Figure 36) to attenuate flows within the drainage system, alum block deployment to increase flocculation of particles and forest drain blocking to reduce connectivity to the stream network were all employed to minimise the impacts of activities on streamwater suspended sediment. The potential for both windfarm construction and associated forest management to increase suspended sediment in streamwater was identified in the EIA provided by the windfarm developer (CRE Energy, 2002). The good working practice used on site, adherence to the Forests and Water Guidelines (2003), and the mitigation measures put in place to reduce the impacts of erosion and sedimentation may have been appropriate and effective, such that the effect on the water quality in terms of POC was insignificant.

4. The detail of POC dynamics may have been missed in this time series because of the approximately bi-monthly sampling regime which did not target storm events, when the greatest transfers of POC from the terrestrial to the aquatic system are likely to occur (Pawson *et al.* 2008; Stutter *et al.* 2008a,b). Dawson *et al.* (2004) observed in peatland catchments in northeast Scotland that baseflow [POC] was mostly between 0.2 mg L^{-1} and 0.8 mg L^{-1} but that [POC] increased substantially during periods of high discharge to a maximum of 22.9 mg L^{-1}. [POC] in streamwater is often temporally highly variable in relation to storm events (Hope *et al.*, 1997a) which may be responsible for greater transfers of POC than observable using routine sampling.

It is likely that the lack of observed windfarm-related increase in [POC] is due to a combination of explanations 2, 3 and 4.

Figure 36. Use of settling ponds at Whitelee to increase the retention time of the water in the catchment so that the suspended load settles out as a mitigation measure to prevent suspended solids and consequently POC reaching streamwater.

4.4.1.3. Assessment of Impact on Total Organic Carbon

There are no environmental standards available to assess for impact on [TOC]. In order to assess for impact in organic C due to windfarm-related disturbance the seasonal signal in [TOC] had to be quantified for each catchment so that any inter-catchment or annual differences in catchment organic C could be identified. [TOC] was used so that data from hydrologic year 2006-2007 from Waldron *et al.* (2009) with different DOC / POC partitioning could be included. Since the periodicity in the TOC time series is not stochastic, that is, not due to random influences, but explained by changes in terrestrial productivity and catchment hydrology, the seasonality was modelled using harmonic regression for each catchment allowing any additional impacts to be identified. Regression analysis was carried out using Minitab® v16 statistical software. Harmonic regression was not carried out using the data from catchment 17/17U due to the interrupted continuity of the time series caused by the construction of flood storage upstream.

Prior to modelling the data, the distribution of the [TOC] time series data for each catchment was tested for normality through a visual inspection of the histogram of residual frequency, the normal probability plot and the plot of the fitted value against the residual values (Figure 37). A harmonic regression was applied to each catchment with covariate year day (as a decimal) as the X variable to model the trend and seasonal signal captured by sine and cosine terms in [TOC] time series (Piegorsch and Bailer, 2005). The regression was carried out first on the four hydrologic years worth of [TOC] to assess for any trends in the data across the four year period (Figure 38, Figure 39 and Table 21).

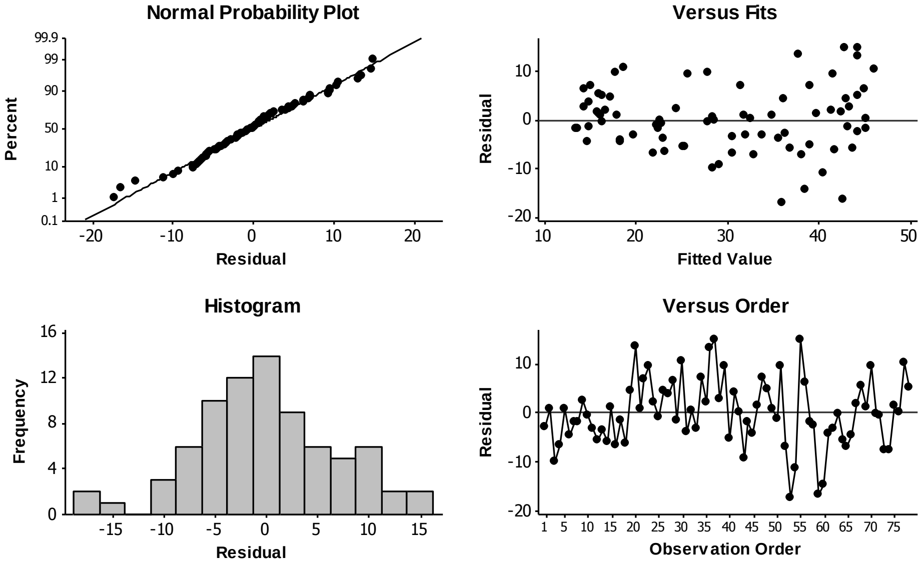


Figure 37. Example of the visual check carried out on the residual plots to check for normality in the [TOC] data, in this case, for catchment 13. The 'normal probability' follows a straight line. The 'histogram of residual frequency' is normally distributed. The 'versus fits' and 'versus order' plots show a random distribution.

Table 21. Harmonic regression of [TOC] with year day as a decimal modelled over four hydrologic years. The P values associated with the Y intercepts were all < 0.001.

Catchment	Y intercept	Year day (slope) coefficient	P value of slope
N-draining			
456	11.9 ± 2.1	1.86 ± 0.70	0.011
9A	13.8 ± 1.4	-0.17 ± 0.64	0.708
9D	8.7 ± 1.0	0.60 ± 0.61	0.091
S-draining			
13	27.5 ± 2.1	0.81 ± 0.70	0.248
14	22.1 ± 1.9	0.58 ± 0.64	0.370
15	26.4 ± 1.8	1.05 ± 0.61	0.087
1	20.2 ± 1.9	0.50 ± 0.64	0.439
1632	22.6 ± 2.0	0.35 ± 0.67	0.609

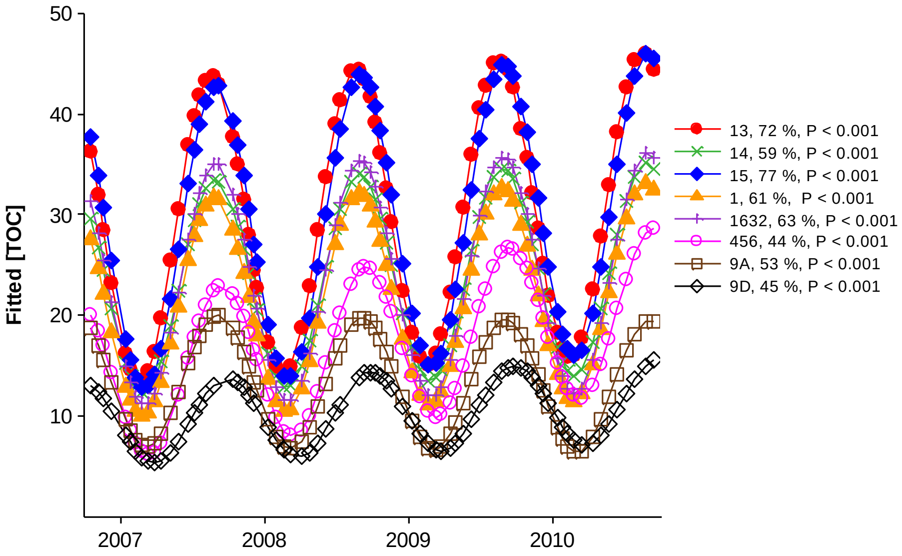


Figure 38. Harmonic regression of [TOC] and year day for four hydrologic years. [TOC] is in mg L^{-1} and 1st January of each year is marked on the X-axis. The R^2 values for the regressions are included in the graph key and the P values of the model fit are all highly significant.

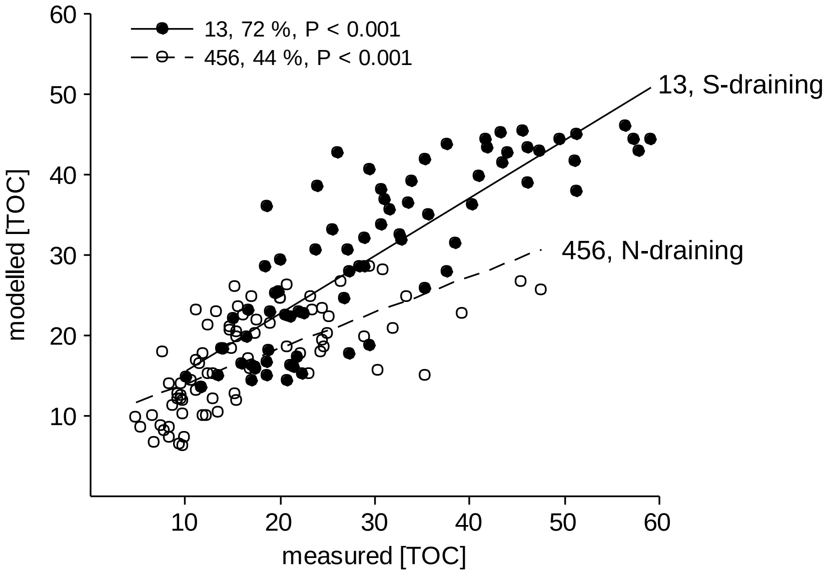


Figure 39. Relationship between measured [TOC] and modelled [TOC] with examples from catchments 13 and 456 to show model fit. [TOC] is in mg L^{-1}.

The fitted [TOC] time series residuals were checked for autocorrelation with a lag of 2 weeks and the graphical output of the autocorrelation function from Minitab v.16 showed that each of the catchments had data points which were independent of the previous data point (Figure 40).

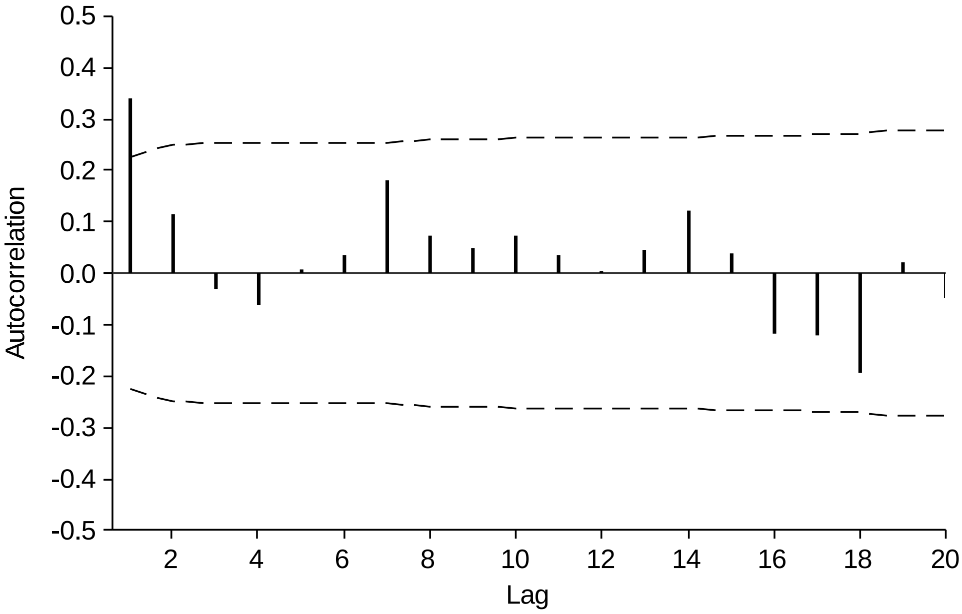


Figure 40. A visual check was performed to test for autocorrelation in the data. An example of a correlogram of the fitted [TOC] residuals, in this case for catchment 13, shows the autocorrection function is close to zero thus there is little time dependence in the data. The 5 % significance limits for the autocorrelations are in the dashed line.

The harmonic regression of [TOC] with year day models the seasonality of TOC reasonably well, with R^2 ranging from 44 to 77 % and all the relationships highly statistically significant ($P < 0.001$) (Figure 38 and Figure 39). Caution must be exercised in the identification of ‘long-term’ trends because it is difficult to interpret trends from a dataset less than a decade in length (Reynolds and Edwards, 1995), as Figure 38 suggests there is a an increasing trend in all catchments. However, the P values of the slope coefficient in Table 21 shows that catchment 456 is the only catchment with statistically significant increases in [TOC] over the four year period, catchments 9D and 15 have weakly significant increases ($P = 0.09$), with the remaining catchments showing no significant trends.

The pre-disturbance baseline period from June 2006 to October 2006 was too short to carry out a before-and-after impact comparison, so the catchment time series for each catchment was split into four hydrologic years from October 2006 to September 2010, each of which were modelled separately to assess for windfarm-related disturbance impact (Figure 41). Harmonic regression allows the identification of changes in annual seasonal pattern and of changes in the ranked position of catchments in terms of the [TOC]. The results of the separate harmonic regressions for each hydrologic year show that in the S-draining catchments the fitted [TOC] model describes the seasonal trend in the data well in 2006-2007 and 2007-2008 (R^2 generally > 75 %, $P < 0.001$) (Figure 41). In the N-draining catchments, the model fit is good for 2006-2007 ($R^2 > 80$ %, $P < 0.001$), but less satisfactory for 2007-2008, with R^2 varying from 52 to 74 %. However, the smallest P value was $P = 0.015$, so the model still describes the variation in the data reasonably well and the relationships provided by the model are still statistically significant (Figure 41).

If the catchments are not affected by windfarm-related disturbance, the modelled [TOC] patterns of the catchments should retain their pattern relative to one another. During 2007-2008 (Figure 41B) catchment 13 has a change in ranked position relative to the other catchments in terms of highest [TOC], whereas during the other years catchment 15, with the greatest percentage of peat-based soils (see Table 7, Chapter 2.4.1), had the highest [TOC]. This inter-annual change for catchment 13 in rank and amplitude (an increase of ~ 10 mg L^{-1} in maximum modelled [TOC]) is evidence of impact in this catchment during the 2007-2008 hydrologic year which is not sustained in the following two years. Controls on streamwater chemistry are identified in Chapter 6, but it is likely the increase in [TOC] is caused by clear-felling and brash mulching carried out in 12 % of the area of catchment 13 during this year. The magnitude of [TOC] increase in catchment 13 is ~ 5 mg L^{-1}, larger than the “relatively modest” impacts of clear-felling on [DOC] observed by Tetzlaff *et al.* (2007). The approximately year-long impact of deforestation activities at Whitelee is shorter than that observed by Cummings and Farrell (2003a) who found increases in streamwater [DOC] lasting up to three years after the start of disturbance. However, the Whitelee catchments exhibited a similar pattern of response to the Irish clear-felled peatland catchments with the increases observed mainly during the maximum phase of the seasonal cycle. Following felling on peaty gley soils in a catchment in mid-Wales there was a slight increase in streamwater [DOC] but at the main catchment outlet, the felling response seems insignificant compared to the normal fluctuations in DOC (Neal *et al.,* 2005). The pattern of increases at Whitelee could be explained by Dai *et al.*’s (2001) conclusion from a study of Hubbard Brook Experimental Forest catchments in New Hampshire, U.S.A. that temporal variations in flowpaths and in-stream processes were more important controllers of streamwater DOC than was the disturbance of felling.

For 2008-2009, regardless of topographic drainage divide, the reliability of the model fit decreases with R^2 ranging from 36 % with a P value of 0.06 (catchment 9A) to 61 % with a P value of 0.001 (catchment 15) (Figure 41). Figure 41C shows that the amplitude of the seasonal signal in the S-draining catchments is less in 2008-2009. The deterioration in model fit and smaller magnitude of amplitude indicates that there was a change in [TOC] pattern in all catchments during 2008-2009. There is a spike in [TOC] in all catchments during April 2009 (Figure 41), which confounds the seasonal pattern. A windfarm-

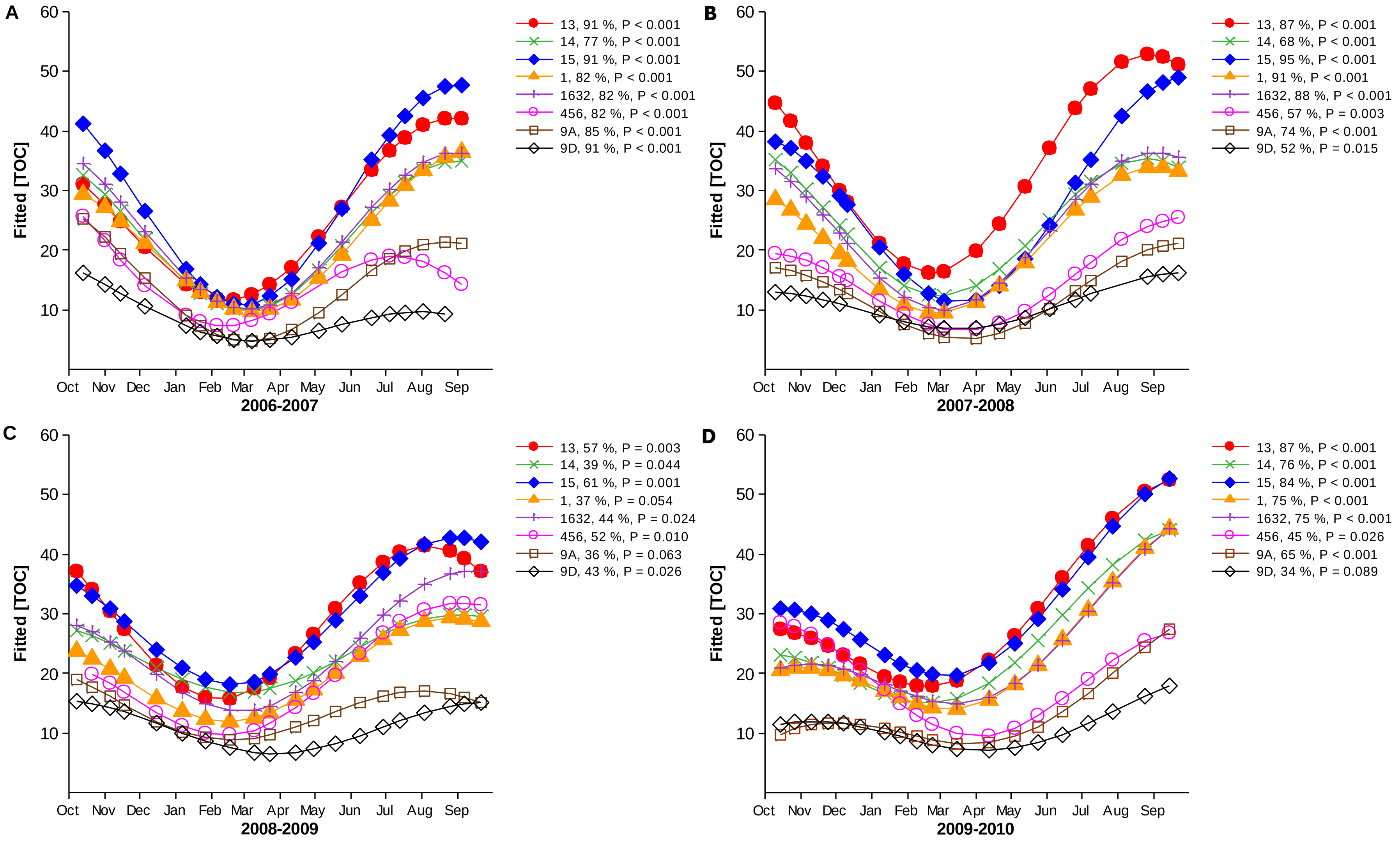


Figure 41. Harmonic regressions of [TOC] with year day, split into four hydrologic years. Panel A shows 2006-2007, Panel B 2007-2008, Panel C 2008-2009, Panel D 2009-2010. The R^2 values and P values for the regression model fit are included in the graph key.

related impact would be expected on an individual catchment basis because construction and deforestation was carried out in focussed pockets of disturbance at different times, which suggests that this spike, which influences the model fit in 2008-2009, is not related to windfarm development. A hydrological or climatic difference during this month driving the availability of a terrestrial C store is the most likely explanation why the modelled seasonal [TOC] time series does not describe the data well compared to the other years of research. Further to this, during 2008-2009 there were six events in the Whitelee catchments with a probability of occurrence of 0.1 %, based on the SEPA Newmilns flow duration curve (see Figure 27, Chapter 4.2.1), including the event with the greatest Q (85 m^3 s^{-1}) recorded for the duration of the research. These high flow events would have increased the connectivity between the available C in terrestrial stores and the stream network throughout the year, not just in the autumn, leading to a lesser seasonal signal in [TOC] during that year.

In 2009-2010 the models describe the [TOC] time series data well again in the S-draining catchments with R^2 increasing to > 75 % with a significance of $P < 0.001$. The model for N-draining catchment 9A fits the data well for 2009-2010 with R^2 of 65 %, $P < 0.001$, but two N-draining catchments show a sustained decrease in model fit over the full duration of research with R^2 in 2009-2010 in catchment 456 as low as R^2 = 45 %, P = 0.03 and in catchment 9D as low as 34 %, P = 0.09. Since windfarm-related disturbance was complete by this stage, it is hypothesised that, rather than any lagged windfarm-related effect, the observed impact on model reliability was due to point source pollution events of [POC] from agriculture (see Chapter 4.4.1.2) in these two catchments driving the loss of seasonal signal.

To summarise, the separate regression analysis for each hydrologic year showed evidence of windfarm-related impact at the sampling points outwith the zone of disturbance using bi-monthly sampling regime through an inter-annual change in [TOC] rank and amplitude in catchment 13 during 2007-2008 – most likely to be explained by the percentage of the catchment area subject to deforestation. This potential control on streamwater chemistry will be examined in the GIS-based analysis in Chapter 6. There was also a distinct change in [TOC] in all catchments during 2008-2009, thought to be driven by changes in hydrology or climate.

4.4.2. Phosphorus

From June 2006 to June 2007 [SRP] and [TP] are comparable in the N- and S- draining catchments and there is homogeneity in the response between catchments (Figure 33 and Figure 34). In all catchments there was a similar seasonal trend to the C dynamics, with the greatest [SRP] and [TP] in late summer/autumn and the least over winter and spring, but with a smaller amplitude than the [DOC] signal. A distinct seasonal signal of [P] in peatland streamwaters has been reported by others (Harriman, 1978; Cummins and Farrell, 2003b) who found the highest [P] in winter, coinciding with increased stream flow. However, the maxima in [SRP] and [TP] were earlier than this at Whitelee, occurring over autumn rather than winter. This may be explained by the difference in timings of greatest rainfall and frozen conditions over winter. Although precipitation at Whitelee is fairly evenly distributed throughout the year, autumn tends to be the wettest period (see Figure 29, Chapter 4.2.3, which is towards the end of the growing season after peak terrestrial productivity. A pool of P is retained in the terrestrial ecosystem during the summer growing period by bio-assimilation and exported as a result of plant decomposition in the autumn (Bowes *et al.,* 2003). When coupled with less plant uptake at the end of the growing season, more P is available to be flushed out through the greater hydrological connectivity due to the Whitelee catchments being wetter for longer periods.

[TP] is more variable in the N-draining catchments than in the S-draining. This phenomenon is likely to be due to the difference in land use between the N- and S-draining catchments, with agriculture more prevalent in the N-draining catchments. The variability in the [TP] time series is likely to be caused by the direct deposition of particulate P in the form of faecal matter in and near the rivers by grazing dairy cattle, which often come down to the stream to drink and may also cause erosion around river banks and disturb P in-stream sediments. Catchment 456 generally has higher and more variable [TP] and [SRP] than the other N-draining catchments which is most likely to be due to the farmyard < 1 km away from the sampling point (Edwards and Withers, 2008).

The seasonal [P] signal was still apparent but the pattern changed in S-draining catchments 13 and 14 from June 2007 with as much as a tenfold increase observed in [SRP] in these two catchments (Figure 33 and Figure 34). Waldron *et al.* (2009) reported the start of this increase in [P] at the end of the [TP] time series of the mean of the S-draining catchments [TP] sampled on the same day.

4.4.2.1. Assessment of Impact on Phosphorus

The Water Framework Directive (2000) UK Technical Advisory Group has provided standards for [SRP] in rivers based on annual mean [SRP] and river type (UKTAG, 2008) (see Chapter 1.3.2 and Table 22). These standards were used to assess for impact of windfarm-related disturbance on streamwater [P], negating the need to conduct harmonic regression analysis on the [P] time series.

Table 22. Standards for phosphorus in rivers, based on [SRP]. Only the standards for the river typologies relevant to the Whitelee catchments are shown.

River type	Annual mean [SRP], μg L^{-1}			
	High	Good	Moderate	Poor
2n	20	40	150	500
4n	50	120	250	1000

Annual mean [SRP] for each of the catchments were calculated for each of the four hydrologic years, including the data from Waldron *et al.* (2009), and compared to the standards for the river type appropriate for each catchment (Table 22). N-draining catchments 9A and 9D have mean annual [SRP] of < 20 μg L^{-1} for the four hydrologic years (Table 23) which, for Type 2n rivers, is a “high” water quality thus these catchments are generally mesotrophic. Similarly catchments 456 and 17U, which are classified as Type 4n rivers, have “high” water quality throughout the duration of research with mean annual [SRP] of < 50 μg L^{-1} (Table 23) which means these catchments are also of low trophic status. S-draining Type 2n catchments 15, 1 and 1632 have a “good” status with mean annual [SRP] for the four hydrologic years of < 40 μg L^{-1} (Table 23). However, there is a clear impact on streamwater [P] in catchments 13 and 14, which are Type 2n rivers and have “good” status in 2006-2007 but deteriorated in 2007-2008 to “moderate” because of a mean annual [SRP] between 40 and 150 μg L^{-1} (Table 23). A full recovery from eutrophication back to “good” water quality status in terms of [SRP] has still not been observed in these two catchments after two further hydrologic years.

Potential sources of P within a catchment were outlined in Chapter 1.3.2 and the controls on streamwater [P] are examined in more detail in Chapter 6, but some provisional explanations for the increases observed in catchments 13 and 14 can be outlined at this stage based on the information about the two catchments and the type and scale of windfarm-related disturbance. P sources entering streams are best grouped into wastewater discharges (for example, septic tank discharges), runoff from impervious surfaces (for example, roads and farmyards) and runoff from pervious surfaces (for example, forestry, cultivated lands and pasture) (Robards *et al.,* 1994; Withers and Jarvie, 2008). In rural catchments such as 13 and 14 at Whitelee, the population uses septic tank systems for wastewater disposal, and if not emptied regularly, or if they do not have adequate soakaway facilities, can impact on streamwater [P]. Farmyard runoff is a mixture of various sources including parlour washings, runoff from silage and manure stores on concrete, livestock sheds, roof water and domestic septic tank discharges as well as open yard runoff (Withers and Jarvie, 2008). Farmyard runoff is therefore another potential source of P to streamwater in rural catchments like 13 and 14. However, the source of the increases in [P] is unlikely to be domestic septic tanks due to the low levels of human settlement in these two catchments, and although both 13 and 14 also have farms upstream of the sampling point, the increase was observed in two catchments simultaneously, suggesting a larger, more diffuse source of P is likely to have impacted both catchments.

Large areas of catchments 13 and 14, 12 % and 10 % respectively, were clear-felled from November 2006 to January 2008 due to bog restoration requirements as part of the HMP (see Table 5, Chapter 2.3.4). An impact on [P] is unsurprising since deforestation is known to have a negative impact on streamwater chemistry, especially in terms of nutrient enrichment (e.g. Nisbet, 2001; Feller 2005). The magnitude of [P] increases, pattern of a decline after peaks in the late summer to tail off in winter followed by a second increase of similar magnitude the next summer, and the timescale of recovery to pre-disturbance levels observed at Whitelee is similar to the response to clear-felling reported in other peatland catchments (see Chapter 1.4.2 for a review of observations from Ahtiainen and Huttunen, 1999; Cummins and Farrell, 2003b and Rodgers *et al.,* 2010).

Table 23. Annual mean [SRP] ± 1 standard deviation for four hydrologic years from 2006.

Catchment	**Annual mean [SRP], μg L^{-1}**			
	2006-2007	**2007-2008**	**2008-2009**	**2009-2010**
N-draining				
456	18.5 ± 7.6	21.1 ± 10.6	28.1 ± 24.5	36.3 ± 36.0
9A	11.7 ± 6.1	12.7 ± 7.9	13.5 ± 8.1	12.4 ± 8.4
9D	10.1 ± 8.4	17.1 ± 17.3	11.9 ± 9.4	10.9 ± 4.8
17/17U	19.2 ± 10.0	22.2 ± 8.6	23.0 ± 17.5	21.0 ± 8.6
S-draining				
13	23.6 ± 16.0	84.7 ± 39.7	70.8 ± 21.1	46.3 ± 11.4
14	21.1 ± 15.2	62.8 ± 40.9	55.2 ± 47.4	47.7 ± 59.8
15	16.2 ± 7.4	22.5 ± 11.0	37.6 ± 26.5	26.6 ± 8.6
1	15.6 ± 9.9	25.3 ± 12.4	22.8 ± 8.2	21.1 ± 8.4
1632	13.9 ± 7.5	28.5 ± 13.3	26.3 ± 8.3	21.1 ± 3.8

The source of some of the P in catchments 13 and 14 could be from the remains of fertilisers used to establish the conifer trees in the 1960s. P as rock phosphate was the principal fertiliser routinely applied in the first rotation at this time and although its input would have been very much lower than is typical of most agricultural systems, it would have been considerably higher than is typical of the low-input agricultural or other uses of blanket peatland (Cummins and Farrell, 2003b). After clear-felling, any remains of this fertiliser could have been washed in-stream in runoff from newly-exposed soils (Malcolm and Cuttle, 1983). With reduced vegetation uptake P levels are likely to exceed greatly plant requirements because felling interrupts the P cycle until the vegetation cover re-establishes (Forestry Commission, 2003).

During harvesting activities, despite the use of brash mats (see Chapter 1.4.2) to reduce the soil disturbance, the forestry machinery may still disturb the forest floor and as a result increase the probability of erosion of particulate matter especially during rain events, consequently increasing P levels in receiving waters (Ensign and Mallin, 2001). After clear-felling, as no significant tree cover remains, soil erosion from the newly-bare peatland surface, which has often been progressively dried due to tree growth (Hope *et al.,* 1994) and become cracked and degraded (Patterson and Anderson, 2000), may increase due to greatly reduced interception and is another likely source of P. Any breaking up of the peat surface is apt to accelerate the mineralisation of nutrients (Vitousek and Melillo, 1979). P is also released from the roots of the felled trees (Ahtiainen and Huttunen, 1999) and after clear-felling, an increase in soil temperature due to increased light penetration to the forest surface can increase decomposition rates (Messina *et al.,* 1997; Perison *et al.,* 1997) and increase P release from the soils (Walbridge and Lockaby, 1994).

The pulse of [P] in streamwater in catchments 13 and 14 is likely to be not due solely to there being a greater pool of available P after disturbance but also there is connectivity which means that P is transported into the stream network. The export of P from the terrestrial ecosystem to streamwater is linked to the P adsorption ability of the soil (Tamm *et al.,* 1974). P is not retained well by peat. The potential of peat to sorb P is extremely low (Fox and Kamprath, 1971; Malcolm *et al.,* 1977). This low P sorption capacity results from the low levels of iron and aluminium in peat to which P can bind (Tamm *et al.,* 1974). Two mechanisms known to cause the transport of this poorly retained P within the landscape are runoff and erosion (Shigaki *et al.,* 2006). A major part of P load after catchment disturbance is derived from movement from the topsoil to the stream by overland flow (McDowell and Wilcock, 2004; Monaghan *et al.,* 2007). Particulate P in particular is likely to increase in runoff at a clear-felled site due to the increase in volume of water reaching the soil surface in the absence of interception by vegetation cover. This water has a greater energy, and therefore erosive power, and when coupled with greater availability of P following clear-felling, a consequent impact on streamwater [TP] and [SRP] could be expected. Where felling has been carried out on podzolic catchments, P released from clear-felling was almost entirely immobilised in the soil and not lost from the site thus there was no noticeable change in streamwater [P], rather [P] were consistently below the analytical detection limit (Stevens *et al.,* 1995). However, this was not the case in peat-dominated Whitelee catchments 13 and 14.

New pathways for water to reach the stream network, less accessible before clear-felling, may become available (Figure 42), allowing nutrients to “by-pass” uptake since terrestrial water becomes rapidly connected to the stream network. Although forest drains in catchments 13 and 14 were blocked during felling, the original plough furrows used to establish the forest in the 1960s may now act as linkages to the streamwaters.

Figure 42. The vegetation has been scraped back off the peat surface at the clear-felled and mulched area in catchment 13 to demonstrate that the original plough furrows have the potential to act as subsurface linkages to stream network.

However, large areas of catchments 1 and 1632, 11 % and 13 % respectively, were also subject to clear-felling yet no increases in [SRP] were observed in these two catchments compared to the drop from “good” to “moderate” water quality status in terms of the standards for annual mean [SRP] reported for catchment 13 and 14.

There are two likely explanations for this:

1) Although similar percentages of the catchment areas were subject to forestry operations, the area of clear-felling in catchment 1 was 7.3 km away from the sampling point and 4.6 km from the sampling point in catchment 1632, whereas it was only 1.0 km upstream to the nearest disturbed area in catchment 13 and 1.8 km in catchment 14. This longer distance from disturbance in catchments 1 and 1632 means that although losses were likely due to extensive felling on peatland, there may have been dilution available between the clear-felled area and the sampling point, and a greater chance that P exiting the felled areas was utilised by bacterial and aquatic organisms upstream of the sampling point. Thus no impact on streamwater chemistry was observed, indicating that distance to disturbance is a key factor influencing the detection of impact on [P].

2) As well clear-felling in catchments 13 and 14, whole tree mulching was also employed, from May 2007 to February 2008 and brash mulching was carried out from May 2007 to July 2008. Although exact figures of the area which was subject to these two forms of mulching are not available, it is known to be extensive compared to the other Whitelee catchments (Personal communication with Ross Kennedy of RTS Woodland and Malcolm Crosby of Forest Commission). Brash mulching was employed so extensively in these catchments because of the need for the quick degradation of brash in order to increase the amount of light reaching the peat surface to speed up the restoration of the peatland habitat and re-vegetation of bog forming plant species as part of the HMP. Whole tree mulching and brash mat mulching were not employed over such a widespread area in catchments 1 and 1632 as these were outside the HMP area where the quick degradation of brash was required. Brash is an important source of leachable nutrients (see Chapter 1.4.2) and when retained intact on site once felling is complete, returns the P to the soil over time. In contrast, when mulched on site like in catchments 13 and 14, this rapid decomposition of the material is known to impact on water quality through the increased likelihood of P leaching (Titus and Malcolm, 1999; Moffat *et al.,* 2006) which is the most likely explanation for the increases observed in streamwater [P].

To summarise, streamwater quality has deteriorated in catchments 13 and 14 with regard to P environmental standards, and a full recovery has still not been observed nearly three years after disturbance commenced. The most likely explanation for the increases reported in these two catchments is a combination of the distance from disturbance to sampling point and the large percentage of the catchment subject to forestry operations.

4.4.3. Nitrogen

[NO_3^-] ranged from as low as the limit of quantification of 0.01 mg L^{-1} to 2.44 mg L^{-1} (Figure 35). These values are comparable to [NO_3^-] observed at Whitelee from June 2006 to September 2007 which ranged from 0.1 mg L^{-1} to 1.9 mg L^{-1} (Waldron *et al.*, 2009). [NO_3^-] were lower in the peatland-dominated S-draining catchments, consistent with the observations in Waldron *et al.* (2009). [NO_3^-] in the S-draining catchments from October 2007 to September 2010 ranged from the limit of quantification to 0.88 mg L^{-1}. This is consistent with other research which has shown that [NO_3^-] in moorland streams is generally very low, typically below 1 mg L^{-1} (Harriman and Morrison, 1982; Reynolds and Edwards, 1995; Adamson *et al.,* 1998, Chapman *et al.,* 2001; Willett *et al.,* 2004; Helliwell *et al.,* 2007a,b; Cundill *et al.,* 2007). In small upland catchments supporting low intensity agriculture or forestry, such as the Whitelee catchments, groundwater supplying the stream as baseflow typically has a low NO_3^- content (Reynolds and Edwards, 1995). The main observation in the [NO_3^-] time series is that there was no obvious increase in any of the Whitelee catchments, and over a year after windfarm-related disturbance commenced, there was no indication of a lagged impact. Other catchments that were subject to extensive clear-felling have shown elevated streamwater [NO_3^-] (Reynolds *et al.,* 1994, Neal *et al.,* 2003a) for up to four years after forestry operations (Tetzlaff *et al.,* 2007) (see Table 3, Chapter 1.4.2), yet no increases were observed at Whitelee.

Although [NO_3^-] in the N-draining catchments was greater than the S-draining (Figure 35) the maximum [NO_3^-] observed in the streams at Whitelee is considerably below the potable drinking water limit of 11.3 mg N L^{-1}, equivalent to 50 mg NO_3^- L^{-1} (EU Drinking Water Directive, 98/83/EC). Controls on [NO_3^-] are examined in more detail in Chapter 6, but it is hypothesised that inter-catchment variation is due to the different land uses with the drainage divide at the Whitelee catchments, with N-draining catchments having greater [NO_3^-] because there is more cattle grazing and more arable land on the lower slopes of the N-draining catchments. [NO_3^-] in streamwater is known to increase where there is more improved pasture, reflecting the inputs from more intensive agriculture (Reynolds and Edwards, 1995). In a study of the River Dee and River Don catchments in Scotland, elevated streamwater [NO_3^-] reflected greater overall agricultural productivity and intensity in these catchments (Edwards *et al.,* 1990).

In both the N- and S-draining catchments [NO_3^-] was greatest over winter and spring with lower [NO_3^-] during summer and autumn, which is the opposite seasonal pattern of the C and P time series. This seasonal [NO_3^-] pattern has been commonly, but not exclusively, observed in several UK studies, many of which were catchments containing either relatively low intensity agriculture or extensive areas of upland, peatland or moorland (Betton *et al.,* 1991; Reynolds *et al.,* 1992; Reynolds and Edwards, 1995; Chapman *et al.,* 2001; Whitehead *et al.,* 2004; Clark *et al.,* 2004; Helliwell *et al.,* 2007a).

The seasonal pattern in streamwater [NO_3^-] is generally explained by the seasonal availability of NO_3^- within the soil for leaching, which is linked to the uptake of NO_3^- by plants during the growing season (Edwards and Thornes, 1973). The greater biological activity during the spring and summer generally means soil NO_3^- availability is low if plant uptake exceeds the rate of N supply from the atmosphere and from NO_3^- production through mineralisation and nitrification (Reynolds and Edwards, 1995), so there is less NO_3^- available to leach into the stream network (Helliwell *et al.,* 2007b). In winter, there is less retention of NO_3^- within the terrestrial ecosystem since transformation and biological uptake of NO_3^- is greatly reduced due to the decrease in biological growth (Helliwell *et al.,* 2007b) and atmospheric inputs increase, which may lead to an increase in soil water [NO_3^-] (Reynolds and Edwards, 1995). This, coupled with greater throughputs of water and increased runoff from soils which become saturated during the autumn and winter, increases the connectivity between the catchment soils and the stream network hence NO_3^- transfers are greater during these two seasons (Reid *et al.,* 1981; Neal *et al.,* 1997; Helliwell *et al.,* 2007b).

The most apparent trend in the NO_3^- time series is that even three years after windfarm-related disturbance commenced there have been no significant increases in [NO_3^-] in any of the catchments like the tenfold increases in [P] observed in catchments 13 and 14. A number of studies in the UK have documented large increases in streamwater [NO_3^-] following tree harvesting (Adamson *et al.,* 1987; Stevens and Hornung, 1990; Adamson and Hornung, 1990; Reynolds *et al.,* 1992). Rapid NO_3^- mobilisation and leaching from felled biomass and enhanced nitrification in soils following harvesting have been well documented in the UK uplands (e.g. Neal *et al.,* 1992; Harriman *et al.,* 2001). These increases in streamwater [NO_3^-] are due to increased rates of mineralisation and nitrification in the organic layers of the soil in response to changes in temperature and moisture regime (Emmett *et al.,* 1991a) combined with a much reduced root demand for N in the absence of uptake by trees (Reynolds and Edwards, 1995) and may last 2 to 5 years, depending upon the rate of re-vegetation (Stevens and Hornung, 1990; Emmett *et al.,* 1991b; Forestry Commission, 2003). It was therefore thought that increases in [NO_3^-] may be observed at the Whitelee catchments due to the extensive forest management and soil disturbance but no clear increases were observed. This could be due to the peatland vegetation taking up any available N before it is able to reach the stream network, or it could be due to the sampling points being located too far downstream from the area of disturbance to observe impact.

4.4.3.1. Assessment of Impact on NO_3^-

Harmonic regression was performed on [NO_3^-] time series from June 2006 to September 2010 to assess for trends in [NO_3^-] over the four year research period. Harmonic regression was not carried out for catchment 17/17U due to the construction of flood storage upstream. One data point (8.4 mg L^{-1}, catchment 9A, May 2009) was omitted from the analysis as it was an extreme high value. The [NO_3^-] data were checked for normality prior to regression – the same approach described for [TOC] time series – and the residuals of the fitted data checked after regression to check for autocorrelation (see Chapter 4.4.1.3). Harmonic regression was carried out on data from each catchment with year day as a decimal as the X variable to model the seasonal signal in [NO_3^-], first on the four year dataset (Figure 43, Figure 44 and Table 24).

The harmonic regression models the [NO_3^-] data less well than [TOC] because there was a greater amount of variation in [NO_3^-] data and seasonal signal was lesser in the [NO_3^-] time series. The model fit over the four years ranges from a weakly significant ($P < 0.05$) R^2 value of 11 % in catchment 9A to a highly significant model fit with an R^2 value of 52 % in catchment 13. The harmonic regressions in Figure 43 suggest that there may be a decreasing trend in [NO_3^-] over the four years and Table 24 shows that the slope coefficients are mostly negative. However, when the slope coefficients are considered with their standard errors, the slope is not different from zero in most of the catchments, and the high P values (ranging from 0.06 to 0.99) show that there are no statistically different trends in six of the catchments. Only catchments 9D and 15 show statistically significant decreases in [NO_3^-] over the four years.

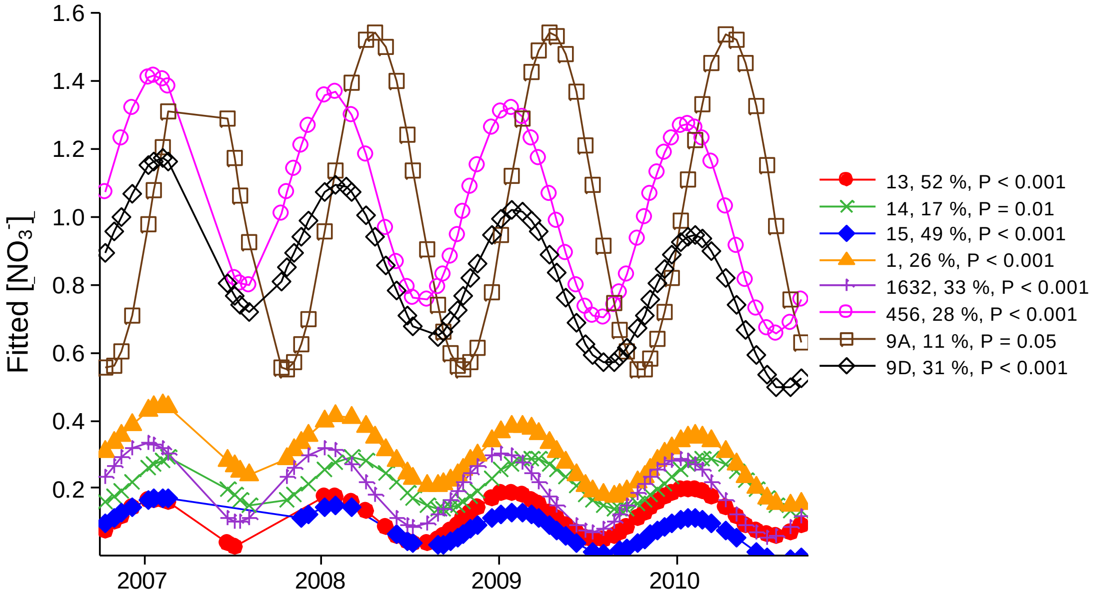


Figure 43. Harmonic regression of [NO_3^-] and year day for four hydrologic years. [NO_3^-] is in mg L^{-1} and 1st January of each year is marked on the X-axis. The R^2 values and P values for the regression model fit are included in the graph key.

Table 24. Harmonic regression of [NO_3^-] with year day as a decimal modelled over four hydrologic years. P values associated with the Y intercepts were all < 0.001.

Catchment	Y intercept	Year day (slope) coefficient	P value of slope
N-draining			
456	1.17 ± 0.14	- 0.05 ± 0.04	0.258
9A	1.05 ± 0.35	- 0.001 ± 0.11	0.993
9D	1.05 ± 0.09	- 0.08 ± 0.03	0.015
S-draining			
13	0.08 ± 0.02	0.01 ± 0.01	0.077
14	0.22 ± 0.04	- 0.002 ± 0.01	0.880
15	0.14 ± 0.02	- 0.02 ± 0.01	0.005
1	0.38 ± 0.05	- 0.03 ± 0.02	0.058
1632	0.24 ± 0.05	- 0.02 ± 0.01	0.291

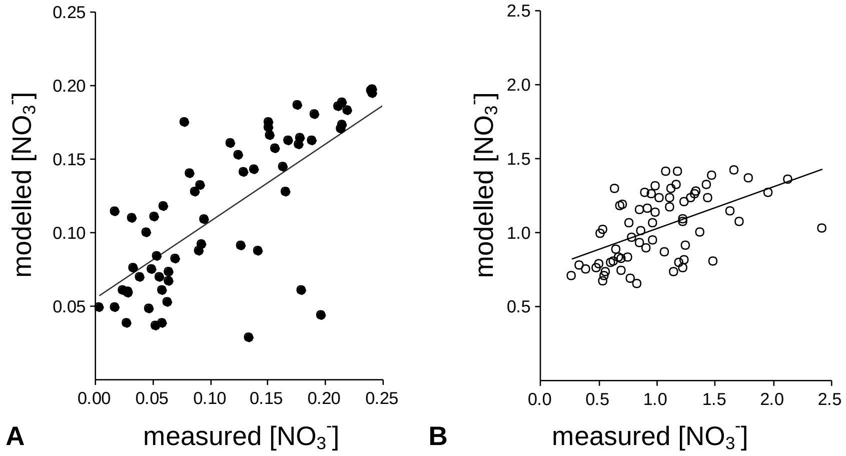


Figure 44. Relationship between measured [NO_3^-] and modelled [NO_3^-] with examples from catchments 13, S-draining, (R^2 = 52 %) (Panel A) and 456, N-draining, (R^2 = 28 %) (Panel B) to show model fit. [NO_3^-] is in mg L^{-1}.

The harmonic regression for [NO_3^-] was performed for each hydrologic year separately because the pre-disturbance baseline period from June 2006 to October 2006 was too short to carry out a direct before-and-after impact comparison. The results for the [NO_3^-] data are more variable than for the [TOC] regression (Figure 45). During 2006-2007 the modelled [NO_3^-] generally had a good fit to the time series data apart from catchments 1, 456 and 9D, where the R^2 values are not as high (≤ 60 %) and the relationships less strongly significant. In 2007-2008 the quality of the fit of modelled [NO_3^-] decreases in all catchments and no highly significant relationships exist between [NO_3^-] and year day apart from in catchment 456 (R^2 = 75 %, $P < 0.001$) (Figure 45).

In 2008-2009 a highly significant negative relationship between [NO_3^-] and year day (R^2 > 74 %, $P < 0.001$) was observed in catchments 13, 15 and 1632, a weakly significant negative relationship (R^2 = 35 %, $P = 0.07$) was observed in catchment 1 and there are no statistically significant relationships in the remaining catchments during this year (Figure 45). The amplitude of the seasonal signal, especially in the N- draining catchments, is much less in 2008-2009 (Figure 45C), with a maximum fitted [NO_3^-] of ~1 mg L^{-1}, compared to the preceding two years which both had greater maximum fitted [NO_3^-]. This deterioration in model fit and different magnitude of amplitude evident across all catchments during 2008-2009 suggests that there is either a hydrological control, such as an increased number of high flow events during this year (see Chapter 4.4.1.3) diluting the seasonal signal as more surface water with a lower [NO_3^-] enters the stream (Stutter *et al*. 2008a). It could also be a climatic control influencing terrestrial sources and production of NO_3^- across the catchments. It is not thought to be due to a windfarm-related impact since that would be expected on an individual catchment basis because disturbance occurs in different catchments at different times.

In 2009-2010 the relationships between [NO_3^-] and year day show the same cross-catchment patterns as 2008-2009 with catchments 13, 15 and 1632 exhibiting statistically highly significant negative relationships between [NO_3^-] and year day (R^2 > 69 %, $P < 0.001$), catchment 1 with a significant negative relationship (R^2 = 52 %, $P = 0.01$) and catchments 14, 456, 9A and 9D with no statistically significant relationships. Figure 45D does, however, clearly show in contrast that the amplitude of the seasonal signal is greater again, with a maximum fitted [NO_3^-] of ~1.4 mg L^{-1}, suggesting that high flow events or a climatic control had had less of an influence on [NO_3^-] during 2009-2010.

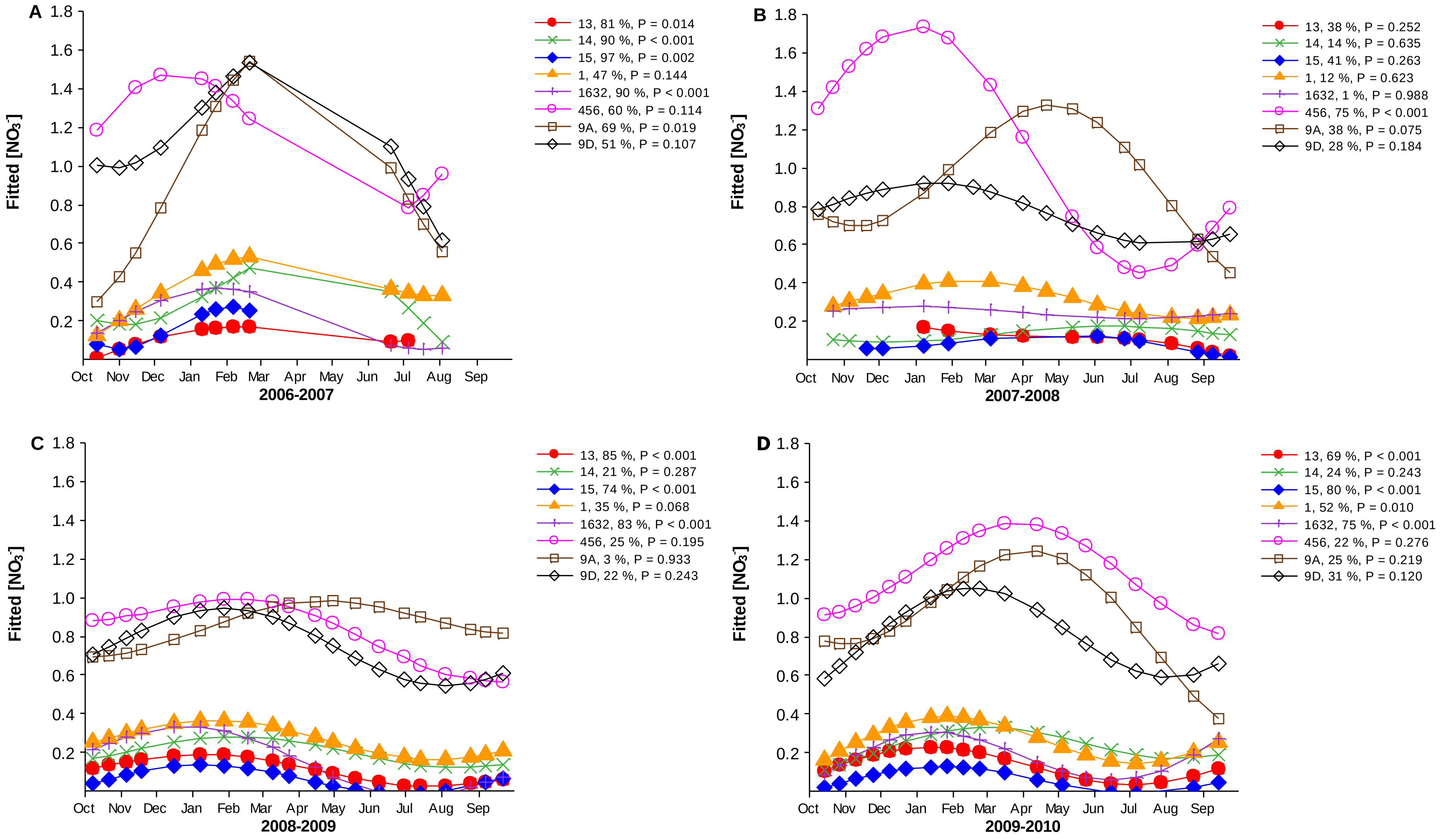


Figure 45. Harmonic regression of [NO_3^-] with year day, split into four hydrologic years. Panel A shows 2006-2007, Panel B 2007-2008, Panel C 2008-2009, Panel D 2009-2010. The outlying data point for catchment 9A in May 2009 was omitted from the analysis. The R^2 values and P values for the regression model fit are included in the graph key.

There is considerable variation in inter-catchment and annual responses in streamwater [NO_3^-] at Whitelee. Chapter 6 examines the controls on streamwater chemistry in more detail but this variation is likely to be caused by varying N inputs in each catchment, due to varying land use, driven by differing soil types. As the N-draining catchments are agriculturally-dominated, the catchments receive more N inputs through fertiliser and manure application. Thus the shapes of fitted [NO_3^-] curves in the N-draining catchments may be more variable than the S-draining catchments. Variations not only occur spatially but also temporally, for example, the maximum fitted [NO_3^-] of all the catchments was catchment 9D in hydrologic years 2006-2007 and 2009-2010, but in 2007-2008 and 2008-2009 [NO_3^-] was considerably lower in this catchment. Land management decisions made in each catchment change from year to year, for example, the rotation of fallow field, grazing areas and arable land, which can explain some of the variation between years in the N-draining agriculturally-dominated catchments. Further to this, not only does the amplitude change but also the phase of the wave differs between years. For example the maximum fitted [NO_3^-] for catchment 456 occurs in December/January in 2006-2007 and 2007-2008, but it is later in 2008-2009 with the maximum fitted [NO_3^-] occurring in February/March and even later in March/April during 2009-2010. The is likely to be due to a cold winter in 2009 and even colder, prolonged winter in 2010 (see Figure 28, Chapter 2.5) delaying the start of the growing season and therefore delaying the application of N inputs, meaning that maximum fitted [NO_3^-] occurs later in these two years. This change in amplitude with year day coinciding with these two cold winters could also be due to NO_3^- release from freeze-thaw and snowmelt (*c.f.* Reynolds and Edwards, 1995).

This variation in inter-catchment and annual response makes the assessment of impact due to windfarm-related disturbance difficult. Nevertheless, in three of the S-draining catchments (13, 15 and 1632) with less improved pasture, a potential windfarm-related disturbance impact may be discernable. The separate harmonic regression models for each hydrologic year have a good fit every year in these catchments with the exception of 2007-2008, when the model fit decreases. This indicates that there is a change in the expected seasonal signal in these catchments during this time, and that it could be hypothesised that this is due to windfarm-related disturbance because the timing of impact coincides with construction and deforestation activity in these catchments.

4.5. Summary of Impacts on Streamwater Chemistry

This chapter has allowed identification of impacts in streamwater chemistry detectable at the sampling points outside the windfarm boundary using an approximately bi-monthly sampling regime to examine streamwater chemistry before, during and after windfarm construction. The harmonic regression analysis showed an impact on [TOC] in catchment 13 during 2007-2008 which changed ranked position relative to the other catchments in terms of highest [TOC]. This was thought to be due to forestry operations within this catchment during this year, however, it is hypothesised that the area of catchment covered by peat has the greatest influence on [C] in streamwater.

The Water Framework Directive (2000) UK Technical Advisory Group Environmental Standards for [SRP] in rivers were used to assess for impact on [SRP]. Whilst the other catchments either had “high” or “good” status based on these standards, catchments 13 and 14 only had “good” status in 2006-2007 but deteriorated in 2007-2008 to “moderate” and a full recovery from eutrophication back to “good” water quality status in terms of [SRP] has still not been observed after two further hydrologic years. As the timing of this deterioration coincided with windfarm-related deforestation in these two catchments, it is hypothesised that the percentage of the catchment deforested controls [TP] and [SRP].

The NO_3^- time series indicates that three years after windfarm-related disturbance commenced there have been no significant increases in [NO_3^-] in any of the catchments like the tenfold increases in [P] observed in catchments 13 and 14. The harmonic regression analysis indicated a potential impact on streamwater [NO_3^-] through a change in the seasonal pattern of [NO_3^-] observed in S-draining catchments 13, 15 and 1632 during 2007-2008. Since the timing of the change coincides with windfarm-related disturbance it is thought to explain these potential impacts, however, it is likely that the percentage of pasture in a catchment will exert the greatest control on [NO_3^-].

5. Streamwater Export Estimates

5.1. Chapter Outline

Using discharge (hereafter named Q) data and the almost bi-monthly time series of concentrations from Chapter 4, monthly and annual streamwater DOC, POC, TP, SRP and NO_3^- export estimates were calculated for the Whitelee catchments. Within this chapter the generation of long-term half-hourly estimates of Q by three methods is discussed and the choice of the most suitable method of estimation of Q for each catchment is explained. Streamwater export estimates for all the Whitelee catchments are presented, interpreted and compared with estimates from other catchments. Finally, the C exports are compared to the suggested C sequestration rate of the Whitelee catchments so that the scale and significance of exports can be assessed.

5.2. Generation of Long-term Half-hourly Q Estimates

In order to calculate exports from the Whitelee catchments a long-term high-frequency estimation of Q was required. Three methods were used to estimate Q at half-hourly intervals. Method 1 used the Q at the SEPA Newmilns gauging site scaled for catchment area, the same method employed by Waldron *et al.* (2009). Method 2 used the relationship between Q measured using an Isco 4150 Area Velocity Flow Logger and Q measured at SEPA Newmilns for the same period to provide a long-term estimate of Q. Method 3 used the relationship between flow measured using an Isco 4150 Area Velocity Flow Logger and stage height measured by an In-Situ Troll 9000 water quality logger (see Chapter 2.5) to provide long-term estimates of Q. Due to equipment constraints Method 3 was carried out for catchment 13 only.

5.2.1. Method 1 – SEPA Q scaled for catchment area

The export estimates calculated previously for the Whitelee catchments in Waldron *et al.* (2009) were based on the assumption that the specific Q for the nearest SEPA gauging station, the River Irvine at Newmilns, (hereafter named SEPA Q), c.3 km west of catchment 1, scaled for each catchment area, described Q in each of the catchments. This method was used in the earlier study because the Whitelee catchments were not gauged at the time of sample collection. Method 1 for generation of long-term Q estimates for this research followed the same approach. The catchment area for the River Irvine at Newmilns is 72.8 km^2, so the half-hourly Q measurements were divided by this value to yield Q in m^3 s^{-1} km^{-2} (specific discharge). This value was multiplied by the study catchment area to give half-hourly Q estimates scaled for catchment area from October 2006 to September 2010. Statistics of Q estimated for each catchment are shown in Table 25 and the hydrographs are shown in Figure 46 and Figure 47.

Table 25. Summary statistics of estimated half-hourly Q by hydrologic year for October 2006 to September 2010 for all the Whitelee catchments. These estimates were calculated using SEPA Q scaled for catchment area.

Catchment	Area (km^2)	Mean Q (m^3 s^{-1})	Median Q (m^3 s^{-1})	Range of Q (m^3 s^{-1})
456	11.7	2006-07 = 0.44 2007-08 = 0.41 2008-09 = 0.42 2009-10 = 0.32	2006-07 = 0.20 2007-08 = 0.21 2008-09 = 0.18 2009-10 = 0.13	0.02 – 13.77
9A	7.9	2006-07 = 0.30 2007-08 = 0.28 2008-09 = 0.28 2009-10 = 0.22	2006-07 = 0.13 2007-08 = 0.14 2008-09 = 0.12 2009-10 = 0.09	0.01 – 9.30
9D	11.6	2006-07 = 0.44 2007-08 = 0.40 2008-09 = 0.41 2009-10 = 0.32	2006-07 = 0.20 2007-08 = 0.21 2008-09 = 0.18 2009-10 = 0.13	0.02 – 13.65
17	15.1	2006-07 = 0.57 2007-08 = 0.53	2006-07 = 0.26 2007-08 = 0.27	0.04 – 13.99
17U	12.0	2008-09 = 0.43 2009-10 = 0.33	2008-09 = 0.19 2009-10 = 0.14	0.02 – 14.12
13	9.4	2006-07 = 0.36 2007-08 = 0.31 2008-09 = 0.32 2009-10 = 0.25	2006-07 = 0.16 2007-08 = 0.16 2008-09 = 0.14 2009-10 = 0.10	0.02 – 10.59
14	14.4	2006-07 = 0.55 2007-08 = 0.50 2008-09 = 0.51 2009-10 = 0.39	2006-07 = 0.24 2007-08 = 0.26 2008-09 = 0.22 2009-10 = 0.16	0.03 – 16.94
15	13.4	2006-07 = 0.51 2007-08 = 0.47 2008-09 = 0.48 2009-10 = 0.37	2006-07 = 0.23 2007-08 = 0.24 2008-09 = 0.21 2009-10 = 0.15	0.02 – 15.77
1	29.4	2006-07 = 1.11 2007-08 = 1.02 2008-09 = 1.05 2009-10 = 0.80	2006-07 = 0.50 2007-08 = 0.53 2008-09 = 0.46 2009-10 = 0.33	0.05 – 34.59
1632	30.0	2006-07 = 1.14 2007-08 = 1.04 2008-09 = 1.07 2009-10 = 0.82	2006-07 = 0.51 2007-08 = 0.54 2008-09 = 0.47 2009-10 = 0.34	0.06 – 35.30

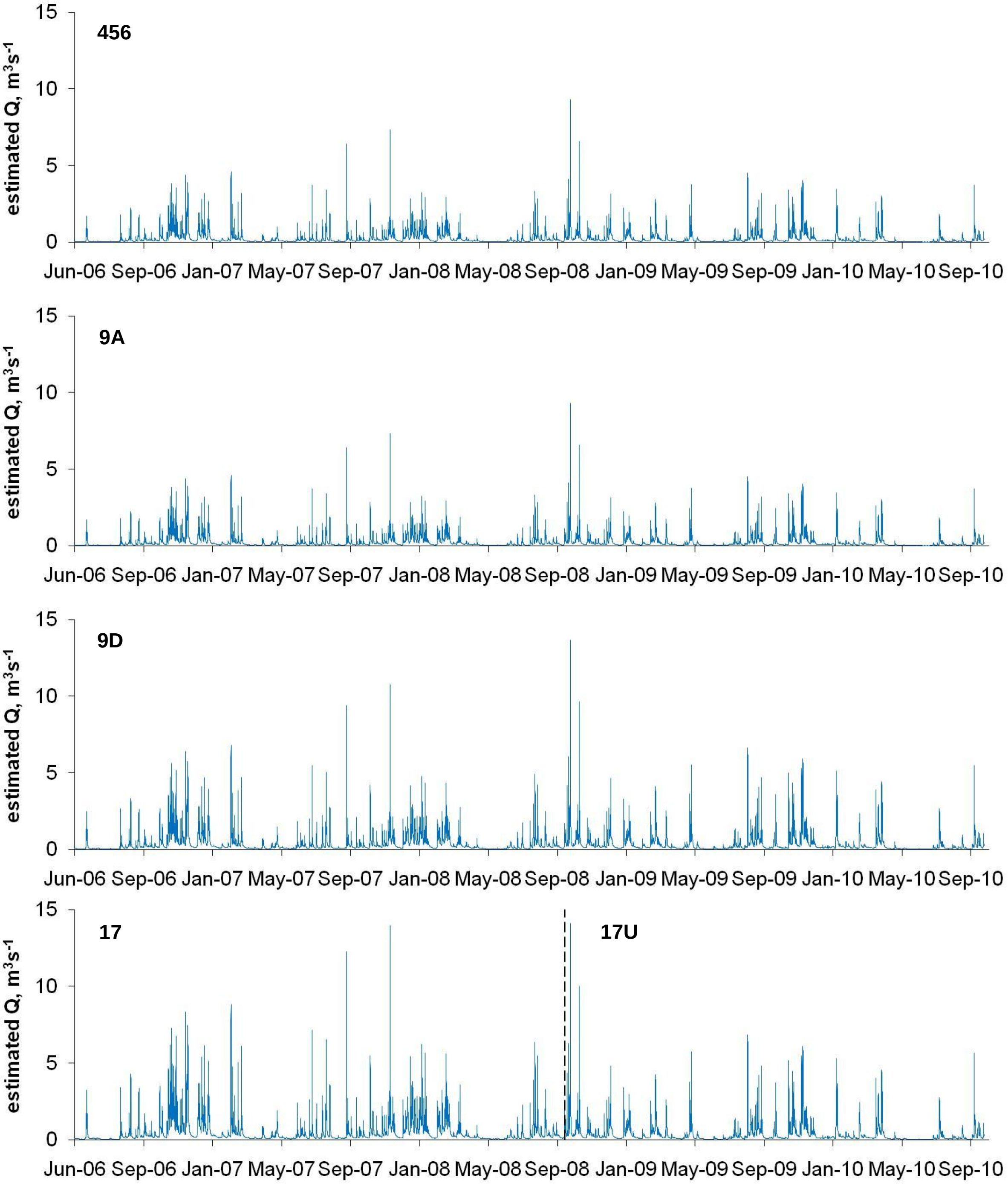


Figure 46. Long-term record of Q at half-hourly intervals for N-draining catchments 456, 9A, 9D, 17 and 17U generated by scaling Q from the nearest SEPA gauged catchment the River Irvine in Newmilns (catchment area 72.8 km^2) by catchment area. Q in catchment 17 was estimated until September 2008 due to the construction upstream of flood storage which altered the flow regime. Q in catchment 17U was estimated from October 2008 onwards, indicated by the black dashed line. Same scale on all y axes for comparison of catchment size.

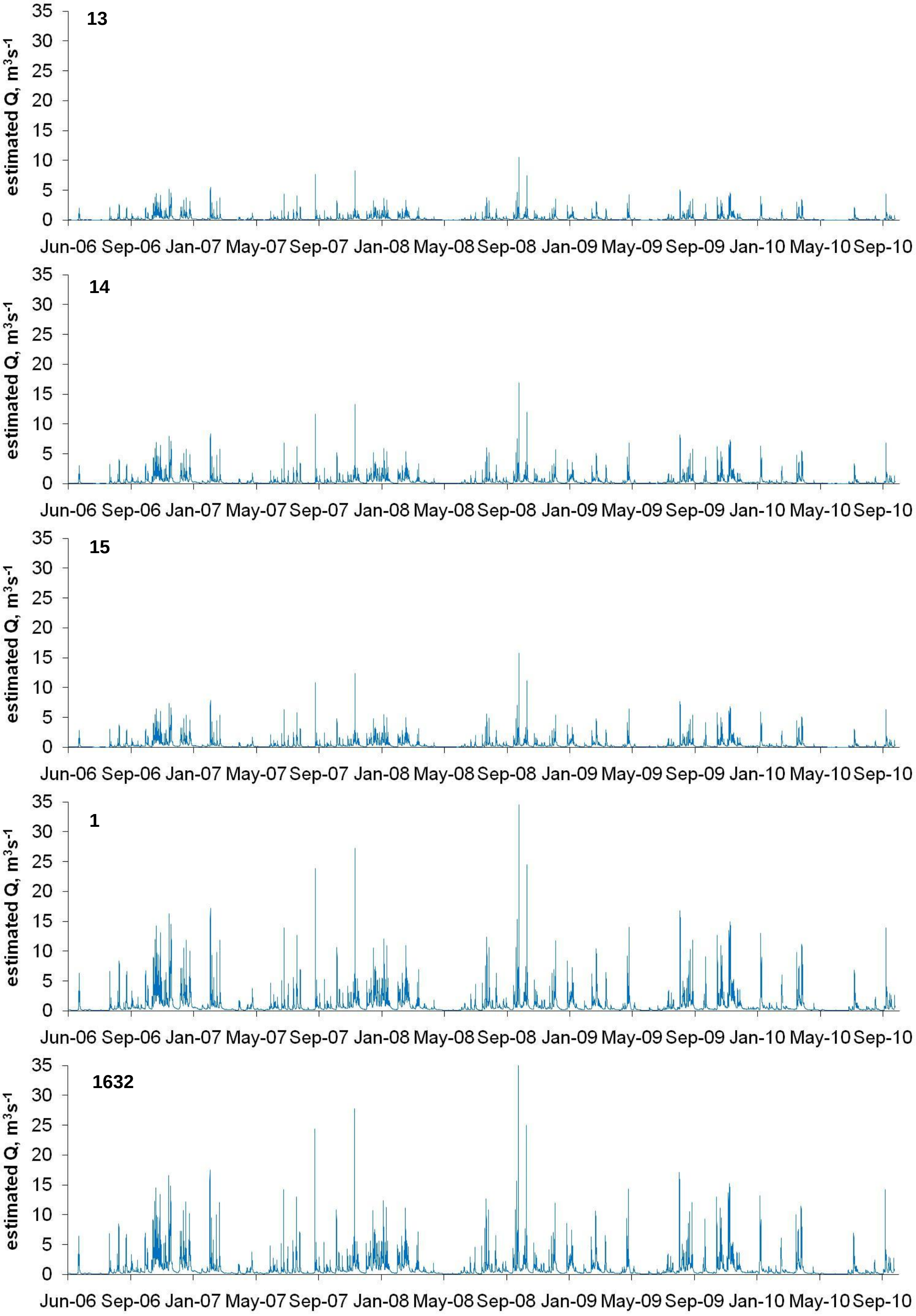


Figure 47. Long-term record of Q at half-hourly intervals for S-draining catchments 13, 14, 15, 1 and 1632 generated by scaling Q from the nearest SEPA gauged catchment, the River Irvine in Newmilns (catchment area 72.8 km^2), by catchment area. Same scale on all y axes for comparison of catchment size.

5.2.2. Method 2 – Relationship Between SEPA Q and Isco Q

An Isco 4150 Area Velocity Flow Logger (hereafter named Isco logger) programmed to measure water depth and velocity at 30 minute intervals, was deployed in seven of the ten Whitelee catchments to capture a range of flow conditions (Table 26). Catchment 1 was not gauged due to the high risk that the equipment would be vandalised. Catchment 456 was not gauged because of the concern that suspended solids could lead to biofilm growth and sedimentation on the sensor, reducing the accuracy of Q measurement. Catchment 17 was not gauged due to the construction of a flood storage facility upstream which was considered to have altered the flow regime during the study period.

Table 26. Summary of where the Isco 4150 Area Velocity Flow Logger was deployed, duration of deployment and the range of Qs measured. The approximate probability of occurrence of these Qs was determined as the probability of occurrence of the SEPA Newmilns Qs at the same time using the flow duration curve for SEPA Newmilns in Chapter 4.2.

Catchment	Duration	Dates of Min. and Max. Q	Isco Q ($m^3 s^{-1}$)	SEPA Q ($m^3 s^{-1}$)	Prob. SEPA Newmilns Q (%)
9A	3 Aug 2010 – 10 Aug 2010 5 Oct 2010 – 8 Nov 2010	19 Oct 2010 23:30 01 Nov 2010 20:30	0.01 5.71	0.83 16.86	58.8 0.9
9D	8 Nov 2010 – 2 Dec 2010	21 Nov 2010 06:00 11 Nov 2010 21:45	0.21 3.11	0.85 11.77	57.6 2.8
17U	15 Dec 2010 – 11 Jan 2011	20 Dec 2010 17:45 4 Jan 2011 22:30	0.03 3.12	0.70 12.50	64.4 2.4
13	22 Dec 2009 – 24 Feb 2010	24 Feb 2010 09:00 15 Feb 2010 18:45	0.01 0.51	0.45 3.64	78.4 19.3
14	10 Sep 2010 – 5 Oct 2010	11 Sep 2010 16:45 13 Sep 2010 18:00	0.07 3.14	1.62 31.98	38.4 0.1
15	7 Jun 2010 – 4 Aug 2010	31 Jul 2010 04:45 15 Jul 2010 09:45	0.06 2.72	0.46 8.41	77.8 5.8
1632	13 Mar 2010 – 29 Mar 2010	22 Mar 2010 00:00 26 Mar 2010 18:45	0.17 9.25	0.49 24.08	75.9 0.3

The logger was deployed close to the water sampling point in each catchment in a section of river with near-laminar flow and where the sensor would be under water even in low flow conditions. The sensor was mounted on a coated lead weight in the middle of the stream bed. The Doppler ultrasonic (500 kHz) sensor on the stream bed measured the average velocity in the flow stream. The acoustic signal emitted by the sensor is reflected by air bubbles or suspended particles in the flow. Thus the time taken for the signal to be received is related to the velocity of water, with quicker times indicating higher flow velocity. A pressure transducer in the sensor unit measured the water depth with a maximum error of ± 0.003 m. The pressure transducer cable was vented so that water depth measurements took account of changes in atmospheric pressure. An offset of 8 cm was input to the Isco Flowlink 4 software to account for the height of the sensor above the stream bed. A detailed survey of the channel bed where the logger was deployed was carried out to construct a water depth to flow area conversion in order to calculate the cross-sectional area of flow from the water depth measured by the sensor. Finally, Q was calculated by multiplying the area of the flow by its average velocity. Half-hourly Q estimates for each catchment from June 2006 to September 2010 were calculated from the relationship between Q measured by the Isco logger (hereafter named Isco Q) and the long-term record of SEPA Q for the period of deployment of the Isco logger.

During deployment in catchment 13 in December 2009 and January 2010 the SEPA Q fluctuated but the Isco Q was almost constant. These data were removed from further analysis because the temperature data from the In-situ Troll 9000 water quality logger showed that the river was frozen at the smaller, more elevated sampling point for catchment 13 during a prolonged very cold period. Hence the relationship was calculated using the February 2010 data only. Although it might be expected that the timing of high flows would differ between catchment 13 and the Newmilns gauging station because of the different catchment areas and thereby reducing the R^2 value of the relationship between the flows measured in the two catchments, there was still a highly significant positive relationship between SEPA Q and Isco Q (R^2 = 94 %, $P < 0.001$) (Figure 48). Relationships between the data after log transformation were also examined but the linear relationship gave the greatest R^2 value and most significant P values.

For catchment 15 the relationship between SEPA Q and Isco Q was skewed by data for the period of greatest flows around 15 July 2010 when the SEPA Q increased at a faster rate than the Isco Q. This could have been due to overbank flow from the channel in catchment 15, that is the water depth exceeded the channel capacity and spilled out laterally, resulting in an underestimate of the cross-sectional area of flow and therefore of Q. However, there was insufficient evidence to exclude any data and the good linear relationship between SEPA Q and Isco Q was used (R^2 = 76 %, $P < 0.001$) (Figure 48).

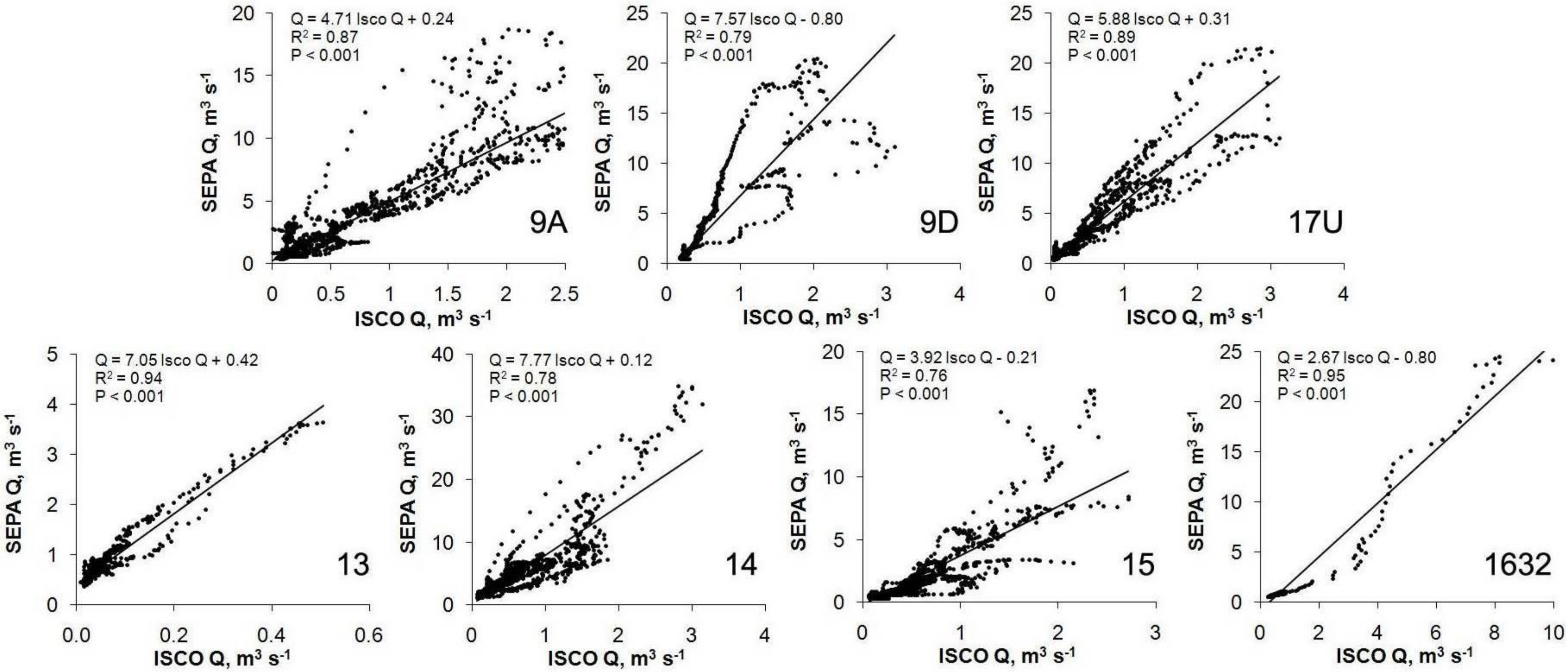


Figure 48. Relationship between SEPA Q and Isco Q for the period of Isco logger deployment in catchments 9A, 9D, 17U, 13, 14, 15 and 1632. The catchment to which each graph refers is labelled in the bottom right corner and the regression equation used to estimate Q is noted on the top left of each graph.

At catchment 1632 there were some anomalous Isco-determined Q values at the end of the Isco logger dataset on the falling limb of a storm hydrograph and these were rejected because the velocity was almost constant. The most likely explanation for the anomalous velocity readings was that the sensor became dislodged from the river bed during event flow. When these data points were removed the R^2 value of the linear relationship between SEPA Q and Isco Q increased from 92 % to 95 % (Figure 48).

Although there are likely to be differences between catchments in the R^2 values for the relationship between SEPA Q and Isco Q due to the different catchment areas, and therefore different timings of high flow events between Newmilns and the Isco-measured Q, the R^2 values were all > 76 % and all were significant ($P < 0.001$) (Figure 48). These likely differences in flow timing may account for the systematic scatter of points around the best-fit lines, for example, in catchment 9D there is a reservoir upstream which may impact on the timings of high flow downstream (Figure 48). From these relationships, time series of half-hourly Q estimates for the seven catchments where the Isco logger was deployed were generated (Figure 49 and Figure 50). Summary statistics of the estimates of Q generated by Method 2 are shown in Table 27.

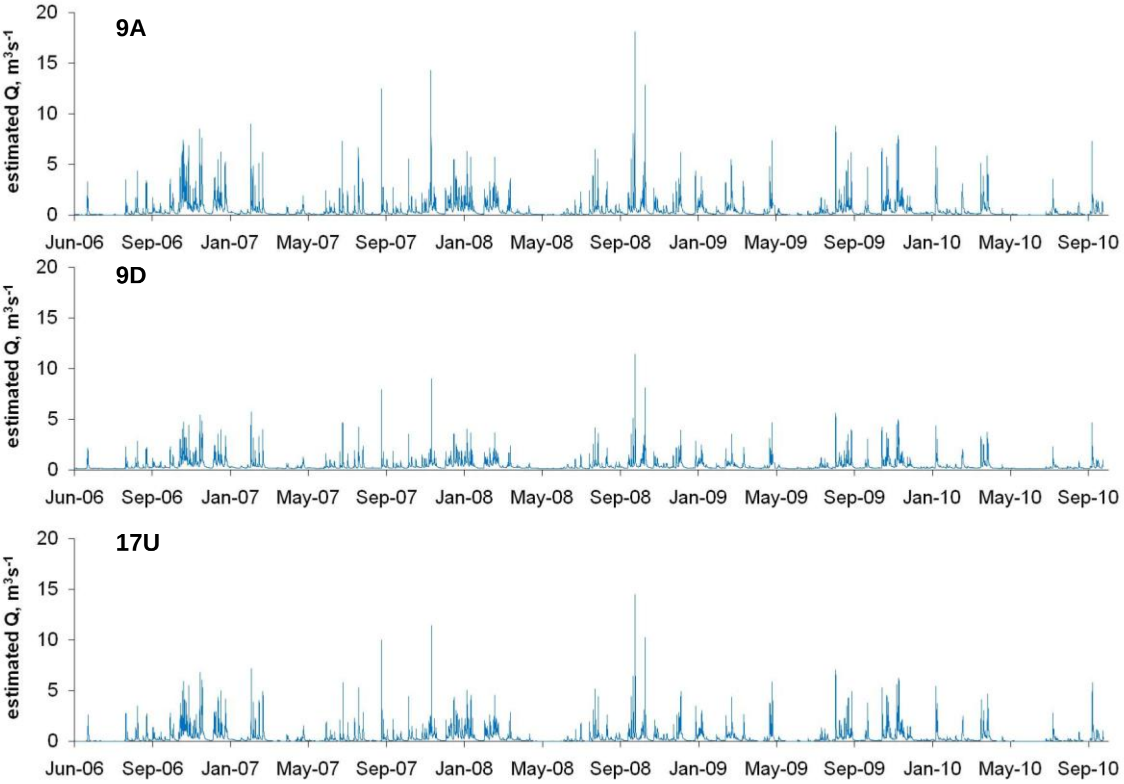


Figure 49. Long-term record of Q at half-hourly intervals for N-draining catchments 9A, 9D and 17U estimated using the relationship between SEPA Q and Isco Q. 456 and 17 are not included because Q was estimated for these catchments using Method 1 only.

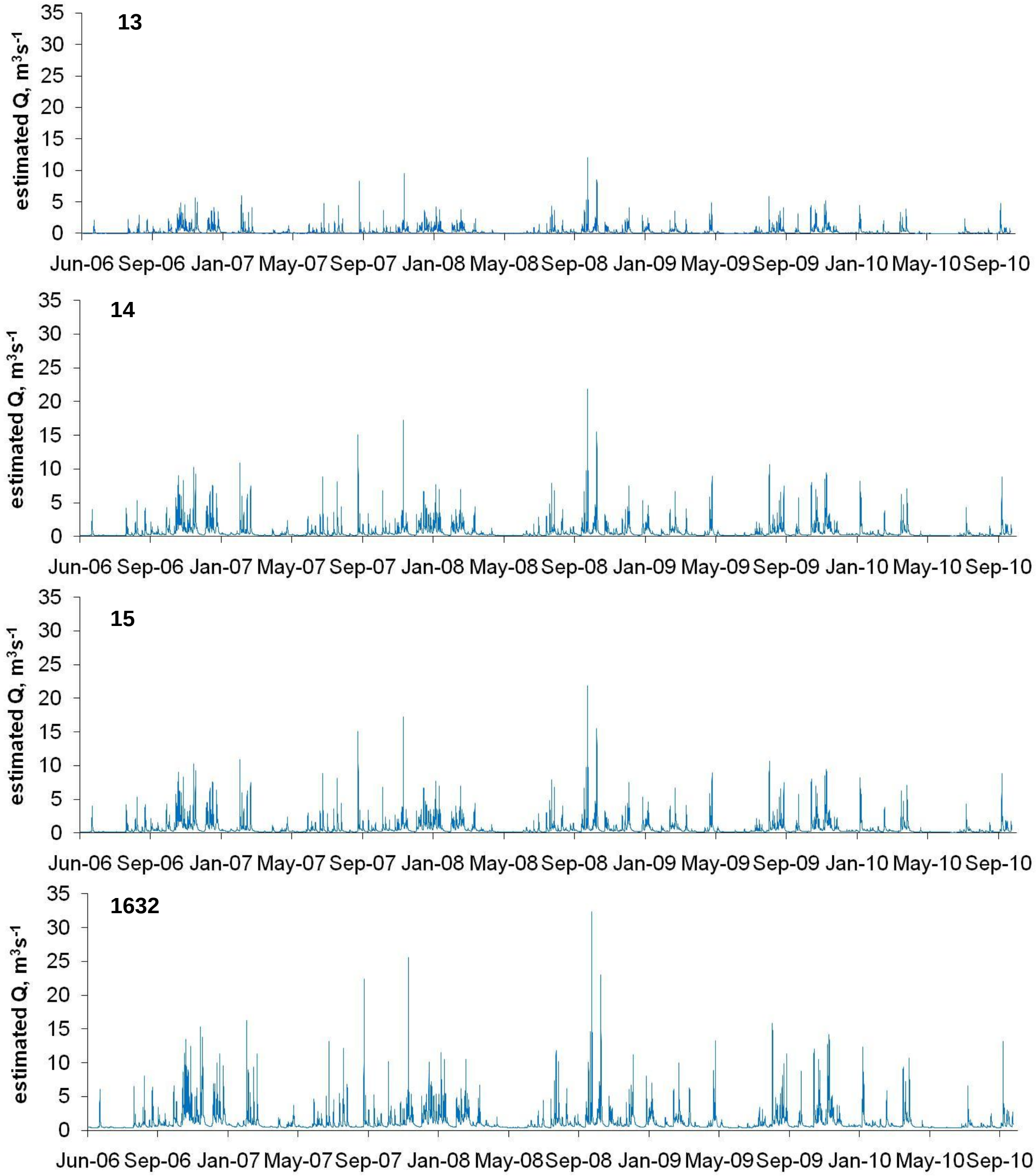


Figure 50. Long-term record of Q at half-hourly intervals for S-draining catchments 13, 14, 15 and 1632 from the relationship between Isco Q and SEPA Q. Q for catchment 1 is not included because Q was estimated for this catchment using Method 1 only.

Table 27. Summary statistics of estimated half-hourly Q by hydrologic year for October 2006 to September 2010 for catchments 9A, 9D, 17U, 13, 14, 15 and 1632. Estimates were generated using the relationship between Isco Q and SEPA Q.

Catchment	Area (km^2)	Mean Q ($m^3 s^{-1}$)	Median Q ($m^3 s^{-1}$)	Range of Q ($m^3 s^{-1}$)	Range of measured Isco Q ($m^3 s^{-1}$)
9A	7.9	2006-07 = 0.53 2007-08 = 0.49 2008-09 = 0.50 2009-10 = 0.37	2006-07 = 0.21 2007-08 = 0.23 2008-09 = 0.19 2009-10 = 0.12	0.01 – 18.13	0.01 – 5.71
9D	11.6	2006-07 = 0.47 2007-08 = 0.44 2008-09 = 0.45 2009-10 = 0.37	2006-07 = 0.27 2007-08 = 0.28 2008-09 = 0.26 2009-10 = 0.21	0.12 – 11.42	0.21 – 3.11
17U	12.0	2008-09 = 0.39 2009-10 = 0.28	2008-09 = 0.14 2009-10 = 0.09	0.01 – 14.43	0.03 – 3.12
13	9.4	2006-07 = 0.33 2007-08 = 0.30 2008-09 = 0.31 2009-10 = 0.22	2006-07 = 0.12 2007-08 = 0.13 2008-09 = 0.10 2009-10 = 0.06	0.01 – 12.10	0.01 – 0.51
14	14.4	2006-07 = 0.34 2007-08 = 0.31 2008-09 = 0.32 2009-10 = 0.24	2006-07 = 0.14 2007-08 = 0.15 2008-09 = 0.13 2009-10 = 0.09	0.01 – 11.01	0.07 – 3.14
15	13.4	2006-07 = 0.63 2007-08 = 0.58 2008-09 = 0.59 2009-10 = 0.45	2006-07 = 0.26 2007-08 = 0.28 2008-09 = 0.25 2009-10 = 0.17	0.01 – 20.59	0.06 – 2.72
1632	30.0	2006-07 = 2.89 2007-08 = 2.67 2008-09 = 2.73 2009-10 = 2.13	2006-07 = 1.39 2007-08 = 1.46 2008-09 = 1.32 2009-10 = 0.99	0.35 – 32.39	0.17 – 9.25

5.2.3. Method 3 – Relationship Between Troll Stage Height and Isco Q

A ratings curve was created using Isco Q measurements for February 2010 (see Method 2) and stage height recorded simultaneously by the In-situ Troll 9000 water quality logger for catchment 13 (see Chapter 2.5) (hereafter named Troll logger) (Figure 51). The positive statistically significant (R^2 = 85 %, $P < 0.001$) linear relationship between Troll stage height and Isco Q was used to produce a long-term time series of 30 minute Q at catchment 13 since October 2007, when the Troll logger was deployed, to September 2010 (Figure 52). Relationships fitted to logarithmic and semi-logarithmic transformations of the data used to construct the ratings curve ($\log_{10}$stage = 0.1222 $\log_{10}$Isco Q + 1.7455, R^2 = 91 %; stage = 4.9747 ln(Isco Q) + 53.75, R^2 = 89 %) produced higher R^2 values than using the untransformed data.

However, using these relationships to calculate long-term time series of Q at catchment 13 yielded unfeasibly high Q estimates at stage heights greater than the stage heights measured during the period when the equation was derived (33 - 55 cm) because of the logarithmic relationship. Therefore the linear relationship between untransformed Troll stage height and untransformed Isco Q was used to obtain the long-term Q estimates at 13. Negative estimated Q values generated by the equation in Figure 51 were replaced with a nominal low flow value of 0.001 m^3 s^{-1} to enable the calculation of exports. This is thought to have little impact on calculated exports since C, P and N exports are normally dominated by high flows (Clark *et al.,* 2007; Pawson *et al.,* 2008; Stutter *et al.,* 2008a,b). Where there were data gaps in the stage height record (5 % of the recorded length) due to logger maintenance and calibration, the relationship between Isco Q and SEPA Q for catchment 13 from Method 2 (see Chapter 5.1.2) was used to estimate Q.

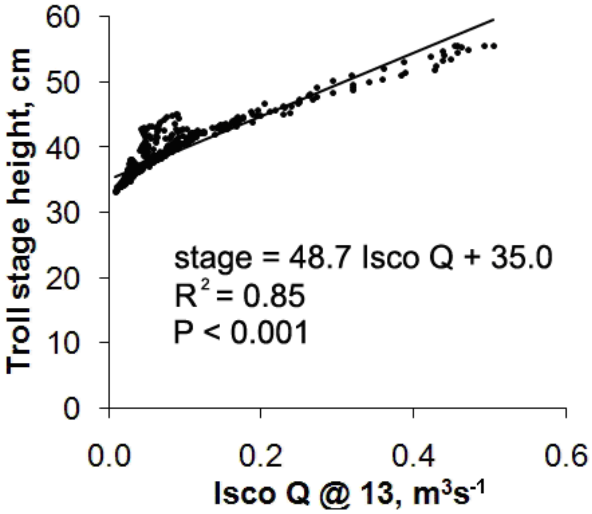


Figure 51. Ratings curve of Isco Q and stage height from the Troll logger in catchment 13 from 9th February 2010 to 24th February 2010 with suspect Isco Q values removed (see Chapter 5.2.2 for explanation).

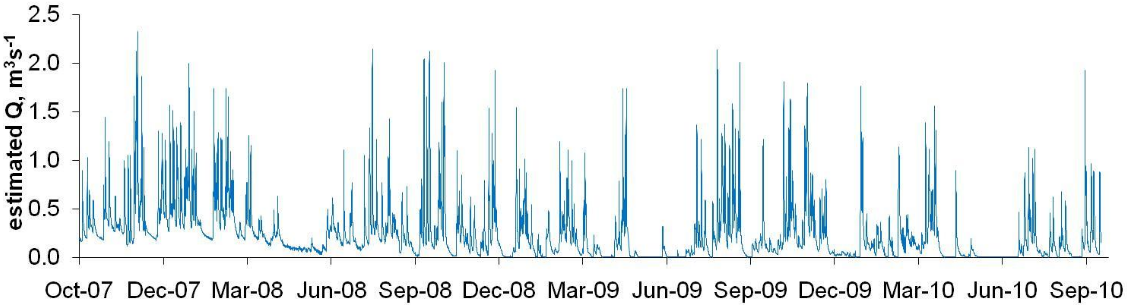


Figure 52. Long-term record of Q at half-hourly intervals for S-draining catchment 13, constructed through a ratings curve between Isco Q and the stage height recorded on Troll 9000 water quality logger deployed since October 2007.

5.2.4. Comparison of Methods to Estimate Q

The range of estimated Q generated by Methods 1 and 2 is reasonable for rivers of these catchment areas and for the most part fits with field observations during event flow. It is assumed that Method 2 for estimating Q is more accurate than Method 1 because it is based on direct measurements of Q in each catchment. Method 2, which does involve a direct measurement of Q, generally gives estimates of Q at low flows which are lower than Method 1 and estimates of high flows which are greater than Method 1. It is likely that Method 1 overestimates Q at low flows and underestimates Q at high flows because it scales Q from a catchment with a much larger area in which variations in flow are expected to be buffered more than in the smaller areas of the study catchments. One inaccuracy in the estimation of Q based on the long-term record of SEPA Q is the differences in the timings of events. Peak flow is likely to occur earlier in the smaller catchments than in the larger SEPA catchment of the River Irvine in Newmilns, where there is likely to be a lag in peak flow timing.

However, using Method 2 to estimate Q results in catchments 9A and 15 having Qs which are higher than would be expected from their areas (Table 27). Catchment 9A had a maximum Q of 18.1 $m^3 s^{-1}$ using Method 2; double the maximum of 9.3 $m^3 s^{-1}$ estimated by Method 1. Catchment 15 had a maximum Q of 20.6 $m^3 s^{-1}$ using Method 2; 25 % greater than the maximum estimated by Method 1 of 15.8 $m^3 s^{-1}$. Based on catchment size, it was expected that estimates of Q from Method 2 for catchment 9A (7.9 km^2) would have a smaller maximum Q than catchment 13 (9.4 km^2), due to its smaller area, when maximum Q for catchment 9A is in fact greater than catchment 13. It was also expected that catchment 15 (13.4 km^2) would have a similar maximum Q to catchment 14 (14.4 km^2) as these catchments have similar areas, but catchment 15 has a maximum Q double that of catchment 14. This could be due to the relatively short time period of deployment of the Isco logger in each catchment, which was not long enough to capture seasonal variability in flows.

Although the approximate probability of occurrence of flows measured by the Isco logger (Table 26) shows that a range of hydrological conditions were captured, the relationship between SEPA Q and Isco Q can only be used with confidence to estimate Q between the minimum and maximum Q measured by the Isco logger (Table 26). For estimates of Q outwith the range of Q measured by the Isco the uncertainties are greater. Since these estimates of Q for catchment 9A and 15 are not realistic when compared to the estimates for the other catchments, Method 2 was not used in the calculation of exports and Method 1 was used for these two catchments instead.

Although the average Qs are reasonably similar between methods, the estimates of Q generated by Method 3 for catchment 13 are the lowest maximum Qs of the three estimation methods (Table 28). The evidence from fieldwork observations of flood debris on the bankside at catchment 13 indicated that high flows had occurred between routine sampling occasions which suggested that Q would have been higher than the estimates generated using Method 3. This suggests that the issue with Method 3 is in regard to estimating high flows. The main explanation for the underestimation of Q using Method 3 is that during high flow at this catchment, water is accommodated laterally rather than vertically. This leads to a lower stage height than expected for a greater volume of water in the channel which could have caused underestimates of Q at high flow. As with the two other estimation methods discussed, the relationship between Troll logger stage height and Isco Q can only be used with confidence to estimate Q between the range of Q measured by the Isco logger. Due to its apparent underestimation of maximum Q, Method 3 was not used to calculate export from catchment 13.

Table 28. Summary statistics of estimated half-hourly Q by hydrologic year for catchment 13 estimated by the three different methods.

	Mean (Q, $m^3 s^{-1}$)	**Median (Q, $m^3 s^{-1}$)**	**Range (Q, $m^3 s^{-1}$)**
Method 1			
2006-2007	0.36	0.16	0.04 - 5.51
2007-2008	0.31	0.16	0.05 - 8.34
2008-2009	0.32	0.14	0.02 - 10.6
2009-2010	0.25	0.10	0.07 - 4.59
Method 2			
2006-2007	0.33	0.12	0.01 - 8.33
2007-2008	0.30	0.13	0.01 - 9.52
2008-2009	0.31	0.10	0.01 - 12.1
2009-2010	0.22	0.06	0.01 - 5.21
Method 3			
2007-2008	0.34	0.26	0.001 - 2.33
2008-2009	0.21	0.10	0.001 - 2.14
2009-2010	0.17	0.08	0.001 - 1.92

Estimates of Q by Method 1 were used in the calculation of exports from catchments 15, 1, 456, 9A and 17. Estimates of Q by Method 2 were used in the calculation of exports from catchments 13, 14, 1632, 9D and 17U.

5.3. Streamwater Export Estimates

5.3.1. Method of Export Calculation

The export of a substance by a river is the product of Q and the concentration of the substance in the river water. Instantaneous values of export are simple to derive but long-term exports are more complicated to calculate. The problems associated with obtaining reliable estimates of river exports have long been recognised (e.g. Ongley, 1978; Verhoff *et al.,* 1980; Walling and Webb, 1981; Rodda and Jones, 1983; Rekolainen *et al.,* 1991; Cooper and Watts, 2002; Johnes, 2007). Long-term export calculations introduce problems because, whereas continuous records of Q are commonly available, concentration data frequently only represents individual samples taken at weekly, or even greater intervals (Walling and Webb, 1985) and therefore there are different export estimation methods with different suitabilities and biases. With the development of high resolution bankside analysers (e.g Jordan *et al.,* 2007), this problem may decrease in the future but currently the resource requirements of such analysers prevents widespread deployment.

The most commonly used methods of export estimation are based on either interpolation or extrapolation calculations (*c.f* Phillips *et al.,* 1999). Much of the literature which has investigated the reliability of export estimation methods has concluded that the accuracy of both methods is questionable (Phillips *et al.,* 1999; Cooper and Watts, 2002; Johnes, 2007). Extrapolation methods use relationships between concentration and Q determined at the same time which results in the known concentration being replaced by an estimated concentration from the empirical relationship to provide a prediction of high-frequency concentrations on the basis of continuously-measured values of Q (Stevens and Smith, 1978; Ferguson, 1986). An extrapolation method was tried first since it does not make the assumption of constant parameter concentration between bi-monthly sampling occasions. The relationships between concentration and Q estimated by both Methods 1 and 2 were examined for all the Whitelee catchments for all parameters (TOC, DOC, POC, TP, SRP and NO_3^-). No significant relationships were found, with R^2 ranging from <1 % to 25 % and n = 82. Therefore, since high-frequency estimates of concentration on the basis of Q measurements could not be generated, an interpolation method was used as follows.

Monthly and annual exports were calculated by multiplying the concentration determined from approximately bi-monthly sampling (mg L^{-1}, Chapter 4.1) with the estimated half-hourly Q (m^3 s^{-1}), outlined in Chapter 5.2.4, to yield an export value in g s^{-1} after corrections for units. This value was multiplied by 60 to convert to g min^{-1}, then multiplied by 30 to obtain the mass exported for each half hour and the half-hourly exports were summed for each month and each hydrologic year. The calculation assumed that the concentration between sampling occasions was constant until the next bi-monthly sampling concentration, while Q varied between sampling. This assumption is not valid as it is not representative of nutrient dynamics, but functions as a means for preliminary export estimates. Monthly and annual exports were divided by the catchment area to give an export per m^2 of catchment area (hereafter termed export) because the comparison of exports between the Whitelee catchments and other rivers must take account of varying catchment size (Russell *et al.,* 1998). Since export estimates were based on intermittent sampling, they are expected to be underestimates because the probability of incorporating within the dataset short-term extreme concentrations which can occur during high flow (Clark *et al.,* 2007; Pawson *et al.,* 2008; Stutter *et al.,* 2008a,b) is significantly reduced (Johnes, 2007). Although continuous discharge data has been incorporated into the export calculations, it is possible that export values were underestimated also due to the flashy hydrological response in each of the Whitelee catchments.

Monthly and annual export estimates for TOC, TP, SRP and NO_3^- were calculated for the four hydrologic years from October 2006 to September 2010. Due to the differing storage methods of samples on return to the laboratory between analysts (see Chapter 3.8) monthly and annual export estimates for DOC and POC were calculated for three years, for the period from October 2007 to September 2010 when a consistent storage method was used.

5.3.2. Monthly Export Estimates

The range of exports is summarised in Table 29. The greatest monthly DOC exports from both N- and S-draining catchments occurred generally in October and November, with the minimum in May and June (Figure 53). In all catchments, the POC exports had minima generally in May and June and maxima in autumn and winter (Figure 54). Monthly POC exports are more variable in the N-draining catchments with 456 often having a higher monthly export than the other N-draining catchments (e.g. December 2007 to January 2008 and August 2009 until January 2010). The greatest monthly TOC exports occurred generally in the autumn, with the minimum in the summer (Figure 55).

For both monthly SRP and TP exports, during the period June 2006 to July 2007, there was general homogeneity in exports between the catchments (Figure 56 and Figure 57). From August 2007, catchment 13 consistently had the greatest export of TP and SRP due to sustained higher [SRP] and [TP] in catchment 13 compared to the other catchments (Figure 33 and Figure 34). During January 2008 and October 2008 the estimated export from catchment 13 was approximately double that of the other catchments. There were two spikes in the SRP export in catchment 456 in November 2009 and January 2010 (Figure 56). There were occasional spikes in monthly export of TP, but not SRP, indicating increases in particulate P and non reactive soluble P in catchment 1 in March 2008, in catchment 9A in September 2006, November 2006 and January 2008, and in catchment 456 in January 2008 and August 2008 (Figure 57). Apart from these occasional spikes, exports in all catchments followed generally similar seasonal patterns for the four years, with the lowest monthly exports occurring from April through to June and the greatest over the autumn months. Although the TP time series (see Chapter 4.4, Figure 34), showed spikes in catchment 14 during May 2009 and June 2010 these high concentrations were not translated into large exports because they coincided with extended periods of low flow.

The greatest monthly NO_3^- exports occurred generally over the winter months in the N-draining catchments (Figure 58).

Table 29. Minimum and maximum monthly exports from the Whitelee catchments. C and N in g m^{-2} per month and P in mg m^{-2} per month.

Parameter	Range of Monthly Exports
DOC	0.01 (17U, Jun 2009) 9.53 (15, Oct 2008)
POC	0.002 (13, May 2008) 0.99 (456, Jan 2010)
TOC	0.01 (17U, Jun 2009) 9.96 (15, Oct 2008)
SRP	0.001 (17U, Jun 2010) 23.1 (13, Oct 2008)
TP	0.001 (17U, Jun 2010) 38.4 (13, Oct 2008)
NO_3^-	0.0001 (15, Jun 2010) 0.60 (17, Sep 2006)

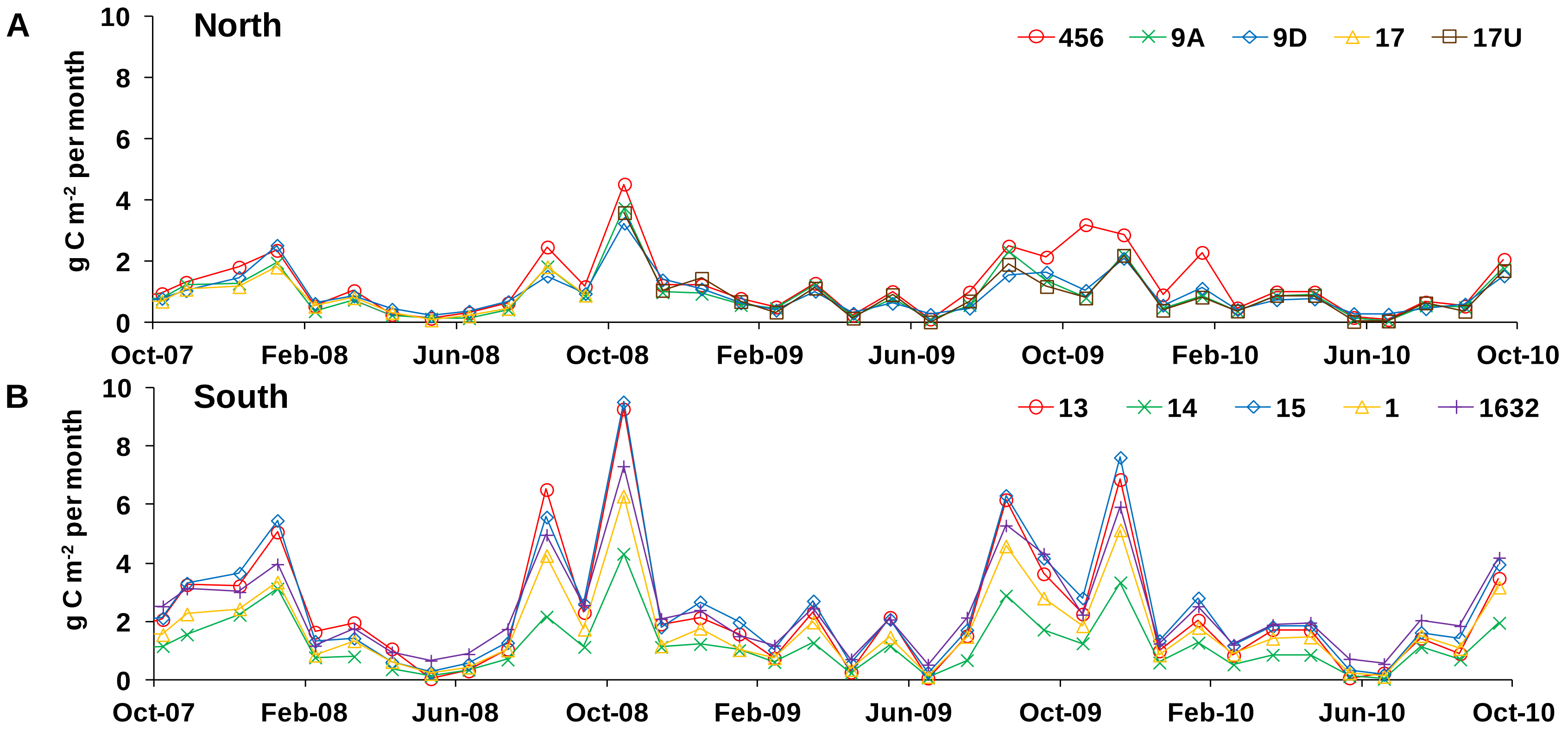


Figure 53. Monthly DOC export with N-draining catchments in Panel A and S-draining catchments in Panel B. Method 1 was used to estimate Q in the calculation of exports from catchments 15, 1, 456, 9A and 17. Method 2 was used to estimate Q in the calculation of exports from catchments 13, 14, 1632, 9D and 17U.

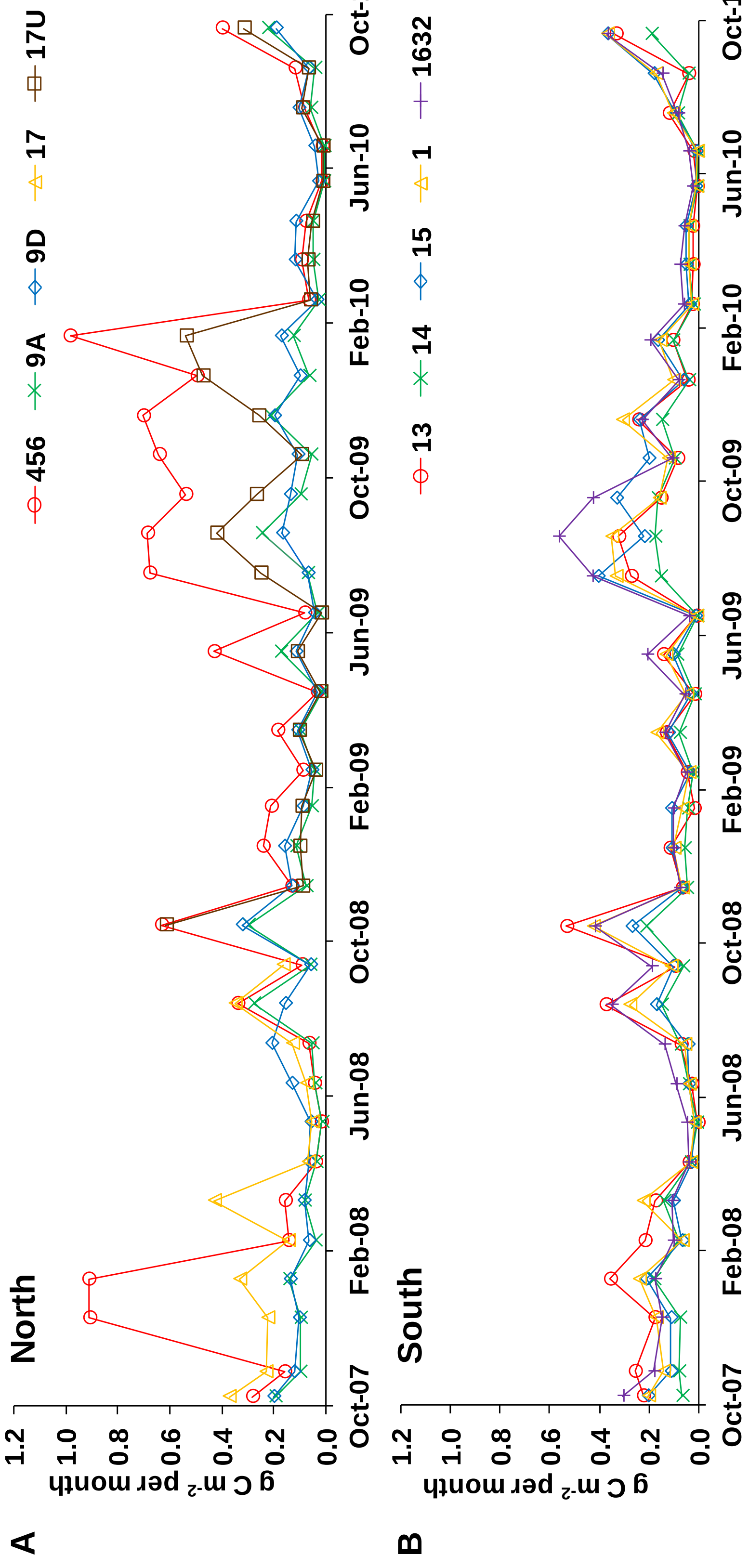


Figure 54. Monthly POC export with N-draining catchments in Panel A and S-draining catchments in Panel B. Method 1 was used to estimate Q in the calculation of exports from catchments 15, 1, 456, 9A and 17. Method 2 was used to estimate Q in the calculation of exports from catchments 13, 14, 1632, 9D and 17U.

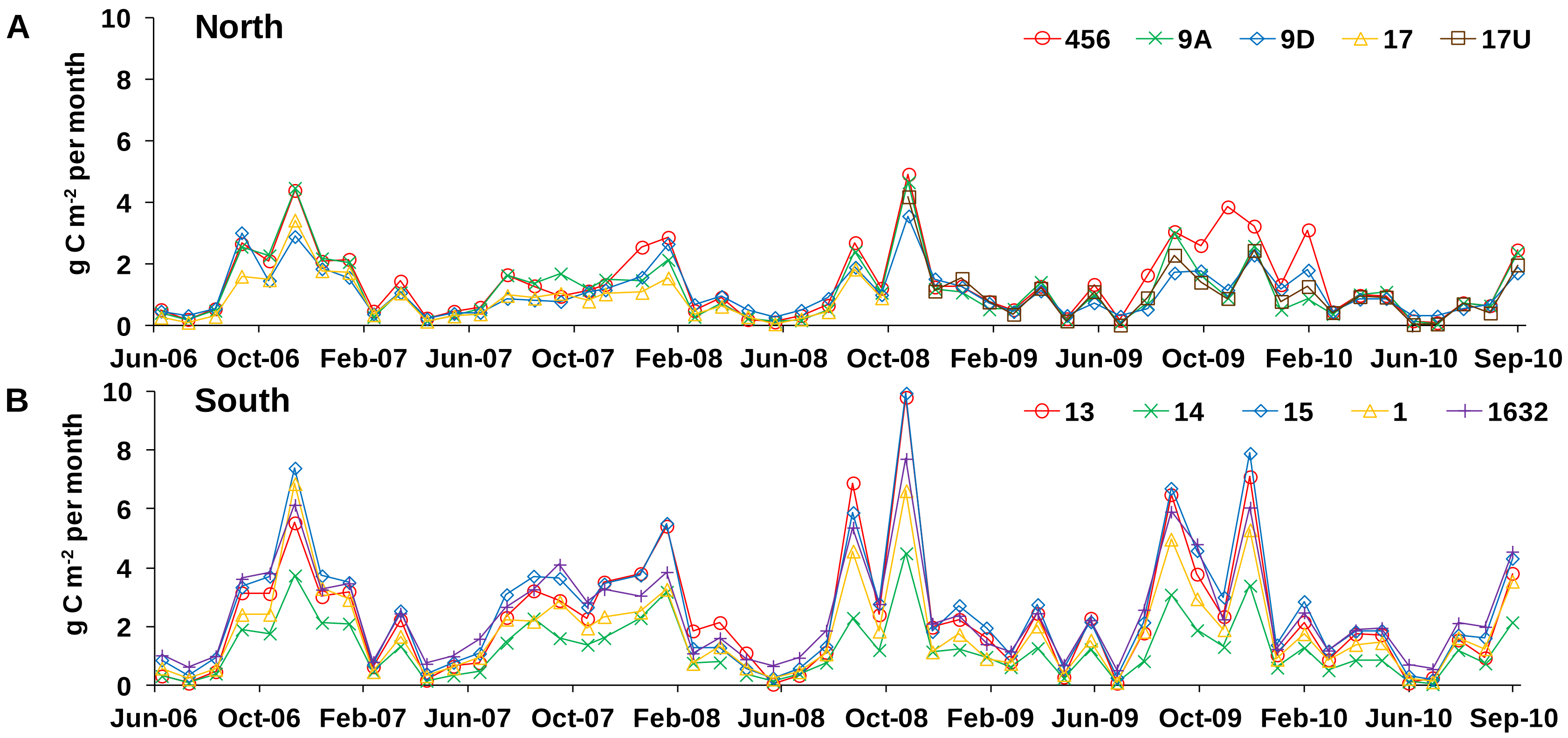


Figure 55. Monthly TOC export with N-draining catchments in Panel A and S-draining catchments in Panel B. Method 1 was used to estimate Q in the calculation of exports from catchments 15, 1, 456, 9A and 17. Method 2 was used to estimate Q in the calculation of exports from catchments 13, 14, 1632, 9D and 17U.

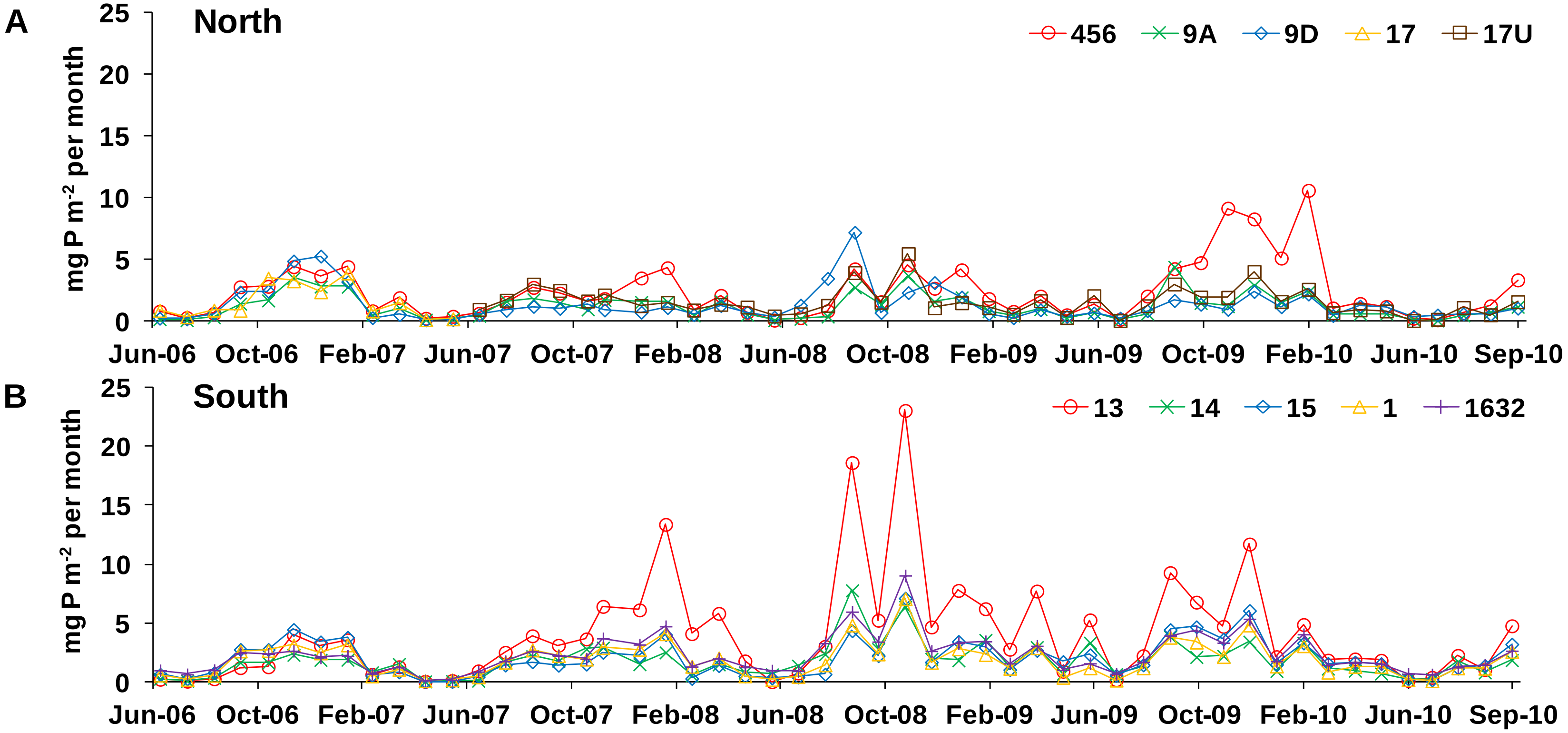


Figure 56. Monthly SRP export with N-draining catchments in Panel A and S-draining catchments in Panel B. Method 1 was used to estimate Q in the calculation of exports from catchments 15, 1, 456, 9A and 17. Method 2 was used to estimate Q in the calculation of exports from catchments 13, 14, 1632, 9D and 17U.

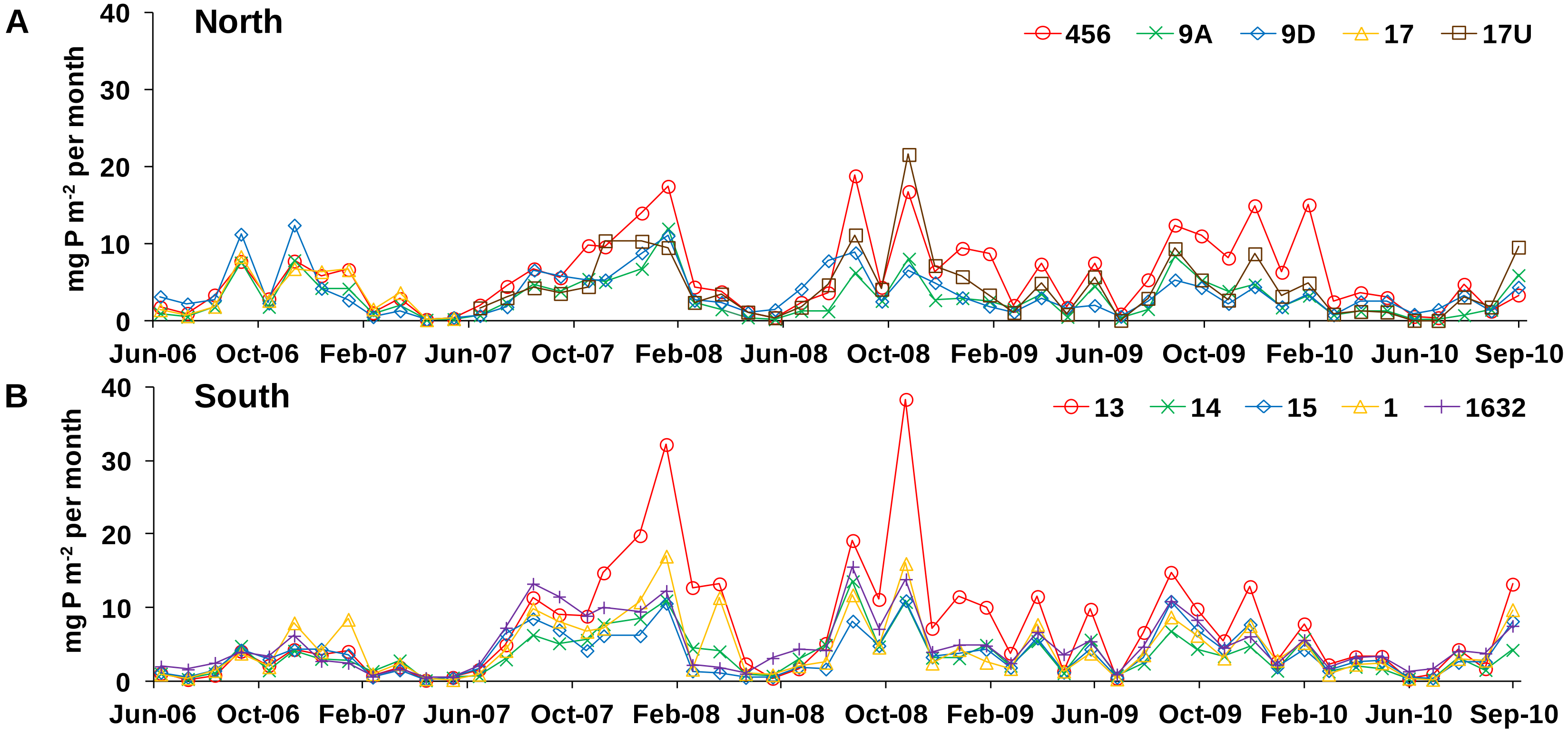


Figure 57. Monthly TP export with N-draining catchments in Panel A and S-draining catchments in Panel B. Method 1 was used to estimate Q in the calculation of exports from catchments 15, 1, 456, 9A and 17. Method 2 was used to estimate Q in the calculation of exports from catchments 13, 14, 1632, 9D and 17U.

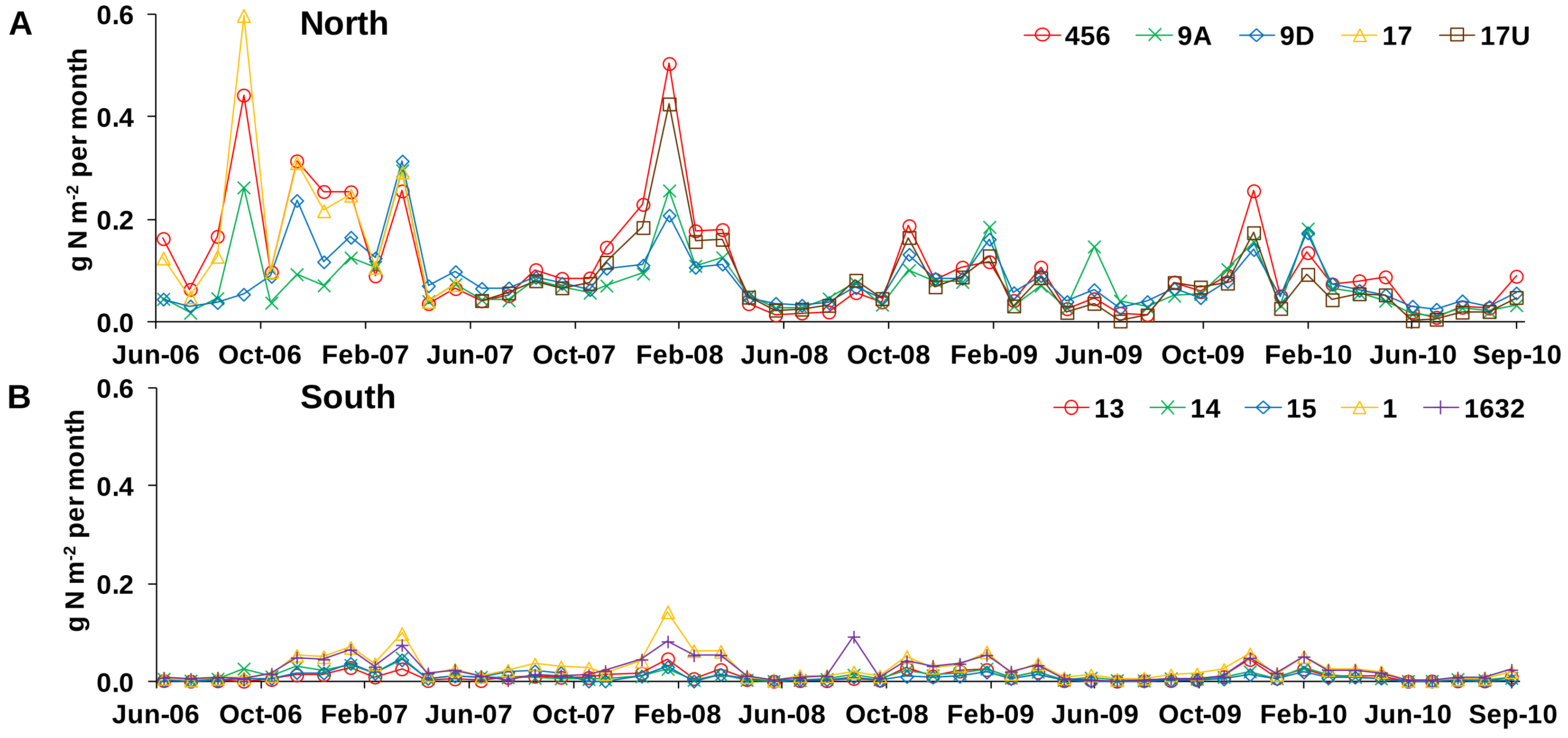


Figure 58. Monthly NO_3^- export with N-draining catchments in Panel A and S-draining catchments in Panel B. Method 1 was used to estimate Q in the calculation of exports from catchments 15, 1, 456, 9A and 17. Method 2 was used to estimate Q in the calculation of exports from catchments 13, 14, 1632, 9D and 17U.

5.3.3. Annual Export Estimates

The range of annual exports is included in Table 30 and annual exports are summarised in Appendix 7. Annual DOC and TOC exports from the S-draining catchments were generally higher than from the N-draining catchments (Figure 59). In all catchments the greatest annual DOC exports occurred in 2008-2009 (Figure 59). Annual POC exports were, on average, 12 % and 6 % of the TOC export in the N- and S-draining catchments respectively. In all catchments the greatest annual POC exports occurred in 2008-2009 with the exception of catchment 13 where the greatest POC export occurred in 2007-2008 (Figure 59).

In the N- and S-draining catchments SRP export accounted for, on average, 41 % and 50 % of the annual TP export respectively. The greatest annual TP exports during the research period were in 2007-2008 except for catchments 17U and 15 where greatest TP export occurred during 2008-2009 (Figure 60). There was no clear pattern indicating in which year the greatest SRP export in the N-draining catchments occurred, but in the S-draining catchments maximum SRP export occurred in the hydrologic year 2008-2009.

The NO_3^- exports were an order of magnitude higher in the N-draining catchments than in the S-draining catchments. The greatest NO_3^- exports occurred generally in 2006-2007, regardless of whether the catchments were N- or S-draining (Figure 61). There is a suggestion in the data that NO_3^- exports decreased over the four years of research.

Table 30. Minimum and maximum annual exports from the Whitelee catchments. C and N in g m^{-2} yr^{-1} and P in mg m^{-2} yr^{-1}.

Parameter	Range of Annual Exports
DOC	9.0 (17U, 2009-10) 42.3 (13, 2008-09)
POC	0.80 (14, 2009-10) 3.93 (456, 2008-09)
TOC	10.7 (17U, 2009-10) 44.9 (13, 2008-09)
SRP	12 (9A, 2009-10) 104 (13, 2008-09)
TP	25 (9A, 2009-10) 206 (13, 2007-08)
NO_3^-	0.07 (15, 2009-10) 1.64 (456, 2006-07)

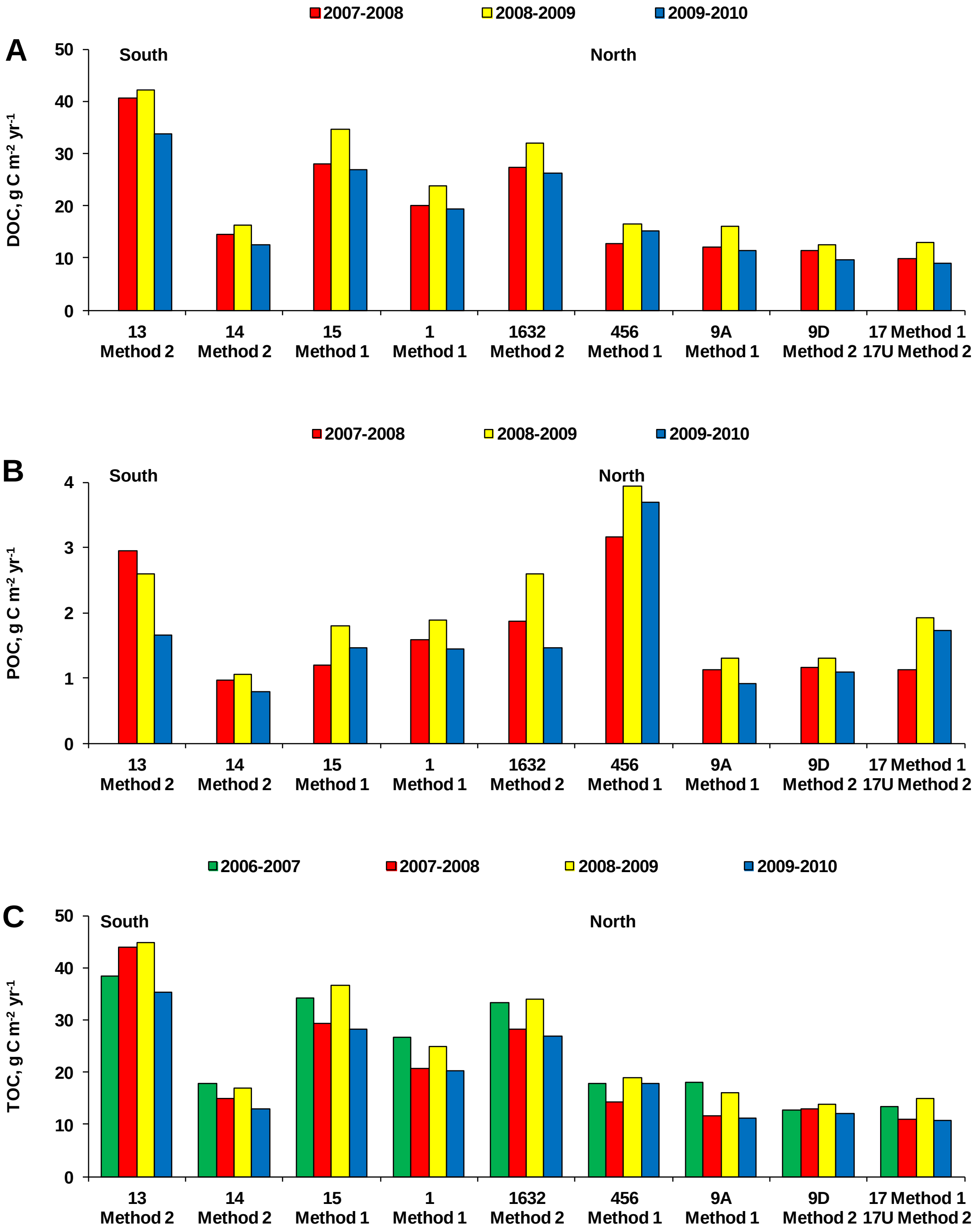
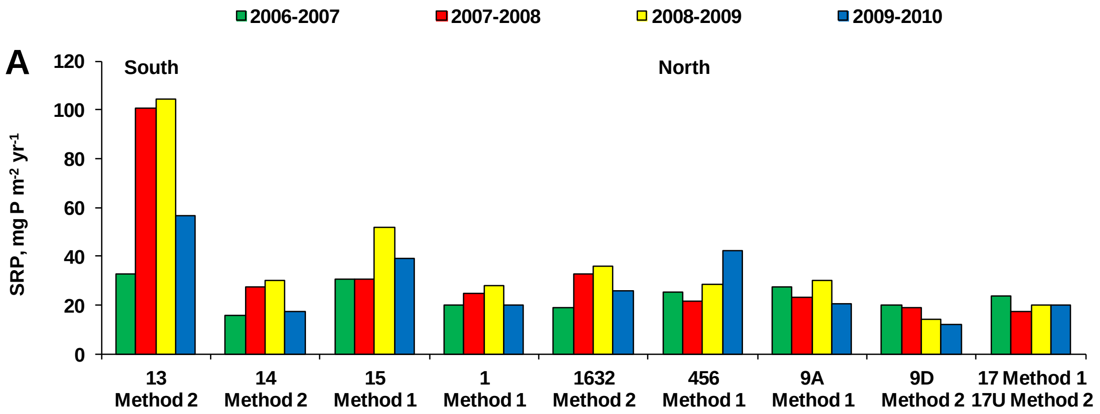


Figure 59. Annual carbon export estimates for the Whitelee catchments with the method used for estimating Q underneath the catchment identifier. Panel A shows the annual DOC export, Panel B the annual POC export and Panel C the annual TOC export. Due to the differing storage methods of samples on return to the laboratory between analysts (see Chapter 3.8) annual export estimates for DOC and POC were calculated only for the period 2007-2010.



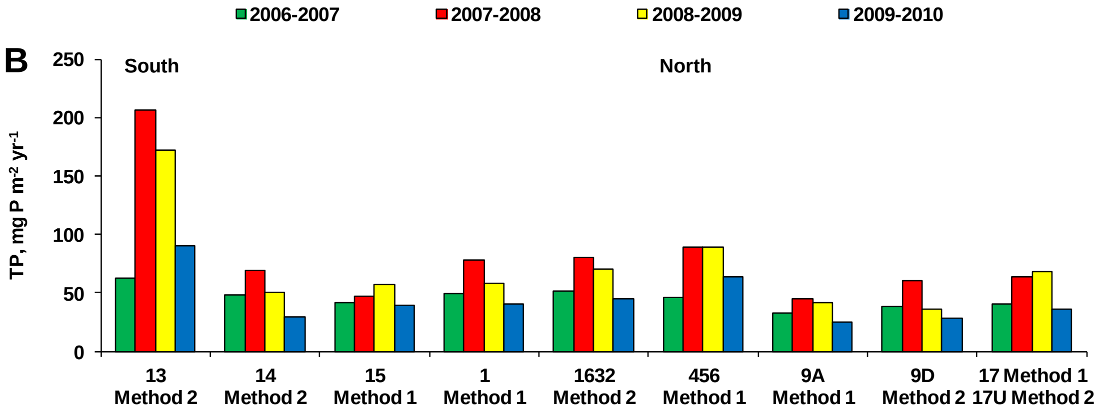


Figure 60. Annual phosphorus export estimates for the Whitelee catchments (mg P m^{-2} yr^{-1}) by hydrologic year for the period 2006-2010. Panel A shows the annual SRP export. Panel B shows the annual TP export.

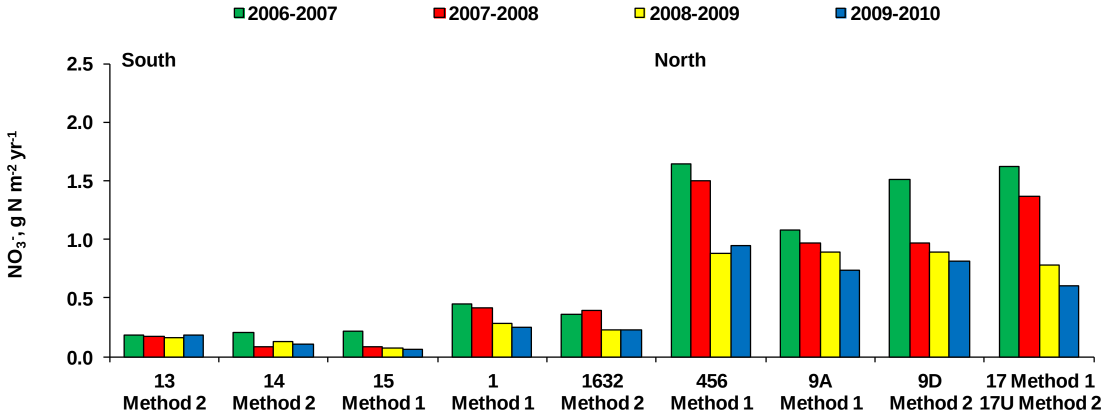


Figure 61. Annual NO_3^- export estimates for the Whitelee catchments by hydrologic year for the period 2006-2010.

5.4. Inter-Catchment and Annual Differences in Exports

5.4.1. Streamwater Carbon Export

5.4.1.1. Inter-Catchment Differences in DOC and TOC Exports

It is estimated that riverine DOC export to British tidal waters is 0.68 ± 0.07 Mt (Hope *et al.,* 1997b). Of this total, rivers in Scotland accounted for 53 %, England 38 % and Wales 9 % (Hope *et al.,* 1997b). Scottish blanket peat is the largest single source of DOC exports in British rivers (Hope *et al.,* 1997b). Table 31 shows that most research into C export in the UK has been carried out in headwater catchments (e.g. Brocky Burn, northeast Scotland) or large river basins (e.g. River Dee and River Don, northeast Scotland) and that there is a paucity of data for C export from meso-scale basins. Table 31 shows export estimates from several Scottish upland catchments with organic rich soils (e.g. Water of Dye, northeast Scotland), a lowland peatland catchment (Black Burn, central Scotland) and actively-eroding peatland catchments (Upper North Grain and Rough Sike, Pennies, England) but there is little data regarding catchments subject to windfarm-related disturbance: only the Garvald Burn, at the Braes of Doune windfarm and this research based at Whitelee windfarm, both in Central Scotland.

The latest export estimates for Whitelee are likely to be underestimates since C exported during storm events may not have been captured by the fortnightly sampling regime. Nevertheless they are generally higher, especially for the S-draining catchments, than exports estimated for other UK peatland-dominated catchments (Table 31), notably the Water of Charr (Dawson *et al.,* 2004), which has comparable catchment characteristics such as area and percentage peat cover. Catchments 13 and 15, the two catchments with the greatest [DOC] and [TOC] (Figure 30 and Figure 32), have a high coverage of peat, with 74 % and 79 % respectively of the catchment covered by peat (see Table 7, Chapter 2.4.1). These two catchments also have the greatest DOC and TOC exports (Figure 53 and Figure 55). DOC export has been found to increase with percentage peat cover in other small (10s of km^2 scale) northern latitude catchments (e.g. Hope *et al.,* 1997b; Billett *et al.,* 2006; Kortelainen *et al.,* 2006) and could explain the difference in DOC and TOC export between the agriculturally-dominated N-draining and peatland-dominated S-draining catchments.

Table 31. Summary of UK catchment studies which included the estimation of aquatic DOC and POC exports. Where TOC data only is available the export estimates straddle both the DOC and POC columns. Either the range of estimates or an annual mean value, with confidence intervals where available, is stated. The results from this research are at the top of the table, with other catchments for comparison grouped by country and listed with the most recent estimates first. This table is reproduced from Dawson and Smith (2007), updated and with available windfarm-related catchment data added.

Details of catchment (area km^2)	**DOC (g C m^{-2} yr^{-1})**	**POC (g C m^{-2} yr^{-1})**	**Reference**
Whitelee (7.9-30.0)	9.0 – 42.3	0.08 – 3.93	This study
Scotland			
Whitelee (7.9-30.)	11.2 – 25.5		Waldron *et al.* (2009)
River Dee (3.4-1837)	3.41 – 9.48		Dawson *et al.* (2011)
Black Burn (3.35)	18.6 ± 16.0 – 32.2 ± 18.7	1.8 ± 0.7 – 5.5 ± 1.8	Dinsmore *et al.* (2010)
Garvald, Braes of Doune (4.5)	24.6		Grieve & Gilvear (2008)
Annett, Braes of Doune (3.5)	19.5		Grieve & Gilvear (2008)
Brocky Burn - upper (0.68)	17.4 – 21.4	0.9 – 2.1	Dawson *et al.* (2004)
Brocky Burn - middle (0.83)	16.2 – 20.6	0.82 – 1.9	Dawson *et al.* (2004)
Brocky Burn - lower (1.3)	14.2 – 19.3	0.59 – 2.8	Dawson *et al.* (2004)
Water of Charr (14.2)	16.9 – 26.2	2.0 – 17.5	Dawson *et al.* (2004)
Small Burn (0.41)	9.5 – 15.0	0.46 – 1.2	Dawson *et al.* (2004)
Burn of Waterhead (3.4)	8.3 – 16.6	0.44 – 1.6	Dawson *et al.* (2004)
Water of Dye - upper (24.6)	8.5 – 14.5	0.54 – 1.9	Dawson *et al.* (2004)
Water of Dye - lower (46.3)	10.3 – 17.8	0.59 – 2.6	Dawson *et al.* (2004)
Black Burn (3.35)	25.7 – 30.9		Billett *et al.* (2004)
Brocky Burn (1.3)	16.9	1.9	Dawson *et al.* (2002)
River Don, Parkhill (1273)	1.8 ± 1.0	0.53 ± 0.4	Hope *et al.* (1997a)
River Dee, Park Bridge (1844)	2.2 ± 1.2	0.19 ± 0.12	Hope *et al.* (1997a)
Dionard (73)	7.0		Hope *et al.* (1997b)
Conon (962)	7.1		Hope *et al.* (1997b)
Thurso (413)	8.8		Hope *et al.* (1997b)
Halladale (205)	10.3		Hope *et al.* (1997b)
Stag Burn (2.4)	3.44		Dawson *et al.* (1995)
England			
Moor House (11.4)	10.3 – 21.8	7.0 – 22.4	Worrall *et al.* (2009)
Moor House (11.4)	0.7 – 6.02		Gibson *et al.* (2009)
Upper North Grain (0.38)	18.5	74.0	Pawson *et al.* (2008)
Cottage Hill Sike (0.2)	6.1 – 7.1		Clark *et al.* (2007)
Upper North Grain (0.38)	10.8	77.3	Evans *et al.* (2006)
Rough Sike (0.83)	9.4	17.7 – 45.0	Evans *et al.* (2006)
Moor House (11.4)	13.4 – 22.5		Worrall *et al.* (2006)
Moor House (11.4)	9.4 – 15.0	2.7 – 31.7	Worrall *et al.* (2003)
Wales			
Upper Hafren (0.93)	8.4 ± 3.8	2.7 ± 1.9	Dawson *et al.* (2002)
Afon Hafren (3.35)	3.57		Neal & Hill (1994)
Afon Hore (3.35)	2.58		Neal & Hill (1994)
South2-Hore (0.14)	2.12		Neal & Hill (1994)
Afon Cyff (0.04)	5.4	0.88	Reynolds (1986)

5.4.1.2. Annual Differences in DOC and TOC Exports

Preliminary TOC export estimates for the Whitelee catchments, calculated for one calendar year running from 3rd July 2006 to June 2007, ranged from 11.2 to 25.5 g C m^{-2} yr^{-1} (Waldron *et al.,* 2009). The latest maximum annual TOC export estimate (44.9 g C m^{-2} yr^{-1}, catchment 13, 2008-2009) is approximately double the TOC export estimate for the same catchment (23.1 g C m^{-2} yr^{-1}, catchment 13) calculated by Waldron *et al.* (2009). This difference in export estimates is likely to be due to the method used to estimate the flow component of the calculation. The preliminary estimates of TOC export from Waldron *et al.* (2009) were calculated using Q estimated by Method 1 (see Chapter 5.2.1) therefore are likely to be less representative as they were not based on direct measurements of Q. The latest estimates are greater because these estimates were calculated using Method 2 estimates of Q (see Chapter 5.2.2). A comparison between exports generated by the two methods used to estimate Q was performed on export data for the five catchments, 13, 14, 1632, 9D and 17U that were estimated using Q calculated by Method 2. Table 32 shows that, for example, catchments 13 had exports as much as 33 % greater using Method 2 to estimate Q rather than Method 1. The exports based on Method 2 to estimate Q are likely to be more representative as they were based on direct measurements of Q in the catchment.

Table 32. Comparison between exports generated by Method 1, scaling SEPA Q, and Method 2, using the relationship between SEPA Q and Isco Q, to estimate Q for the export calculations for the five catchments, 13, 14, 1632, 9D and 17U where Method 2 was used. The direction of the difference between the exports calculated using the two Q estimation methods is a summary of the trends observed for TOC, DOC, POC, TP, SRP and NO_3^- exports. The % difference is the average % difference for the catchments across the full range of years for TOC, DOC, POC, TP, SRP and NO_3^- exports. See Appendix 8 for the full data set for all five catchments.

Catchment	Method 2 > or < than Method 1	% difference
13	>	33
14	<	39
1632	>	22
9D	>	15
17U	<	10

Monitoring the catchments at Whitelee which have different amounts of disturbance enables the identification of disturbance effects on C exports. DOC exports are usually high immediately after disturbance (Hope *et al.,* 1994), although variable results have been observed in other catchments. Clear-felling has been reported to produce little change in DOC export (McDowell and Likens, 1988), a slight increase in DOC export

(Hobbie and Likens, 1973; Moore and Jackson, 1989) and also reduced DOC exports (Meyer and Tate, 1983). DOC exports have been reported to be lowest in undisturbed catchments and highest in catchments which had been clear-felled (Moore and Jackson, 1989). There are no clear inter-catchment differences between the Whitelee catchments, therefore at sampling points outwith the immediate zone of disturbance, there is no discernable impact on DOC export related to windfarm-related disturbance.

Annual TOC and DOC export from the Whitelee catchments were calculated for only four and three years respectively; consequently any comparison to long-term trends in DOC export (*c.f.* Monteith *et al.,* 2007) is not possible. However, this length of record does allow annual comparisons. There was no clear trend in the annual TOC exports but one was apparent in the annual DOC exports, with the greatest exports for all catchments occurring during 2008-2009. These greatest exports are likely to be due to annual hydrological variability and a function of high Q occurring when DOC is available for flushing from catchment soils. The total volume of half-hourly Q at SEPA Newmilns and the total annual rainfall were the greatest during 2006-2007 (see Table 19 and Table 20, Chapter 4.2) and there were 10 high flow events with a probability of occurrence of ≤ 0.1 % (see Figure 27, Chapter 4.2.1), with the largest occurring in February and December. Although the highest annual flow volume and rainfall occurred in 2006-2007, it is hypothesised that it did not result in the greatest TOC export because the highest flows occurred in months when DOC availability is low in catchment soils. During 2008-2009 there were six events with a probability of occurrence of 0.1 %, with two during October 2008, including the event with the greatest Q (85 $m^3 s^{-1}$) recorded for the duration of the research, occurring when there was high DOC availability in UK upland peat catchments (Naden and McDonald, 1989; Cummins and Farrell, 2003b; Billett *et al.,* 2004; Worrall *et al.,* 2006; Clark *et al.,* 2007; Dawson *et al.,* 2008) which may account for the highest DOC exports occurring in this year for all catchments.

In 2009-2010 there was no windfarm-related disturbance, which could explain why the exports of TOC and DOC were lower than for the previous two years. However, a simpler interpretation is the lower volume of Q compared to previous years. The annual Q volume at SEPA Newmilns in 2009-2010 was around three quarters of the annual Q volumes for the three previous years (see Table 19, Chapter 4.2) with the maximum Q less than half the maximum recorded in the previous year and the annual rainfall totals (Table 20, Chapter 4.2) were lower for 2009-2010 compared to the other years. Although unable to confidently determine a relationship based on three years worth of data, when rainfall is plotted against DOC export (Figure 62) the general trend is for DOC export to be greater with greater rainfall, the same as the relationship observed in Clark *et al.,* (2007) for the Cottage Hill Sike catchment.

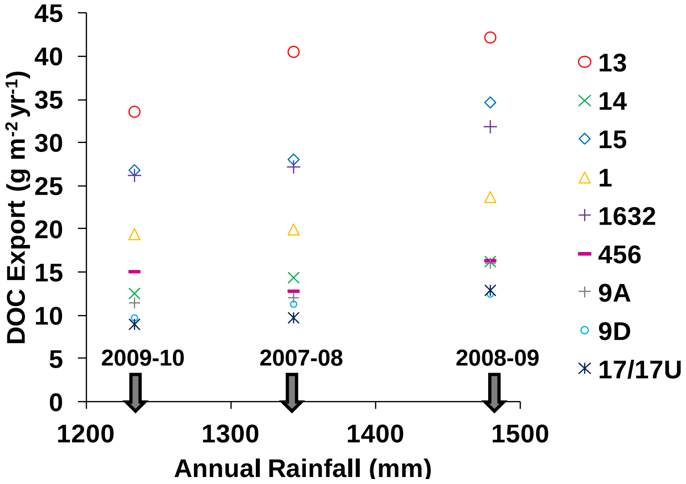


Figure 62. Rainfall and DOC export for the Whitelee catchments, with the total rainfall data from the three SEPA tipping bucket rainfall gauges nearest to the Whitelee area averaged to give approximate annual rainfall across the catchments.

The TOC and DOC export data from Whitelee suggests that percentage peat cover, seasonality in [DOC] and variability in Q have more impact on annual DOC exports than windfarm-related disturbance.

5.4.2. Streamwater POC Export

5.4.2.1. Inter-Catchment Differences in POC Exports

The C export estimates reported in this research are consistent with Waldron *et al.* (2009) in that DOC is the largest component of aquatic TOC export, with POC export representing a small percentage of TOC export, ~ 9 %, in the latest estimates for Whitelee. This figure is comparable to the other UK catchments (Table 31). For example, the POC export of the Rivers Dee and Don is ~ 10 % of the TOC export, and for the Black Burn POC export is ~ 5 % of the TOC export, occasionally 8 % in high flow (Billett *et al.,* 2004; Dinsmore *et al.,* 2010). There are only two exceptions to this. The first is the Water of Charr where POC is a higher percentage, 30 %, of TOC export (Dawson *et al.,* 2004). This catchment is > 80 % peatland and, due to its larger catchment size (14.2 km^2) compared to the surrounding catchments, there is enough stream energy to transport POC generated from the extensive areas of peat in the catchment, some of which are exposed and actively-eroding (Dawson *et al.,* 2004). The second exception is the Upper North Grain catchment in the Pennines, England. This catchment has 90 % peat coverage which is actively-eroding, where the majority (88 %) of aquatic C export is as POC (Evans *et al.,* 2006). As the percentage of TOC export which is POC is low (< 10 %) it suggests the Whitelee catchments are not actively-eroding to a large extent.

However, at Upper North Grain, 95 % of POC export occurred in only 8 % of the catchment monitoring time (Pawson *et al.,* 2008). Significant erosion of disturbed peatland may be occurring at Whitelee during high flow but, as the POC export estimates for Whitelee are based on a bi-monthly sampling routine, they may be underestimates since significant transfers of POC from the terrestrial to aquatic environments are likely during high flow events (Pawson *et al.,* 2008). The change in the nature of hydrological flow pathways, possible increases in quantity and power of Q and likely increases in [POC] source could explain why the greatest annual POC export occurred in catchment 13 during 2007-2008 co-incident with disturbance.

There was homogeneity in the response of POC exports between catchments for monthly and annual POC exports during the period of research but there were spikes in monthly POC export from catchment 456 (Figure 54). Annual POC exports were on average 12 % and 6 % of the TOC export in the N- and S-draining catchments respectively. These spikes and inter-catchment differences with drainage divide, as explained earlier in Chapter 4.4.1.2, are probably due to inputs from agricultural sources rather than the windfarm development.

5.4.2.2. Annual Differences in POC Exports

In the less agriculturally-dominated S-draining catchments, the timing of greatest annual POC export estimates over the three years was expected to be in the same year across the catchments, but this was not the case. The greatest annual POC export in the S-draining catchments occurred during 2008-2009 except for catchment 13 which had the greatest annual export in 2007-2008 (Figure 59), driven by the greatest monthly POC exports of the S-draining catchments for approximately six months during 2007-2008 (Figure 54). The different temporal pattern of POC export for catchment 13 is likely to be caused by windfarm-related disturbance, notably the close proximity of deforestation. Clear-felling has been reported to increases aquatic POC exports (Hope *et al.,* 1994). The sampling site in catchment 13 is 1 km from the area of extensive forestry operations; the nearest of all the sampling sites to an area of disturbance (see Chapter 6). Although the annual POC export of 2.95 g C m^{-2} yr^{-1} for catchment 13 during 2007-2008 was not the greatest annual POC export of all the Whitelee catchments, the change in annual trend indicates that windfarm-related forestry operations could be increasing [POC] in streamwater.

With a large area of catchment 13 subject to forestry operations (12 % of the catchment) during 2007-2008, Q could also have increased due to the increased accessibility of flow pathways caused by the removal of tree cover, (see Figure 42, Chapter 4.4.2.1), increasing the connectivity of terrestrial C stores to streamwaters. After the removal of vegetation cover in many peatlands, dominant overland and near-surface flow accelerate peat exposure, resulting in enhanced POC export (Holden *et al.,* 2007). The clear-felling and subsequent mulching will create a greater store of POC on the peat surface, for example, loosened soil particles and mulch material. With the reduction of vegetation cover there may be increased subsurface erosion of preferential pathways leading to greater connectivity between the peatland and streamwater, which may lead to unexpected aquatic carbon and nutrient losses in some catchments (Holden *et al.,* 2006a). With less interception of rainfall due to reduced tree cover, there is likely to be a greater quantity of overland flow, which has greater erosive power than other hydrological flow pathways, and may entrain loosened soil particles and mulch material, and thus POC, from the newly-bare peat surface which has often undergone cracking and increase transport of POC into the stream network (Dawson and Smith, 2007).

The extent and timing of disturbance in catchment 14 was similar, with clear-felling and mulching of 10 % of catchment 14 (see Chapter 4.4.2.1) conducted at the same time as in catchment 13. However, one of the headwater tributaries of catchment 14 drains into the Craigendunton reservoir upstream of the sample point and this may be acting as a buffer supporting sedimentation of POC and thus precluding a similar increase in annual POC export during 2007-2008 in catchment 14 to that observed in 13. Other than this slight change in pattern in response for catchment 13, the values for POC export from the Whitelee catchments show little evidence of increased erosion associated with windfarm-related disturbance.

5.4.3. Carbon Balance at Whitelee

Aquatic C exports are critical in terms of peatland C balance since aquatic C exports from undisturbed peatland rivers have been reported to equal C sequestration in the peatland (Schlesinger, 1990; Billett *et al.,* 2004). It was therefore important to compare the annual TOC export estimates for the Whitelee catchments to the C sequestration rate of the peatland. C sequestration rates of UK peatlands range between 5 and 50 g C m^{-2} yr^{-1} (Dawson and Smith, 2007). Auchencorth Moss, a 3.5 km^2 lowland ombotrophic raised bog 25 km east from Whitelee, has an estimated C sequestration rate of 25 g C m^{-2} yr^{-1} (Hargreaves *et al.,* 2003). ^{210}Pb dating of three peat cores collected from just outside the Whitelee field site have a C sequestration rate of 18.7 g C m^{-2} yr^{-1} (Waldron *et al.,* 2009).

If these two figures for C sequestration rate are representative of the Whitelee catchments, the streamwater DOC and TOC exports calculated in this research ranging from 26.3 to 42.3 g C m^{-2} yr^{-1} and 26.9 to 44.9 g C m^{-2} yr^{-1} respectively for S-draining catchments 13, 15, 1 and 1632, exceed the suggested C sequestration rates. These exports are likely to be underestimates due to the assumptions in the method of calculation; and as a full streamwater C budget including dissolved gases (CO_2 and CH_4) and inorganic C has not been constructed for the Whitelee catchments, streamwater C losses are likely to be even larger and the suggested sequestration rate exceeded even more. This means that in order for the Whitelee catchments to remain sequestering C, the minimum amount of C fixed has to equal the amount lost via the streamwater pathway plus 18 g C m^{-2} yr^{-1} against a background of increasing [DOC] and export in freshwaters across northern temperate latitudes (Monteith *et al.,* 2007).

5.4.4. Streamwater Phosphorus Exports

5.4.4.1. Inter-Catchment Differences in P Exports

The Whitelee data provides preliminary P exports for disturbed peatland catchments for which little data exists. The annual aquatic TP exports, in the Whitelee catchments, with the exception of catchment 13, were < 90 mg P m^{-2} yr^{-1} (Figure 60) revealing that these catchments contribute more than the most recent estimates of background P export (see Chapter 1.3.2). The greater export values from all Whitelee catchments are likely to be caused by the mixed land use, with, in addition to conifer forest plantation, stocking of dairy cattle on the improved pastures of the N-draining catchments and rough grazing of mainly sheep and occasional cattle on the areas of open moorland in the S-draining catchments. Livestock within a catchment are known to be potential sources of P (e.g. Heathwaite *et al.,* 2003). As discussed in Chapters 4, water quality at the sampling point in catchment 456 is thought to be impacted by episodic runoff from the farmyard of a nearby dairy farm (*c.f.* Edwards and Withers, 2008) and by the cattle having direct access to the stream. This can explain why N-draining catchment 456 often had the greatest monthly TP and SRP exports of the N-draining catchments for many consecutive months during 2009-2010, leading to the maximum SRP export in catchment 456 occurring during this year. The P export estimates from the agriculturally-dominated N-draining catchments estimates are, however, low compared to catchments where there are large areas of intensive, high input agriculture. Catchment P exports from agricultural land are typically in the range < 10 – 600 mg TP m^{-2} yr^{-1} (Ryden *et al.,* 1973; Haygarth and Jarvis, 1999; Kronvang *et al.,* 2007).

In catchment 13 the annual SRP exports exceed the maximum TP export for a catchment determined by Waldron *et al.* (2009). Monthly SRP and TP exports for catchment 13 did not follow the same temporal pattern as the other catchments (Figure 56 and Figure 57). The elevated exports of SRP and TP from catchment 13 from 2007 to 2009 are likely to have been caused by extensive windfarm-related forestry operations as explained in Chapter 4. TP exports of 206 mg P m^{-2} yr^{-1} from catchment 13 for the year when most clear-felling and mulching was conducted (2007-2008) were 41 times higher than TP export from unmanaged boreal forest catchments in Finland (5 mg TP m^{-2} yr^{-1}) (Kortelainen *et al.,* 2006). Exports from catchment 13 are more than double the TP exports from the more agriculturally influenced N-draining Whitelee catchments, although still less than diffuse TP export from three agriculturally-dominated catchments in the West of Scotland, UK, which ranged from 394 – 559 mg TP m^{-2} yr^{-1} (Hooda *et al.,* 2000). Even in 2009-2010, when there is evidence in catchment 13 of the elevated [P] decreasing (see Figure 33 and Figure 34, Chapter 4.3.2), TP and SRP exports in this year from catchment 13 are comparable to the maximum exports of TP and SRP in the other catchments for the 4-year study period (Figure 60).

Many studies have reported increases in [P] due to clear-felling (e.g. Lebo and Herrmann, 1994; Ahtiainen and Huttunen, 1999; Ensign and Mallin, 2001; Nisbet, 2001; Cummins and Farrell, 2003b; Feller 2005) but few have presented P export estimates. For an area of forested blanket peat in Co. Mayo, Ireland, estimated monthly total reactive phosphorus (TRP) exports from the undisturbed forested upstream part of a catchment (0.72 km^2) and the harvested downstream area of the same catchment (0.11 km^2) were 0.08 – 1.87 mg P m^{-2} and 0.09 – 5.73 mg P m^{-2}, respectively (Rodgers *et al.,* 2008). Annual TRP exports from the harvested part of the catchment at 224 mg P m^{-2} yr^{-1} were an order of magnitude higher than from the undisturbed area at 20 mg P m^{-2} yr^{-1}. In a clear-felled catchment in Burrishoole, clear-felling on peat was observed similarly to increase TRP export in streamwater, with sustained impact for four years (Rodgers *et al.*, 2010). This is similar to the timescale of increased exports observed at Whitelee. At Burrishoole, in the second year alone after clear-felling, 230 mg TRP m^{-2} yr^{-1} was exported from a 0.25 km^2 catchment, with up to 515 mg TRP m^{-2} exported from the catchment into streamwater in the first three years following harvesting. Although the TRP exports from this study in Ireland are expected to be less than the Whitelee TP exports because the TP exports also include the fraction of unreactive phosphorus (see Figure 3, Chapter 1.3.2), the order of magnitude of the estimated TRP exports is similar to the TP export from catchment 13, the most impacted of the Whitelee catchments, which over the four years of this study exported an estimated 530 mg P m^{-2}. Sources of TP in catchment 13 related to deforestation could be the residual rock phosphate fertiliser used to establish and maintain the tree coupe in the 1960s and loosened soil particles and mulch material in runoff from the newly-exposed soils (Forestry Commission, 2003). Another source of SRP in catchment 13 is likely to be from the breakdown of the mulched brash mat (Moffat *et al.,* 2006) which is known to increase P leaching over 12 to 18 months (Forestry Commission, 2003).

5.4.4.2. Annual Differences in P Exports

The greatest catchment annual DOC and POC exports generally occurred in 2008-2009 but any annual differences in the P exports are less clear. The greatest annual TP exports generally occurred in 2007-2008 and in the S-draining catchments the maximum SRP export occurred in hydrologic year 2008-2009 (Figure 60). As SRP and C exports have the same annual trend in the S-draining catchments this suggests that they share a similar source and/or flow pathways. C exports are thought to be strongly influenced by hydrology (see Chapter 5.4.1.2) and, since the greatest export of SRP occurred during the wettest of the years studied, this indicates that SRP exports are also strongly influenced by hydrology. The greater transfer of SRP from the catchment to the streamwater during this wetter year is likely to be caused by a higher degree of hydrological connectivity in which there would have more linked soil flow pathways, over a range of scales from micropores to peatland piping (Holden *et al.,* 2006b) and over a longer period of time for transfer of water containing high [SRP] from the terrestrial system to the stream network. The greatest SRP exports were seen during 2008-2009, a combination of an available source of P and the greatest connectivity due to being the wettest year of the research period.

In addition P is likely to be transported during high flow events (Jordan *et al.,* 2007, Stutter *et al.,* 2008a,b) of which there were several during 2008-2009, with four during October 2008 at the end of the growing season when there is less terrestrial P uptake and more available P to be washed in-stream. Waldron *et al.* (2009) found statistically significant positive linear relationships between [SRP] and [DOC] in the Whitelee catchments and hypothesised that if catchment SRP and C exports are derived from the same source, or share similar export pathways, then the concentrations will be positively correlated; and if they are derived from different source or share different export pathways, a positive correlation will not exist. This more recent research observed similar annual trends in SRP and C exports and therefore supports the hypothesis in Waldron *et al.* (2009) that the SRP source is closely linked to the C source and/or they share the same export mechanism pathways.

The greatest TP exports from Whitelee occurred in 2007-2008, a year earlier than the greatest C and SRP exports which generally occurred in 2008-2009. This difference in annual patterns suggests that TP has a different mobilisation mechanism to SRP. SRP is most likely to be mobilised in wet periods in winter when limited biological uptake from the soil and the soil profile is wet so that there is a high degree of hydrological connectivity. Exports of particulate P, (TP - SRP), occur mainly during high flow events in surface runoff and sub-surface runoff (Withers and Jarvie, 2008) at any time of year when overland flow and erosion are most favoured. During 2007-2008 there was more TP available in the catchments due to windfarm-related forestry operations but over time less TP was available (see Figure 34, Chapter 4.3.2), and the greatest transfers expected with the highest flows during 2008-2009 were not observed.

The P exports from Whitelee are low compared, for example, to exports in wastewater from sewage treatment works (*c.f.* Bowes *et al.,* 2003) or runoff from a dairy farmyard (*c.f.* Edwards and Hooda, 2007). However, even the low level exports of P from Whitelee are still significant because streamwater draining peatland is naturally nutrient-poor, with biological activity usually P-limited (Forestry Commision, 2003), therefore even a small increase in exports can impact on streamwater quality. This can have implications for complying with the Water Framework Directive (2000) and its regulatory requirement to achieve “good” ecological status in a range of waterbodies by 2027.

5.4.5. Streamwater NO_3^- Exports

5.4.5.1. Inter-Catchment Differences in NO_3^- Exports

There are numerous studies of N hydrochemistry in streamwater. A few studies have considered NO_3^- in peatland streams (e.g. Chapman *et al.,* 2001; Lepistö *et al.,* 2001; Clark *et al.,* 2004; Kortelainen *et al.,* 2006; Lepistö *et al.,* 2006; Helliwell *et al.,* 2007a,b; Cundill *et al.,* 2007; Austnes *et al.,* 2010). A smaller number of studies have reported NO_3^- exports (e.g. Neal *et al.,* 2003; Mattsson *et al.,* 2005), and an even smaller number of studies report exports for disturbed peatland catchments (e.g. Waldron *et al.,* 2009).

There were three main temporal and spatial patterns in the Whitelee aquatic N export estimates. Firstly, there is a clear seasonal pattern in N export from all catchments in which the greatest NO_3^- exports occurred over the winter months, with summer minima (Figure 58). This seasonal pattern has been observed in many other UK catchments in terms of [NO_3^-]. For example, from analysis of data for 743 British rivers Betton *et al.* (1991) reported that 80 % exhibited maximum [NO_3^-] in the winter months. The same seasonal trend in [NO_3^-] has been reported in upland rivers in mid-Wales and throughout Scotland (Reynolds *et al.,* 1992; Chapman *et al.,* 2001; Whitehead *et al.,* 2004; Clark *et al.,* 2004; Helliwell *et al.,* 2007a,b) As discussed in Chapter 4.4.3, this is thought to be controlled by seasonal patterns in catchment biological activity with the growing season.

The second pattern is that there are clear inter-catchment differences in the magnitude of streamwater NO_3^- exports. S-draining catchments 13, 14 and 15 have a mean streamwater NO_3^- export over the 4 years of study of 0.14 g m^{-2} yr^{-1}. Given the low intensity of the agriculture in these catchments, streamwater [NO_3^-] are therefore low in these catchments hence the S-draining peatland-dominated catchments 13, 14 and 15 have the lowest exports. Similar magnitudes of annual NO_3^- exports have been reported from a blanket peat catchment, Moor House, Pennines, UK, of 0.03-0.21 g m^{-2} yr^{-1} (Adamson *et al*., 1998) and a mean of 0.13 g m^{-2} yr^{-1} for Finnish catchments of mainly forestry, peatland and lakes (Mattsson *et al*., 2005). In a study of Finnish catchments retention of NO_3^- within the catchments was observed to be high in northern N-limited forest ecosystems and even higher in peatlands. Consequently [NO_3^-] in peatland waters is low (Lepistö *et al.,* 2001).

S-draining catchments 1 and 1632 have a mean streamwater NO_3^- export over the 4 years of 0.33 g m^{-2} yr^{-1}, more than double that of the other S-draining catchments. N-draining catchments 456, 9A, 9D and 17/17U have an even greater mean NO_3^- export over the 4 years of 1.07 g m^{-2} yr^{-1}. Catchments 1 and 1632 are also peatland-dominated but have larger areas and therefore the length of stream to sampling point is much longer, increasing the opportunity for NO_3^- input to streamwater. These two catchments also have larger areas of pastures with sheep grazing and catchment 1 has the most settlement of all the S-draining catchments, both potential sources of NO_3^- inputs. The N-draining catchments only have peatland in their upper reaches, thus so much larger proportions of the catchment areas comprise improved pastures and the grazing of dairy cattle. The influence of this agricultural activity is evident in the greater NO_3^- exports.

The inter-catchment differences in the streamwater NO_3^- exports from Whitelee are consistent with observations from Finnish catchments where agricultural activities resulted in an approximate tenfold N loss per unit area compared to forest land (Lepistö *et al.,* 2001). Furthermore, in streams draining four different upland regions of Scotland NO_3^- exports were found to be strongly correlated with the percentage of agricultural land in the catchment (Chapman *et al.,* 2001). Increases in NO_3^-export with increasing proportions of agricultural land have been reported for catchments in Finland (Lepistö *et al.,* 2001; Mattsson *et al.,* 2005) and the USA (Jordan *et al.,* 1997; Qualls and Richardson, 2003) probably related to application of fertilisers and higher biological productivity. The Whitelee estimates are lower than estimates of export from the Severn, Avon, Exe and Dart rivers in the southern UK, which have TON exports of 1.50, 1.94, 1.88 and 2.65 g m^{-2} yr^{-1} respectively (Russell *et al.,* 1998). Although TON exports will be higher than aquatic NO_3^- exports as they also include NO_2^-, this is likely to account only for a small fraction of TON export. Thus the higher exports for these four rivers compared to the Whitelee catchments reflects the greater number of septic tanks, greater areas of pasture and the likely application of fertiliser at a higher rate to maximise grazing potential and silage production.

5.4.5.2. Annual Differences in NO_3^- Exports

There is a general trend of decreasing streamwater NO_3^- exports over the 4 four years of research (Figure 61). By 2009-2010 there has been a ~ 50 % reduction in exports compared to 2006-2007 exports. Since the annual pattern of streamwater NO_3^- exports is different to that of the C and P exports, it appears that hydrology exerts less control on NO_3^- exports and suggests that sources of NO_3^- are limited in the Whitelee catchments, quickly taken up by peatland vegetation. An increase in rainfall may suppress nitrification and release of NO_3^- in the soil (Rodgers *et al.,* 1983) which could explain this decreasing trend but Table 20 in Chapter 4.2.3 shows no obvious increase in rainfall. A decreasing trend in flow during the study period may drive the decreasing NO_3^- exports because less NO_3^- would be flushed out of the soil, however, Figure 26 in Chapter 4.2.1 does not show a decreasing trend in flow across the 4 years. It is therefore hypothesised that a decrease in temperature may result in reduced nitrification and release of NO_3^- in the soil or decreasing atmospheric deposition of N may explain the general trend of decreasing streamwater NO_3^- exports rather than windfarm-related disturbance.

5.5. Summary of Streamwater Exports

There were no clear patterns in the annual TOC exports but the greatest annual DOC exports occurred in all catchments in 2008-2009 with the difference attributed to a greater number of high flow events occurring when there was a high DOC availability in the catchments. The greatest annual POC exports also occurred in 2008-2009 with the exception of catchment 13 where the greatest POC export occurred in 2007-2008. The different temporal pattern of POC export for catchment 13 was thought to be caused by the close proximity to extensive forestry operations.

Annual DOC and TOC exports from the S-draining catchments were generally higher than from the N-draining catchments, thought to be due to the greater proportion of peat-based soils in the S-draining catchments, with C exports from catchments 13, 15, 1 and 1632 for each hydrologic year of the four years of research exceeding the suggested C sequestration rate of 18 g C m^{-2} yr^{-1} for the Whitelee peatland.

There was no clear pattern in which year greatest P exports occurred, however, the greatest P exports were always from catchment 13, most likely to be caused by windfarm-related forestry operations. The greatest NO_3^- exports generally occurred in 2006-2007, with NO_3^- exports an order of magnitude higher in the N-draining catchments than in the S-draining, thought to be due to differences in land use since the N-draining catchments are dominated by agriculture.

6. Controls on Streamwater Concentration and Export

6.1. Chapter Outline

The main aim of this chapter is to investigate the controls on streamwater C, P and N concentration and export and to assess if there is an impact of windfarm-related disturbance on these in the Whitelee catchments or not. Although inferences have been made throughout Chapters 4 and 5 to explain the inter-catchment and annual differences in streamwater chemistry, an approach is required which tests these explanations. Windfarm construction began at Whitelee in November 2006. The pre-disturbance streamwater chemistry data determined by Waldron *et al.* (2009) are too short in length (five months) to perform a reliable and representative before-and-after impact comparison. Thus by comparing low- and maximum- disturbance phases in the time series presented in Chapter 4 it is possible to identify potential impacts of windfarm-related disturbance. To determine the most likely controls of C, P and N, multiple regression analysis was carried out using median concentration and export for DOC, POC, TOC, SRP, TP and NO_3^- for the two phases of the time series. These were regressed with the outputs of a geographic information system (GIS) analysis to describe the physiography of each catchment and to quantify the extent of windfarm-related disturbance. The rationale and methodology of a GIS-based approach are outlined at the beginning of this chapter, the multiple linear regression methodology and results are described next. The chapter concludes with an assessment of the impact of windfarm-related disturbance on streamwater chemistry and exports.

6.2. GIS Analysis of the Whitelee Catchments

6.2.1. Rationale for GIS-Based Approach

A GIS approach was used in order to quantify catchment characteristics with the potential to control streamwater chemistry and exports. This approach was chosen because GIS is adept at processing large volumes of spatial data and has the analysis tools to order information in new formats and to create high quality map outputs which make the different catchment characteristics and windfarm-related disturbance visually comprehensible. Although errors will be introduced through the use of the various software analysis tools, as there is no control catchment in this study, this approach allows catchments of varying types and scales of disturbance to be compared. A GIS-based approach to understand the biogeochemistry of rivers has been used effectively for investigating the complex effects of land use change on streamwater chemistry and to establish statistically relationships between streamwater chemistry and catchment characteristics which identify the most likely controls (e.g. Ballester *et al.,* 2003; Brandt *et al.,* 2004; Xie *et al.,* 2005; Davies and Neal, 2007; Yuan *et al.,* 2008). Furthermore, as GIS is already widely used in other windfarm-related planning decisions, a desk-based GIS approach was chosen also because it can be adopted readily by policy makers, windfarm developers, environmental regulators, environmental consultants and land managers involved with windfarm construction.

6.2.2. Catchment Physiography

The GIS analysis of the Whitelee catchments was split into two categories: (i) catchment physiography and (ii) windfarm-related disturbance. In order to distinguish windfarm-related disturbance, other catchment characteristics which may influence streamwater chemistry had to be quantified and in this section the rationale is outlined for which potential controls were included in the GIS analysis of the catchments.

6.2.2.1. Catchment Area and Maximum Flow Length to Sampling Point

Several studies have noted that catchment area can be an important control on streamwater chemistry, for example, it can influence the efficiency of sediment delivery (Walling, 1983); and, in catchments with mixed land use, [C] and [N] in streamwater were negatively correlated with catchment area, reflecting the retention and decomposition of dissolved organic matter in the catchment (Mattsson *et al.* 2005). In a large catchment, the flow paths from C, P and N sources within the catchment to the stream network are longer and consequently C, P and N have a greater opportunity to be exposed to various biogeochemical processes before reaching the stream. Moreover, in large catchments, large areas of the catchments are not closely connected to the stream network resulting in decreasing load compared to the near stream zone (Mattsson *et al.* 2005). Conversely, [NO_3^-] in an agriculturally-dominated catchment has been observed to increase as catchment area increases due to increasing source size (Edwards and Withers, 2008). However this was at the < 10 km^2 catchment scale compared to Mattsson *et al.* (2005) where the catchments were considerably larger, ranging from 10s to 10 000s km^2 in area.

C and P dynamics are controlled by catchment area with streamwater concentrations decreasing with increasing catchment area in catchments ranging from 10 to 10 000 km^2 in area, attributed to in-stream transformations of C and P (Russell *et al.,* 1998). In the case of DOC, DOC exports in catchments < 10 km^2 in area tend to decrease with increasing catchment size owing to dilution by groundwater which contains low [DOC] (Grieve, 1990). Even though there is variable evidence concerning catchment size as a control of streamwater chemistry, catchment area and maximum flow length to sample point are important descriptors to be included in the GIS analysis of the Whitelee catchments.

6.2.2.2. Soil Type and Hydrology of Soil Type

Many previous studies have found that elevated [C] and export were associated with a high proportion of peatlands within a catchment (e.g. Hope *et al.,* 1994; Hope *et al.,* 1997a,b; Dillon and Molot, 1997; Aitkenhead *et al.,* 1999; Eckhardt and Moore, 1990; Mattsson *et al.,* 2005; Xie *et al.,* 2005; Kortelainen *et al.,* 2006). [DOC] has been reported to be positively correlated to percentage peat and inversely related to the extent of mineral soils (Dawson *et al.,* 2011). Streamwater [DOC] has been found to increase downstream, reaching a maximum in the centre of the catchment, and then decreasing in the lower part of the catchment – a pattern which was linked to spatial changes in the soil C pool (Billett *et al.,* 2006). Sub-catchment analysis of the soil C pool and DOC export showed that the strong relationship between the percentage of peat coverage and streamwater DOC in the upper part of the catchment did not hold downstream, where freely draining mineral soils become spatially more important (Billett *et al.,* 2006). Further downstream, the relationship between organic C in the soil and the stream becomes weaker while other processes (for example, inputs from minerals soils and allochthonous within-stream processing of DOC) become more important (Billett *et al.,* 2006).

In studies of unmanaged and managed Finnish catchments statistically significant relationships between percentage peatland and P export were not observed (Kortelainen *et al.,* 2006). In contrast, larger sources of P from peatlands have been reported compared to mineral soils (Dillon and Molot, 1997) and thought to be due to the weak P adsorption capacity of peatland, so a high proportion of the P available within a catchment can be exported downstream (Nieminen and Jarva, 1996).

The significance of catchment properties, particularly soil type, in determining streamwater [NO_3^-] has been demonstrated for moorland catchments in northeast Scotland (Black *et al.,* 1993). Peatlands were least able to retain N, and, if the availability of inorganic N is in excess of that required for biological activity, there is significant export in streamwater from peatland-dominated areas (Black *et al.,* 1993). A negative relationship has been observed between [NO_3^-] and the percentage of peatland within a catchment (Helliwell *et al.,* 2007a). [NO_3^-] in catchments dominated by peat with its large C pool were observed to be much less than in catchments dominated by mineral soil with its smaller C pool (Helliwell *et al.,* 2007a).

As the percentage of different soil types in a catchment is an important factor recognised by many studies to influence C, P and N dynamics it was included in the GIS analysis of potential controls of streamwater chemistry in the Whitelee catchments. However, soil type alone does not give an indication of the flow pathways and connectivity between the terrestrial and aquatic ecosystems. Many studies of controls on streamwater chemistry have also included an indicator of the movement of water through the soil, for example, standard percentage runoff as an indication of soil hydrological response (Helliwell *et al.,* 2007a) or a hydrological soil group code which is a measure of the infiltration capacity of water in a soil (Yuan *et al.,* 2008). However, soil drainage characteristics are not always observed to be a significant control on [DOC] (Eckhardt and Moore, 1990). As there is the potential for the hydrology of soil types (HOST) to control streamwater chemistry at Whitelee, a classification of this property in UK soils was included in the GIS analysis of the catchments.

6.2.2.3. Land Use

Land use plays an important role in determining streamwater chemistry. Agricultural land has been shown to be an important control of [NO_3^-] and export, with N in surface waters increasing with the increasing percentage of agricultural land, related to the application of fertilisers (Jordan *et al.,* 1997; Russell *et al.,* 1998; Nedwell *et al.,* 2002; Xie *et al.,* 2005; Mattsson *et al.,* 2005; Helliwell *et al.,* 2007b). Both agriculture and forestry have been shown to contribute to N export, but agricultural lands have approximately a tenfold N loss per unit area than forested land (Lepistö *et al.,* 2001). Agriculturally-dominated areas within a catchment have been reported to be highly positively correlated to streamwater [NO_3^-] (Ferrier *et al.,* 2001; Davies and Neal, 2007) but weakly related to [SRP] (Davies and Neal, 2007) although significant positive relationships have been found to exist between grassland cover and [SRP] (Ferrier *et al.,* 2001). As well as percentage peatland, forestry is an important source of DOC within a catchment due to a greater amount of organic material within these catchments (Grieve, 1994). Since land use other than the windfarm development is important in controlling streamwater chemistry, land use was included in the GIS analysis of the Whitelee catchments.

6.2.2.4. Slope

Slope has been identified by many as an important control of streamwater chemistry because it influences the connectivity between the terrestrial and the aquatic ecosystems, with several studies using mean slope angle to describe the topography of the catchment. Catchment topography exerts an important control on N and P dynamics and on particulate transport through its effect on sediment conveyance and delivery (Russell *et al.,* 1998). Large areas of flat morphology will have a longer average water residence time in the catchment, whereas steep slopes result in a higher share of surface runoff with respect to total runoff. A significant negative relationship was observed between mean slope and both [TP] and export in Finnish catchments but a strong significant relationship was not reported with [PO_4^-] or export (Kortelainen *et al.,* 2006). A significant positive relationship was observed between mean slope and surface water [NO_3^-] (Helliwell *et al.,* 2007a,b) and greater proportions of steeper slopes in a catchment have been associated with enhanced NO_3^- leaching (Smart *et al.,* 2005). Catchment slope can strongly influence both DOC and POC exports (Ludwig *et al.,* 1996). [TOC] was observed to be correlated negatively with slope angle, with streamwater [TOC] in valley floor moorland catchments double the concentrations in streamwater draining moorland catchments with steeper slopes (Grieve and Marsden, 2001). However, slope is not always an influential control on streamwater [DOC] (Eckhardt and Moore, 1990; Ballester *et al.,* 2003). For these reasons it was decided that slope should be included in the GIS analysis of the Whitelee catchments.

6.2.3. GIS Analysis Methodology

This section outlines the methodology for the GIS analysis of the Whitelee catchments using ESRI® ArcGIS™ 9.2 software. The GIS analysis output files named throughout the following sections are in italics for clarity. Appendix 9 contains tables summarising raw and derived GIS data files and includes information on file type and a description of the file contents.

6.2.3.1. Catchment Physiography

6.2.3.1.1. Catchment Area and Flow Length to Sampling Point

The first step in the GIS analysis of the Whitelee field site was to delineate the catchment boundaries and to establish the catchment areas and maximum flow length of stream to sampling point. This involved several stages. The elevation data of the area in the form of OS Land-Form PROFILE^{TM} profile digital terrain model (DTM) tiles at 1:10,000 scale was downloaded from www.edina.ac.uk/digimap. The downloaded data tiles were imported into ArcMap™ through data conversion from NTF files to ASCII format. The tiles were merged using the data management tool 'raster mosaic' to create the layer *dtmraster*. In order to use the spatial analyst hydrology tools on the *dtmraster* layer, a hydrologically correct topographic surface needed to be created. The 'fill' tool was used to fill the surface sinks in the digital terrain model input layer and to prepare a layer, *dtmfill*, for surface analysis. The spatial analyst hydrology tools were used to analyse this new hydrologically correct layer.

The next step in the surface hydrology analysis of the Whitelee area was to determine the direction of flow through each cell. The 'flow direction' tool indentifies the flow direction of a cell by comparing its elevation to that of its eight neighbours. The output from this, *flowdirofdtm*, was put into the 'flow accumulation' tool to calculate for every cell the amount of water which flows into the cell from all the uphill cells which drain through it. This produced the *flowaccum* dataset and the high value cells in this output were considered to be in a stream. The symbology was manipulated to determine the flow value for generating a stream network which resembled that on a 1:25,000 scale map of the area. From this, the set null function was used to make a raster stream network output, *strmnet*.

The 'stream link' tool was used to give each stream segment in the previous output a unique ID in a new layer called *strmlnk*. There were many short segments in this layer which did not connect with other segments, so the surface hydrology tools and map algebra processing were used to remove stream segments of 5 cells or less. The 'stream order' tool was run using the Strahler ordering method to assign stream order to each stream segment based on the number of upstream segments connected to it. The 'stream to feature' tool was used to convert the raster stream segments in the *strmorder* layer into line features in the *streamnetwork* layer. The 'region group' tool was used on the *streamnetwork* layer to assign unique basin identifiers to the streams, creating the *strmgrp* layer. The eight cell option was used to define the connectivity, so that the cells could also be connected by the corners as well as by their sides. To calculate the maximum accumulated flow within each stream region, the ‘zonal statistics’ tool was used on the *strmgrp* layer to define the region and the *flowaccum* layer to provide the summary values for each region. This created the zon*flowmax* layer.

A shapefile of grid references for the sample points, *GPSlocations*, was uploaded from a handheld GPS and, using the ‘identify’ tool, the elevation of each sample point was generated from the elevation data in the DTM added to the attributes of each sampling point. Using the *GPSlocations* file and the *flowaccum* layer, a separate point shapefile for each sampling location was created. This was named *WL#* (# indicates the ID number unique to each catchment). This point feature was then converted to raster, named *catchment#* and linked with *flowaccum* so that the ‘watershed’ tool could be used to delineate the catchment area, named *catch#*. This raster *catch#* was converted to a polygon feature, named *areacatch#.* The area of the catchment in km^2 was calculated using the ‘calculate geometry’ tool and added to the attribute table of the catchment area. The maximum possible stream flow length to the sampling point in km was calculated using the ‘flow length’ tool in the hydrology spatial analyst toolbox and added to the attribute table, as was the grid co-ordinate of the sampling point. A summary of catchment data for each of the Whitelee catchments is provided in the sampling point locations and catchment characteristics description in Table 7 in Chapter 2.4.1.

6.2.3.1.2. Soil Type and Hydrology of Soil Type

A shapefile, *WhiteleeSoil*, of the soil type and HOST data (*c.f.* Boorman *et al.,* 1995) was purchased from the Macaulay Land Use Research Institute (MLURI, now the James Hutton Institute). HOST is a hydrologically-based classification of UK soils where soils are assigned to a class on the basis of their physical properties with reference to the hydrogeology of the substrate. Using the ‘clip’ tool in the extract function of the ArcMap™ analysis tools on the *WhiteleeSoil* shapefile with the catchment areas generated in Chapter 6.2.3.1.1 as the clip feature, an output of a file with the geometry of the catchment area and the attributes for that shape was created from the input file, following the method used by Cundill *et al.* (2007). From this, the soil type and HOST were determined for each catchment. By exporting this attribute table for the catchment into Microsoft® Excel, the percentage of each soil type and HOST expressed relative to the catchment area was calculated for each catchment. The soil types found at Whitelee are alluvial, humic gleys, non-calcareous gleys, peat, blanket peat (defined by MLURI as peat > 1m deep), peaty gleys, peaty podzols, humus-iron podzols, and brown forest soils (see Table 33 and Figure 7, Chapter 2.2). Of the 29 HOST classes, the Whitelee catchments contain 12 HOST classes (Table 34). There are predominant HOST classes at Whitelee – 15, 24 and 29 – all poorly draining. A description of soil type and hydrological conditions of soil type in each HOST class is included in Table 35. The percentage of HOST classes associated with each soil type at Whitelee are shown in Table 36.

6.2.3.1.3. Land Use

The percentage of each land use expressed relative to the catchment area was generated for each catchment using the same procedure as Cundill *et al.* (2007). The catchment area was the clip feature and the input was a shapefile of the Whitelee area of the Coordination of Information on the Environment (CORINE) Land Cover Map for 2000 at the scale of 1:100,000, called *LandUse.* This was the most up-to-date licensed data for land use available through the University of Glasgow. The data was produced jointly by the European Commission and the Member States, which record 44 land use classes. Of the 44 land use classes, 11 are recorded in the Whitelee catchments, the main ones being coniferous forest, natural grassland, pastures and peatbog (Table 37).

6.2.3.1.4. Slope Analysis

Using the DTM layer, *dtmraster*, mean and maximum slopes were calculated in degrees for each of the Whitelee catchments utilising the ‘extract by mask’ tool in the extraction menu of the spatial analysis tools, with the catchment area as the input feature mask to produce a file named *slope#*. The mean and standard deviation, and maximum slopes in each catchment were determined from the statistics table in the ‘layer properties’ window. A common slope category system was created for all the catchments using the ‘reclassify’ tool in the analyst tools, and a layer file called *Reclass of slope #* was created for each catchment. The attribute table of number of cells for each catchment was exported to Microsoft® Excel and the count of each slope angle in each category, expressed as a percentage relative to the number of cells in the catchment, was calculated (Table 38).

Table 33. Soil type in each catchment expressed as a % relative to catchment area. Soils data was provided by the Macaulay Land Use Research Institute. Blanket peat is defined by MLURI as peat > 1m deep.

Catchment	Alluvial	Humic gley	Non-calcareous gley	Blanket Peat	Peat	Peaty gley	Peaty podzol	Humus-iron podzol	Brown forest soil	Made-up/ Built-up/ Quarries/ Complex	Lochs/ reservoirs
13	1.9	7.4	6.2		73.5	8.4	2.6				
14	4.9	3.0	11.4		65.4	4.3	5.2		0.1	0.9	4.8
15	4.2	3.8	1.1		78.5	11.0	0.6		0.4	0.4	
1	1.5	9.3	17.7	0.8	50.2	10.7	0.4		8.2	0.9	
1632		0.7	12.4	42.7	23.7	14.6	0.6		4.5	0.3	
456	2.6		72.6	17.6	14.4	2.6			0.9	0.8	
9A	4.3	9.0	5.6		42.8	14.7	3.5		13.0		
9D	1.3	16.9	5.1		23.9	11.2	7.9	2.1	23.0		4.3
17	3.9	8.5	35.9	1.1	0.8		0.4	0.6	1.9	1.2	1.3
17U	1.8	4.9	58.4	15.1	19.6	27.5	3.2		13.4	0.5	

Table 34. Summary of HOST classes in each catchment expressed as a % relative to catchment area . HOST data was provided by the Macaulay Land Use Research Institute. ND indicates no data is available. See Table 35 for a description of each HOST class.

Catchment	5	8	9	10	12	14	15	17	18	24	26	29	ND
13				1.9			11.0			13.6		73.5	
14				4.9			8.4	0.1		14.4	1.1	65.4	5.7
15	0.4			4.2			11.5			5.0		78.5	0.4
1	7.5			2.0		0.7	10.0	0.8		25.8	1.1	50.9	0.9
1632					10.8		15.2	4.5		13.1		55.6	0.3
456	0.4	2.0	0.5		14.4		2.6	0.1	0.4	61.2		17.6	0.8
9A	9.0			4.3		1.3	18.3	3.9		20.4		42.8	
9D	9.8			1.3		11.8	19.1	15.4		14.5		23.9	4.3
17	5.5		0.7	3.2		4.1	14.4	8.6		40.4		20.6	2.5
17U			1.8		0.8		16.7	1.9		63.2		15.1	0.5

Table 35. Description of soil type and hydrological conditions in soil associated with the 12 HOST classes occurring in the Whitelee catchments. Information sourced from http://www.macaulay.ac.uk/host/

HOST Class	Soil Type	Hydrological Conditions
5	humus-iron podzols, brown earths with brown calcareous soils, alluvial sands and gravel	freely drained
8	immature loamy textured alluvial soils	free & imperfectly drained
9	alluvial soils	imperfect to poorly drained
10	alluvial soils and mineral groundwater gleys	poorly drained
12	predominantly peaty gleys, peaty alluvial soils and peaty podzols	poorly drained
14	mineral non-calcareous gleys and humic gleys	poorly drained
15	peaty gley, peaty podzols and peaty rankers on porous rock types	poorly drained
17	brown earths, humus-iron podzols, some brown magnesian soils, sub- and alpine soils	freely drained
18	mineral non-calcareous gley soils	imperfectly drained
24	non-calcareous mineral gleys	imperfect to poorly drained
26	peaty gleys	poorly drained
29	blanket peats (> 1 m deep)	poorly drained

Table 36. % HOST classes associated with each soil type at Whitelee.

	HOST Classes											
Soil Type	5	8	9	10	12	14	15	17	18	24	26	29
Alluvial		5	21	74								
Humic gley				4		12				84		
Non-calcareous gley						2				98		
Blanket peat												100
Peat					37							63
Peaty gley							94				6	
Peaty podzol							100					
Humus-iron podzol								100				
Brown forest	49							49	2			

Table 37. Land use coverage in each catchment from the CORINE Land Cover Map for 2000 expressed as a % relative to catchment area. The forested land use class is the % of the catchment forested before windfarm development from the CORINE Land Cover Map for 2000. *The deforested land use class is due to the windfarm development and is from data provided by the Forestry Commission.

Catchment	Peatbog	Coniferous Forest		Moors & Heath	Natural Grassland	Pasture	Transitional Forest	Agricultural Natural Vegetation	Sport & Leisure	Construction	Urban	Waterbody
		Forested	*Deforested									
13	25.8		12.2		52.4	10.9						
14	25.2	21.4	10.3	8.3	15.1	16.1						3.7
15	7.6	73.8	3.5		3.5	7.1	4.5					
1	6.9	39.5	10.7		1.1	31.7	9.6				0.4	
1632	7.0	45.2	13.2		12.4	18.0	4.2					
456	3.9	4.0	0.8	5.0	2.5	72.3	6.0	3.9	1.7			
9A	8.3	53.5	0.5	2.7	2.7	32.3						
9D	1.3	4.6	2.3	5.9	45.0	36.6						4.3
17	2.6	18.3	2.0	2.3	16.4	55.6				0.8	0.7	1.3
17U	1.5	20.4	3.9	0.1	7.8	64.8				0.5		

Table 38. Slope statistics for each catchment expressed as a % relative to catchment area. Units for slope are degrees.

Catchment	0 - 2.5	2.6 - 5.0	5.1 - 10.0	10.1 - 15	15.1 - 20	20.1 - 25	25.1 - 30	30 +	mean	maximum
13	54.5	34.4	9.0	1.3	0.6	0.2	0.1	0.0	3.1 ± 2.5	35.6
14	56.5	28.9	10.9	2.5	0.7	0.2	0.1	0.0	3.0 ± 3.0	39.3
15	45.3	31.2	17.5	4.4	1.2	0.3	0.1	0.0	3.1 ± 2.6	37.7
1	37.9	34.1	19.1	4.9	2.4	1.0	0.4	0.2	4.3 ± 4.5	59.6
1632	48.7	36.9	11.7	2.1	0.5	0.1	0.0	0.0	2.9 ± 2.5	38.5
456	54.6	35.4	9.4	0.5	0.1	0.0	0.0	0.0	2.9 ± 2.4	39.2
9A	27.9	34.2	26.6	7.0	3.1	0.8	0.2	0.1	5.1 ± 4.4	44.8
9D	28.8	37.9	25.8	5.7	1.4	0.4	0.1	0.0	5.0 ± 4.2	40.0
17	32.5	40.0	21.7	4.0	1.3	0.3	0.1	0.0	4.4 ± 3.8	44.8
17U	34.6	44.5	18.6	1.8	0.4	0.1	0.0	0.0	3.8 ± 2.7	31.2

6.2.3.2. Windfarm-Related Disturbance

Windfarm construction is not solely about erecting turbines; a major part of the impact can be associated with other windfarm infrastructure, such as borrow pits and access tracks, and felling of forest. Therefore the location and extent of such activities must be known in order to assess for impacts on streamwater chemistry and exports. An overview of windfarm-related disturbance and associated deforestation in the Whitelee catchments is provided in Table 7 in Chapter 2.4.1.

6.2.3.2.1. Turbine and Borrow Pit Locations

Grid co-ordinates of the as-built (rather than proposed) locations of turbine bases obtained from Scottish Power Renewables were inputted as a DBF file and from this a shapefile of the turbine locations was created, called *TurbineLocations*. Where available, the mean peat depth before construction was calculated from survey data at 10 m intervals at each turbine location obtained from Scottish Power Renewables and was added to the attribute table of the turbine locations. The locations of the borrow pits were also digitised using the ‘trace’ tool from geo-referenced DWG files received from Scottish Power Renewables and a shapefile *BorrowPits* was created.

6.2.3.2.2. Windfarm Access Tracks

The windfarm boundary was digitised from a geo-referenced DWG file received from Scottish Power Renewables using the ‘trace’ tool in ArcMap™, to give a shapefile called *DevelopmentBoundary*. Similarly, the access tracks were digitised from geo-referenced DWG files received from Scottish Power Renewables using the ‘trace’ tool in ArcMap™. The road polylines were changed from dashed road centrelines to continuous lines to give a shapefile for all the Whitelee catchments called *AccessTracks*. The access tracks in this shapefile are the road locations as-built rather than the proposed road layout from the EIS, since the proposed layout may have changed during construction due to difficult ground conditions. Using the ‘clip’ tool with the catchment area as the clip feature, data from the *AccessTracks* separate shapefiles were created for each catchment of the location of access tracks, *AccessTracks_#.* From this, the length of each road in each catchment in km was calculated using the ‘measure’ tool.

6.2.3.2.3. Deforestation

Shapefiles called *Forestry*, *ShortRotation* and *FelledAreasWindfarm* outlining forest management in the Whitelee catchments during the research period from June 2006 to September 2010 were received from the Forestry Commission. No spatial data was available regarding the extent of mulching in each catchment. The attribute table for *FelledAreasWindfarm* contained the year of clear-felling. *Forestry* was more up to date and spatially accurate than the coniferous forestry class in the CORINE Land Use data and the felling plans included in the Environmental Impact Statement (CRE Energy, 2002). The area of clear-fell in each catchment, *#deforest*, was determined using the 'clip' tool with the catchment area as the clip feature and the resulting attribute table was exported to Microsoft® Excel where the percentage of the catchment deforested expressed relative to the catchment area was calculated (Table 37). A detailed summary of the forestry operations carried out in each of the Whitelee catchments is provided in Table 5 in Chapter 2.4.1 and Figure 6 in Chapter 2.2.

6.2.3.2.4. Distance to Windfarm-Related Disturbance

The 'raster calculator' in the map algebra tools of the spatial analyst toolbox was used to measure the stream distance from the sampling point to the nearest windfarm-related disturbance in each catchment.

6.3. Multiple Linear Regression

To identify the catchment characteristics important in the release of C, P and N, two multiple linear regression analyses were carried out in order to model the controls on both streamwater concentration and export. The relationship of both concentration and export with catchment physiography and windfarm-related disturbance was compared not only to gain information about potential sources of C, P and N but also about the impact of hydrological pathways on C, P and N movement within the catchment. Multiple linear regression analysis was chosen because it is an approach which has been successfully employed in other studies (e.g. Ballester *et al.,* 2003; Mattsson *et al.,* 2005; Billett *et al.,* 2006; Helliwell *et al.,* 2007a) to determine the correlation between catchment characteristics and streamwater chemistry responses. A best subsets approach to regression analysis was carried out using Minitab® v16 statistical software.

6.3.1. Multiple Linear Regression Inputs

6.3.1.1. Dependent Variable

As the pre-disturbance streamwater chemistry data determined by Waldron *et al.* (2009) was for too short a time period to perform a direct before-and-after impact comparison, two regression analyses were carried out, for a low- and a maximum- disturbance phase. The low-disturbance phase was from June 2006 to August 2007 (personal communication with Scottish Power Renewables and Forestry Commission), and the maximum-disturbance phase was from September 2007 until May 2009 when infrastructure construction and windfarm-related deforestation was completed. In the case of DOC and POC time series, concentration and export data for each catchment exist only for the maximum-disturbance phase so no comparison of controls on streamwater chemistry can be made to the low-disturbance phase. Catchments 17 and 17U were not included in the regression analysis because the time series were shorter in these catchments (see Chapter 2.4).

6.3.1.1.1. Dependent Variable - Concentration

The dependent variable used for the regressions with [DOC], [POC], [TOC], [SRP], [TP] and [NO_3^-] were median concentrations calculated for each catchment for both the low- and maximum-disturbance phases (see Appendix 10). The number of sampling occasions used to calculate median concentrations was 23 in the low-disturbance phase and 34 in the maximum-disturbance phase. Median values for concentration were chosen as they are influenced less by extremes in the data than mean values. Median values have been used as the dependent variable in other multiple linear regression-based studies to identify the controls on streamwater chemistry (e.g. Xie *et al.,* 2005; Kortelainen *et al.,* 2006).

6.3.1.1.2. Dependent Variable - Export

The dependent variable for the regressions with DOC, POC, TOC, SRP, TP and NO_3^- exports was the median value of monthly exports for the duration of each phase (see Appendix 10). The median value for the low-disturbance phase was calculated from 14 months of data and for the maximum-disturbance phase from 21 months of data.

6.3.1.2. Potential Controls on Streamwater Concentrations and Exports

To avoid the duplication of data through the inter-relationships between potential controls, to reduce the number of potential controls and to select the most important potential controls for the regression analysis, the potential controls were checked for multicollinearity. This was done by plotting all the potential controls in a correlation matrix. A highly significant correlation was found between catchment area and stream flow length ($r = 0.872$, $P = 0.005$) which is expected as the greater the catchment area the longer the flow path of the river. It was therefore decided to divide the catchment area by the length of the river in each catchment because of this multicollinearity in order to provide a variable which represents the connectivity within the catchment and the potential for in-stream cycling.

There was a highly significant positive correlation between catchment area and access track length ($r = 0.902$, $P = 0.002$). This is not surprising as the greater the catchment area, the greater the number of turbines which could be sited in the catchment and consequently the greater the length of access track required. There was also a highly significant positive correlation between the access track length and the number of turbines ($r = 0.949$, $P < 0.001$). Therefore only the length of the access track was used in the regression as it is also a proxy for the number of turbines.

There were significant correlations between the soil type and the hydrology of soil type which were expected because HOST classes are assigned on the basis of soil physical properties (Table 32). As these correlations would result in the duplication of information, HOST classes rather than soil type were inputted into the regression. Many of the HOST classes covered < 2 % of a catchment area and were considered not to influence streamwater chemistry strongly enough to be included as a potential control. Due to the limited number of variables which can be inputted into the regression analysis, the three main HOST classes of the 12 HOST classes in the Whitelee catchments – classes 15, 24 and 29 – were chosen to feature in the regression. HOST classes 15 and 29 were grouped together to form one potential control. This was done on the basis that these two classes largely represent poorly-drained peat-based soils, whereas HOST class 24 represents imperfectly to poorly-drained non-calcareous mineral soils (Table 35). As HOST indirectly accounts for slope since soil formation and therefore soil type is strongly influenced by topography (Boorman *et al.,* 1995), slope was not included in the regression analysis.

The selection of the other potential controls inputted into the regression analysis was driven by the most likely controls hypothesised throughout Chapter 4 and 5 to explain the variation in streamwater chemistry observed at Whitelee, such as the proportion of peat-based soils, the area of pasture within a catchment and the extent of windfarm-related forestry operations.

The 11 CORINE land use classes present at Whitelee were simplified into two main land use potential controls: coniferous forestry and pasture. The percentage coniferous forestry potential control figures are different for the low- and maximum-disturbance phase since the maximum-disturbance phase takes into account the area of windfarm-related deforestation in each catchment. Peatbog is another land use class which is extensive at Whitelee and likely to influence streamwater chemistry. However as HOST class 29, which represents blanket peatland, was already included in the regression analysis the peatbog land use class was not used.

For the low-disturbance phase, five catchment physiography potential controls were selected to be inputted into the regression analysis (Table 39). Since the number of potential controls inputted into the regression cannot be greater than the number of observations – in this case the observations from eight catchments – (catchment 17U excluded), the five controls describing catchment physiography identified as influential for each parameter for the low-disturbance phase were inputted into the regression for the maximum-disturbance phase plus the three potential controls describing windfarm-related disturbance (Table 39). When the regressions were carried out the variance inflation factors, which quantify the severity of multicollinearity, were plotted as a final check and these were all < 3 for the regressions showing that multicollinearity was minimal.

Table 39. Overview of the potential controls inputted into multiple linear regressions with median values for each catchment of streamwater concentration and export as the dependent variables.

	Potential controls
Catchment physiography	Stream flow length per catchment area (km km^{-2}) % area HOST classes 15 and 29 % area HOST class 24 % coniferous forest (low- and max- disturbance) % pasture
Windfarm-related disturbance	% deforested access track length (km) Stream distance from sampling point to nearest disturbance (km)

6.3.2. Multiple Linear Regression Results

The results of the best subset regressions are presented individually for C, P and N in turn. The equation chosen for each parameter to describe the variation in streamwater concentration and in export was selected due to their high R^2 and low Mallows Cp value.

6.3.2.1. Carbon

The best fit equations for median [C] and export obtained by the regression analysis for both the low- and maximum- disturbance phases are shown in Table 40.

6.3.2.1.1. Concentration

The relationship between median [TOC] and the catchment characteristics for the low-disturbance phase was highly significant (R^2 = 99 %, P = 0.005) at the 95 % confidence level. Four catchment physiography controls model [TOC] before any windfarm-related impact on streamwater chemistry. The percentage of peat-based soil in a catchment was expected to exert a positive control on [TOC] (Hope *et al.,* 1994; Hope *et al.,* 1997a,b; Dillon and Molot, 1997; Aitkenhead *et al.,* 1999; Eckhardt and Moore, 1990; Mattsson *et al.,* 2005; Xie *et al.,* 2005; Kortelainen *et al.,* 2006), and the regression analysis indicated a positive relationship between [TOC] and HOST classes 15 and 29, which represent peat-rich soil types (blanket peat, peaty podzols, peaty gleys). This positive control is attributed to the size of the soil C pool (Dawson *et al.*, 2001a; Dawson *et al.*, 2004; Billett *et al.*, 2006; Dawson *et al.*, 2008, Dawson *et al.*, 2011).

The regression analysis identified that the percentage coniferous forest cover positively influenced [TOC] during the low-disturbance phase. In a study of one forested and two moorland catchments in southwest Scotland, the mean streamwater [DOC] of the catchment forested with Sitka spruce and lodgepole pine, the same species as the Whitelee forests, was observed to be twice that of the moorland catchments (Grieve, 1990). It has previously been demonstrated that plantation forestry on organic soils can alter DOC export in several ways by impacting on the thickness and nature of soil organic horizons (Miles, 1985) and influencing the proportion of water flowing through the different soil horizons with more water flowing through surface organic horizons and less at depth due to drainage associated with plantation forestry (Hornung and Newson, 1986).

Table 40. Best fit equations obtained by the regression analysis of median catchment [C] and exports during both the low- and maximum- disturbance phases. N = 8 catchments. Units for [C] are mg L^{-1}. Units for export are g C m^{-2} $month^{-1}$. The names of the controls are in brackets for clarity.

Concentration				
Disturb. Phase	**Parameter**	**Equation**	**R^2**	**P value**
Low	TOC	= - 43.8 - 18.2 (flow length per catchment area) + 1.01 (% HOST classes 15 and 29) + 0.20 (% coniferous forest) + 0.63 (% pastures)	99 %	0.005
Maximum	DOC	= 2.69 + 0.19 (% HOST classes 15 and 29) + 0.42 (% deforested)	78 %	0.022
	POC	= 0.77 + 0.02 (% HOST class 24) + 0.09 (% deforested) - 0.05 (access track length)	96 %	0.004
	TOC	= 24.2 - 24.0 (flow length per catchment area) + 0.18 (% HOST classes 15 and 29) + 2.02 (% deforested) - 1.47 (access track length)	87 %	0.110
Exports				
Disturb. Phase	**Parameter**	**Equation**	**R^2**	**P value**
Low	TOC	= 0.24 + 0.02 (% HOST classes 15 and 29) + 0.02 (% coniferous forest)	68 %	0.058
Maximum	DOC	= 1.84 + 0.02 (% coniferous forest) - 0.22 (distance to nearest disturbance)	90 %	0.003
	POC	= 0.33 - 0.22 (flow length per catchment area) + 0.001 (% HOST class 24) + 0.01 (% deforested) - 0.01 (access track length)	96 %	0.018
	TOC	= 0.35 + 0.02 (% HOST classes 15 and 29) + 0.01 (% coniferous forest)	64 %	0.076

There is a greater input of more mobile organic compounds to the soil from throughfall below a forest canopy (Malcolm and McCracken, 1968) and the development of a forest litter layer is likely to increase the production of DOC. Hence Sitka spruce forest has been shown to be associated with larger mean [DOC] in the underlying soil solution than beneath acid grassland vegetation (Reynolds *et al.,* 1988) and moorland (Grieve and Marsden, 2001). Establishment of coniferous forestry in the UK uplands typically requires drainage of highly organic soils which results in a lowering of the water table, causing increased decomposition rates due to increased aeration, and thereby reducing the potential for DOC retention within the soil (e.g. Holden *et al*., 2004; Worrall *et al*., 2004b). As [DOC] is the main component of [TOC] at Whitelee, streamwater [TOC] is expected to be driven by the controls on [DOC]. Thus these influences on source and flow pathways on DOC may explain why [TOC] and export in the catchment increases with a greater proportion of coniferous forestry.

The stream flow length per catchment area was also identified as a control on [TOC] for the low-disturbance phase, exerting a negative influence on [TOC], showing that the greater the stream density within the catchment, the lower the [TOC]. This control may be interpreted as the effect of residence time of water in the soil on [TOC]. The less well connected the catchment soil C store is to the river network (low stream density), the longer the residence time of the water in the soil and the greater the [TOC] due to more time for leaching of DOC from the soil.

The proportion of pasture within the catchment was also found to exert a positive control on [TOC] during the low-disturbance phase which was unexpected. Improved pastures typically contain less soil C than peatlands since soil conditions underlying pastoral lands are much less favourable for the accumulation of organic matter and therefore a negative relationship was expected between [TOC] and pasture. However, this unexpected positive control is likely to be driven by spikes in the [POC] time series in catchment 456 downstream of a dairy cattle farm (see Figure 31**,** Chapter 4.3.1.2).

The regression analyses for the maximum-disturbance phase show that significant relationships at the 95 % confidence level described the variation in [DOC] (R^2 = 78 %, P = 0.022) and [POC] (R^2 = 96 %, P = 0.004), but not for [TOC] (R^2 = 87 %, P = 0.110). As expected, peat-based HOST classes 15 and 29 exert a positive control on [DOC] due to the greater soil C pool of these two HOST classes. However, HOST class 24 soils (imperfectly and poorly drained non-calcareous mineral gleys) rather than HOST classes 15 and 29 exert a positive control on [POC]. Since the peat, and therefore soil C pool, from personal observation show no evidence of active erosion, HOST classes 15 and 29 were not expected to control [POC]. The positive relationship between the percentage of HOST class 24 soils and streamwater [POC] is likely to be due to the fact that HOST class 24 soils are more extensive in the agriculturally-dominated N-draining catchments (Table 30) so this control is also representing the effect of agricultural activity on [POC].

It was considered from the time series and harmonic regression analysis presented in Chapter 4.3.1 and 4.4, that, as well as the proportion of peat-based soils in a catchment controlling C dynamics, deforestation may result in an increase in streamwater [C] because this has been observed in other catchment studies (Hobbie and Likens, 1973; Cummins and Farrell, 2003a; Neal *et al.,* 2004; Neal *et al.,* 2005; Tetzlaff *et al.,* 2007). Indeed the regression analysis indicates that during the maximum-disturbance phase, there are positive relationships between the percentage of the catchment deforested and [DOC] and [POC]. These relationships are likely to be caused by increased brash and litter material and more favourable conditions for organic matter decomposition at the exposed soil surface provided by deforestation, creating a larger soil store of soluble and particulate C for mobilisation in streamwater.

It was expected that [POC] would be influenced by the area of the catchment which is pasture since spikes in the POC time series for the N-draining catchments suggested that the dominant pasture land use in these catchments influences POC loss (see Figure 31**,** Chapter 4.3.1.2). However, the regression analysis has not identified the percentage of pasture as a control of [POC] and this is likely to be due to the fact that HOST class 24 is more extensive in the agriculturally-dominated N-draining catchments. In addition to HOST class 24 and the proportion of the catchment deforested exerting positive controls on the variation in [POC] during the maximum-disturbance phase, [POC] is also controlled by a negative relationship with access track length. This is an unexpected relationship and is interpreted as evidence that the mitigation measures employed to minimise the impacts of activities on streamwater suspended sediment, such as settling ponds (Figure 36), alum block flocculation and forest drain blocking, have been effective in minimising POC reaching the stream network.

6.3.2.1.2. Export

The regression equations for median monthly export of TOC during the low-disturbance and maximum-disturbance phases had lower R^2 values (68 and 64 %, respectively) compared to the equations for [TOC] during these phases and were not significant at the 95 % confidence level (P = 0.058 and 0.076, respectively). Both equations indicated that the same controls, HOST classes 15 and 29 and coniferous forest, influence TOC export regardless of windfarm-related disturbance. These two positive controls were also identified as controls of [TOC] during the low-disturbance phase (see Chapter 6.3.2.1.1 for explanation).

A highly significant relationship at the 95 % confidence level (R^2 = 90 %, P = 0.003) describes the variation in DOC export during the maximum-disturbance phase. It was thought that deforestation would be positively related to DOC export as well as [DOC]. However, rather than the proportion of the catchment deforested controlling DOC export during the maximum-disturbance phase, the percentage of the catchment which was coniferous forest was found to be positively related to DOC export. A possible explanation for why the percentage deforested was not positively related to DOC export is that the increase in [DOC] in the Whitelee S-draining catchment 13 associated with deforestation was observed during the maximum phase of the seasonal cycle (see Figure 30, Chapter 4.3.1) and the effect of felling on [DOC] seemed insignificant compared to seasonal fluctuations in [DOC]. Deforestation may also have not been identified as a control on DOC export because the higher [DOC] associated with felling occurred earlier than the timing of highest flows during the year. Furthermore, only one catchment showed enhanced [DOC] therefore the relationship is stronger with the proportion of forestry rather than the felled area. The forested areas remain a source of DOC within the catchment with continual fresh litter production and organic matter decomposition, whereas the felled areas become depleted as a source of DOC fairly rapidly after deforestation.

HOST classes 15 and 29 were also not identified as a control of DOC export (in contrast to [DOC]), rather stream distance to nearest disturbance was found to exert a control, with the shorter the distance to nearest windfarm-related disturbance, the greater the DOC export. In terms of a windfarm-related control, it therefore appears that the type of windfarm-related disturbance is not influential, but that the connectivity between available DOC and the stream network is important. From a study of felling at Hubbard Brook, New Hampshire, U.S.A., it was observed that temporal variations in flowpaths were more important controls of streamwater [DOC] than the area disturbed by felling (Dai *et al.,* 2001).

A significant relationship (R^2 = 96 %, P = 0.018) at the 95 % confidence level describes POC export during the maximum-disturbance phase. The same three controls which explained the variation in [POC] during the maximum-disturbance phase – a positive relationship with HOST class 24, a positive relationship with the percentage deforested and a negative relationship with access track length – describe the variation in POC export, plus one other control; a negative relationship with flow length per catchment area. An explanation for this relationship is not clear since it indicates that the greater the connectivity within the catchment, the lower the [POC].

6.3.2.2. Phosphorus

The best fit equations for median [P] and export obtained by the regression analysis for both the low- and maximum- disturbance phases are shown in Table 41.

6.3.2.2.1. Concentration

Median [SRP] during the low-disturbance phase of the time series (R^2 = 75 %, P = 0.032) was controlled positively by the main HOST classes in the Whitelee catchments. The most likely explanation for this is that sources of P in the catchments are relatively small and uniform so that streamwater [P] is linked to the P adsorption ability of the soil type within the catchment. P is not retained well by HOST classes 15 and 19 because the potential of blanket peat to sorb P is extremely low (Fox and Kamprath, 1971; Malcolm *et al.,* 1977; Nieminen and Jarva, 1996) due to the low levels of iron and aluminium (Tamm *et al.,* 1974), thus more SRP reaches the stream network.

In contrast, the HOST classes are not found to be as influential on [SRP] during the maximum-disturbance phase whereas a significant relationship exists at the 95 % confidence limit (R^2 = 93 %, P = 0.010) between median [SRP] and three windfarm-related disturbance controls. In the assessment of impact on [SRP] time series (see Chapter 4.4.2.1) it was hypothesised that the most likely control on streamwater [SRP] was the extent of the catchment subject to deforestation and the regression analysis for the maximum-disturbance phase provides evidence supporting this hypothesis. Deforestation is known to have a negative impact on streamwater chemistry, especially in terms of nutrient enrichment (e.g. Ahtiainen and Huttunen, 1999; Nisbet, 2001; Cummins and Farrell, 2003b; Feller 2005; Rodgers *et al.,* 2010).

Table 41. Best fit equations obtained by the regression analysis of median [P] and exports during both the low- and maximum-disturbance phases. N = 8. Units for [P] are μg L^{-1}. Units for P export are mg P m^{-2} $month^{-1}$.

Concentration				
Disturb. Phase	**Parameter**	**Equation**	**R^2**	**P value**
Low	SRP	= - 7.83 + 0.25 (% HOST classes 15 and 29) + 0.32 (% HOST class 24)	75 %	0.032
	TP	= 18.2 + 0.71 (% HOST class 24) + 0.36 (% pasture)	73 %	0.038
Maximum	SRP	= 36.9 + 3.92 (% deforested) - 1.65 (access track length) - 4.21 (distance to nearest disturbance)	93 %	0.010
	TP	= 30.8 + 0.96 (% HOST class 24) + 8.81 (% deforested) - 4.35 (access track length)	90 %	0.020
Export				
Disturb. Phase	**Parameter**	**Equation**	**R^2**	**P value**
Low	SRP	= - 2.85 + 0.04 (% HOST class15 and 29) + 0.05 (% pasture)	53 %	0.148
	TP	= 5.78 + 1.42 (flow length per catchment area) - 0.05 (% HOST classes 15 and 29) - 0.04 (% HOST class 24)	84 %	0.046
Maximum	SRP	= 1.43 + 0.01 (% HOST classes 15 and 29) + 0.29 (% deforested) - 0.16 (access track length)	86 %	0.037
	TP	= 38.4 - 11.9 (flow length per catchment area) - 0.27 (% HOST classes 15 and 29) - 0.27 (% HOST class 24) + 1.95 (% deforested) - 1.43 (access track length)	97 %	0.086

An increase in streamwater [SRP] after deforestation is likely to be from a combination of potential sources: the remains of fertilisers used to establish the conifer trees in the 1960s washed in-stream in runoff from newly-exposed soils (Malcolm and Cuttle, 1983), reduced uptake of soil P by vegetation (Forestry Commission, 2003), P release from the roots of the felled trees (Ahtiainen and Huttunen, 1999), increased decomposition rates at the newly-bare soil surface (Walbridger and Lockaby, 1994; Messina *et al.,* 1997; Perison *et al.,* 1997) and leaching from brash material which is an important source of SRP (Taylor, 1991; Stevens *et al.,* 1995; Nisbet *et al.,* 1997; Titus and Malcolm, 1999; Moffat *et al.,* 2006).

Access track length was also identified as a control on [SRP] during the maximum-disturbance phase, indicating an unexpected negative relationship, with increasing track length associated with lower [SRP]. This decrease in [SRP] with access track length was not observable during the time of maximum disturbance in the time series figure (Figure 33, see Chapter 4.3.2). It was hypothesised that windfarm-related disturbance, especially in the case of access tracks with their improved drainage, would increase the transfer of nutrients from soil to water. The most likely explanation for this negative relationship is the adsorption of P by mineral material used to construct the windfarm access tracks which reduces the amount of SRP in the catchment available to reach the stream network. The construction stone is likely to have been tested only for inertness in terms of leaching prior to construction rather than for likelihood of chemical uptake.

The third control on median [SRP] in the maximum-disturbance phase was stream distance to nearest windfarm-related disturbance, with the shorter the distance, the greater the [SRP]. This emphasises that median [SRP] is not only influenced by the source of available P due to deforestation but also the connectivity between the source and the stream network. The shorter the flow paths to the stream network, the lower the chance of retention of P within the catchment due to various biogeochemical processes, including sorption to any available mineral soil and mineralization, before reaching the stream.

During the low-disturbance phase [TP] is described by a significant positive relationship (R^2 = 73 %, P = 0.038) with both the percentage of HOST class 24 and the proportion of pasture within the catchment. It is thought that these two controls are linked as HOST class 24 is more extensive in the agriculturally-dominated N-draining catchments. The variation in the [TP] time series is also positively controlled by these two controls through the direct deposition of particulate P in the form of faecal matter in and near the stream network by grazing dairy cattle, which often come down to the stream to drink and may also cause erosion around river banks and disturb P in-stream sediments. In addition to this source of TP, [TP] measured at the sampling point in catchment 456 is thought to be impacted by episodic runoff from a nearby farmyard.

During the maximum-disturbance phase median [TP] is also described by a significant relationship (R^2 = 90 %, P = 0.020) in which % HOST class 24 remains a control, with two windfarm-related disturbance controls also identified. As expected, the percentage of the catchment deforested exerts a positive control on [TP]. In addition to the potential sources already described for [SRP] from deforestation, [TP] may also increase after deforestation because of the greater susceptibility to erosion of the newly-bare peat surface, which is often dry, cracked and degraded (Patterson and Anderson, 2000), especially during rain events due to greatly reduced interception (Vitousek and Melillo, 1979; Ensign and Mallin, 2001). The length of access track per catchment has a negative influence on [TP], similar to the control on [SRP]. As well as the potential adsorption of P by the mineral construction material used in the windfarm access tracks, particulate P is also likely to be reduced in catchments where there is greater length of access track and turbine bases since there will be a greater presence of silt traps to retain particulates, therefore less TP reaches the stream network, as already described for POC (see Chapter 6.3.2.1.1).

6.3.2.2.2. Export

All the regression equations for describing the variation in [P] are significant and enable identification of windfarm-related disturbance as an important control through comparison of controls on concentrations in low- and maximum-disturbance phases. However, although the majority of regression equations for describing the variation in P export have R^2 values of 84 - 97 %, only two are significant. The relationship to describe the variation in SRP export is not significant during the low-disturbance phase (R^2 = 53 %, P = 0.148), but is significant for the maximum-disturbance phase (R^2 = 86 %, P = 0.037). Both the percentage of HOST classes 15 and 29 and the proportion of the catchment deforested positively influence SRP exports during the maximum-disturbance phase, reflecting, in the case of the HOST, the poor retention of P by peat-based soils, and, in terms of deforestation, increases in the source of available P within the catchment (see Chapter 6.3.2.2.1).

Variation in TP export is described by a weakly significant relationship (R^2 = 84 %, P = 0.046) during the low-disturbance phase, but not during the maximum-disturbance phase (R^2 = 97 %, P = 0.086). The relationship for the low-disturbance phase TP export is not only weakly significant but identifies controls which are difficult to interpret as the relationship is not as expected. There is a positive relationship between TP export and flow length per catchment area in the low-disturbance phase, yet a negative influence between TP export and flow length per catchment area in the maximum-disturbance phase. The percentage of HOST classes 15 and 29 may be expected to exert a positive control on TP export because streamwater [P] is linked to the P adsorption ability of the soil within the catchment which, in the case of these two peat-based soil classes, would be low (see Chapter 6.3.2.2.1) thus more P would reach the stream network. However, a negative relationship is shown which is interpreted most simply that the larger the area covered by these soils the less P there is – suggesting they are not a source of P.

Although the relationships between TP export flow length per catchment area and the percentage of HOST classes 15 and 29 cannot be explained and the relationships between the potential controls and P export do not describe the variation in the data very well, the approach is strong enough to show that there are changes in controls between the low- and maximum- disturbance phases due to windfarm-related disturbance.

6.3.2.3. Nitrogen

The best fit equations for median [NO_3^-] and export obtained by the regression analysis for both the low- and maximum- disturbance phases are shown in Table 42.

6.3.2.3.1. Concentration

During the low-disturbance phase, a highly significant relationship (R^2 = 94 %, P = 0.001) exists at the 95 % confidence limits between median [NO_3^-] and two controls. The percentage of HOST class 24 exerts a negative control on [NO_3^-] which may be indicative of denitrification occurring in these waterlogged gley soils (Ryden, 1983), reducing the NO_3^- available for leaching into streamwater. It could also be that the percentage of HOST class 24 is a surrogate indicator of the S-draining catchments which have lower coverage of this HOST class and fewer NO_3^- sources. As expected (see Chapter 4.4.3), the

Table 42. Best fit equations obtained by the regression analysis of median [NO_3^-] and exports during both the low- and maximum-disturbance phases. N = 8. Units for [NO_3^-] are mg L^{-1}. Units for NO_3^- export are g N m^{-2} $month^{-1}$.

Concentration			
Disturb. Phase	**Equation**	**R^2**	**P value**
Low	= - 0.08 - 0.02 (% HOST class 24) + 0.04 (% pasture)	94 %	0.001
Maximum	= - 0.01 - 0.02 (% HOST class 24) + 0.03 (% pasture)	90 %	0.003
Export			
Disturb. Phase	**Equation**	**R^2**	**P value**
Low	= - 0.11 + 0.07 (flow length per catchment area) + 0.001 (% coniferous forest) + 0.002 (% pasture)	91 %	0.014
Maximum	= - 0.23 + 0.15 (flow length per catchment area) + 0.002 (% coniferous forest) + 0.004 (% pasture)	76 %	0.097

proportion of pasture exerts a positive control on [NO_3^-], consistent with the results from other studies (Jordan *et al.,*1997; Russell *et al.,* 1998; Lepistö *et al.,* 2001; Nedwell *et al.,*2002; Xie *et al.,* 2005; Mattsson *et al.,* 2005; Helliwell *et al.,* 2007a,b) and is attributed to more sources of NO_3^- as the percentage of pasture increases from diffuse inputs, such as inorganic fertilizer use, organic manure application and excretion from grazing animals (Robards *et al.,* 1994).

The assessment of impact on streamwater [NO_3^-] in Chapter 4.3.3.1 indicated that in S-draining catchments 13, 15 and 1632 a potential windfarm-related disturbance impact was discernable through a change in the expected seasonal signal coinciding with windfarm-related disturbance in these catchments. However, the same two controls – HOST class 24 and percentage pasture – explain most of the variation in [NO_3^-] in highly significant relationships during both the low- and maximum-disturbance phases suggesting that the difference observed in the time series in these three S-draining catchments cannot be explained by either the windfarm-related construction or the forestry operations considered here.

6.3.2.3.2. Export

Similarly, the results of the regression for both the low- and maximum- disturbance phases show that the same three controls influence NO_3^- export. However, a statistically significant relationship only exists for NO_3^- export during the low-disturbance phase (R^2 = 91 %, P = 0.014) because one does not exist for the maximum-disturbance phase at the 95 % confidence limits (R^2 = 76 %, P = 0.097). As well as the percentage of the catchment which is pasture, which was expected to exert a positive control on streamwater NO_3^- export (see Chapter 6.3.2.3.1), the flow length per catchment area also exhibits a positive control on NO_3^- export, indicating that connectivity between N sources within the catchment and the stream network is important in determining NO_3^- export. In a Finnish catchment study, large catchments, with extensive areas not closely connected to the stream network resulted in decreasing load compared to the near stream zone (Mattsson *et al.* 2005).

Furthermore, the proportion of the catchment covered by coniferous forest also has a positive influence on NO_3^- export at Whitelee, with greater exports from the catchments containing greater coniferous forest cover. [NO_3^-] has been observed to be significantly larger in forested streams compared to moorland streams as a result of changes in the soil N cycle due to the different vegetation types (Reynolds and Edwards, 1995; Chapman *et al.,* 1999). The forest vegetation has a much greater ability to capture inputs of occult and dry deposition than moorland vegetation and thus the forested catchments receive larger inputs of atmospheric N (Reynolds *et al.,* 1997) and forestry can promote nitrification within the soil, making more NO_3^- available for leaching into runoff and thereby increasing streamwater [NO_3^-]. No controls associated with windfarm-related disturbance were found by this research to influence NO_3^- export.

6.4. Summary of Windfarm-Related Controls on Streamwater Chemistry

The results of the GIS analysis-supported multiple linear regression presented and discussed in this chapter confirm, as hypothesised in Chapters 4 and 5, that during the maximum-disturbance phase windfarm-related disturbance influences streamwater C and P dynamics in the Whitelee catchments through the relationships listed in Table 43. Although windfarm-related disturbances control some aspects of streamwater dynamics, it is clear from the regression analysis that other catchment characteristics, such as flow length per catchment area, HOST and land use also influence streamwater concentrations and exports. For example, the regression analysis also showed that there were no statistically significant windfarm-related controls on streamwater N dynamics (Table 43), and that N dynamics are influenced by factors such as stream density, HOST class and land use.

Table 43. Summary of windfarm-related controls on streamwater chemistry.

Windfarm-Related Disturbance	Concentration	Export	Direction of relationship
% deforested	DOC, POC, SRP, TP	POC, SRP	positive
access track length (km)	POC, SRP, TP	POC, SRP	negative
distance to nearest disturbance (km)	SRP	DOC	negative

6.4.1. Deforestation

The percentage of the catchment area subject to deforestation exerts a significant positive control on streamwater [DOC], [POC], [SRP] and [TP] and POC and SRP exports. Concentrations and exports of these parameters increased with a greater percentage deforestation within the catchment. The sources of C and P in the catchment area are likely to increase after forestry operations due to brash and felling litter, increased organic matter decomposition and erosion of the newly-exposed soil surface. P sources may also increase after deforestation from the remains of fertilisers used to establish the conifer trees, increased soil P resulting from reduced vegetation uptake of P levels, and P release from the roots of the felled trees.

6.4.2. Access Tracks

The length of access track was observed to exert a significant negative control on both the concentration and export of POC, SRP and TP, with concentrations and exports decreasing with increasing access track length. This is thought to be due to two reasons. Firstly, the effective employment of settlement ponds, flocculation blocks and ditch blocking where new drainage was installed alongside tracks which reduced the amount of particulate matter reaching the stream network, and secondly, the adsorption of P by the mineral material used for access track construction.

6.4.3. Distance to Nearest Disturbance

The regression analysis also identified that the nearer the sampling point to the nearest windfarm-related disturbance, the greater the [SRP] and DOC export. This emphasises that [SRP] and DOC export are controlled not only by size and availability of the P and C sources, but also by the connectivity between the source and the stream network. For example, clear-felling was carried out in catchments 13, 14, 1 and 1632, yet an impact on the time series was observed only in catchments 13 and 14, 1.0 km and 1.8 km respectively away from the nearest disturbance, whereas no impact was observed in catchments 1 and 1632, 7.3 km and 4.6 km downstream of deforestation (see Chapter 4.4.2.1). Consequently, it may be that the sampling points in some catchments are too far away from areas of disturbance to show any effect, highlighting the importance of hydrological pathways, the role of dilution and in-stream cycling of P and C in mitigating disturbance-related impacts downstream.

7. Concluding Remarks: Synthesis of Research, Windfarm-Related Impacts and Recommendations for Suitable Management and Future Research

7.1. Chapter Outline

This chapter consists of four further sections. The first section summarises the outcomes of this research, highlighting the key findings of C, P and N dynamics in relation to the first four aims outlined in Chapter 1.6. The second section summarises the overall impact of windfarm-related disturbance on streamwater chemistry. The third section uses the synthesis of these findings to address the fifth aim of this research, also outlined in Chapter 1.6, and makes two recommendations for best practice at future windfarm developments on peatland. The final section proposes seven ideas for further research into streamwater chemistry at windfarm developments hosted on peatlands based on the findings of this research.

7.2. Concluding Remarks Regarding Aims of Research

There is a greater need now more than ever, due to climate change, an increase in [DOC] in freshwaters (*c.f* Monteith *et al.,* 2007) caused by various factors (*c.f.* Clark *et al.* (2010), the continued development of onshore renewables and the growing economic and political importance of C sequestered naturally, to understand the dynamics of Scotland's C stores and to preserve them. The impact of windfarms on peatland streamwater chemistry has gradually been attracting interest from the scientific community (*c.f.* Grieve and Gilvear, 2008; Waldron *et al.,* 2009). The research reported in this thesis has built on the pre-disturbance data of streamwater chemistry for the Whitelee catchments from Waldron *et al.* (2009) and has provided valuable insight into the impacts which occur, their magnitude and their duration. This proved to be challenging because streamwater chemistry is highly dynamic at a range of temporal scales such as high flow events, seasonal responses and long-term climatic changes, thus this too had to be characterised in order to discern impact.

Chapter 1.4 explained that windfarm-related disturbance can be separated into two types – windfarm construction activities associated with installing the windfarm infrastructure, and forestry operations to improve air flow or to meet HMP requirements. This research has been successful in separating the impacts of these two types of windfarm-related disturbance. The results of the research carried out at Whitelee can be used to advise best practice at other windfarm developments on peatland, especially where extensive forestry operations are required, and are relevant to any other type of development on peatland which share similar disturbance mechanisms.

As well as identifying impacts on streamwater chemistry due to windfarm-related disturbance, during this research improvements in analytical protocols were developed (see Chapter 2); namely, the colour correction protocol, filtration protocol, and pore size investigation in conjunction with Adam (2009), and the impacts of sample storage on [C]. Since many of the water samples were collected from peat-dominated catchments they were highly coloured, leading to interferences in the peak height determined colorimetrically on the Technicon Autoanalyser II which resulted in over-estimates of [P] and [N]. Using the colour correction methods developed by Adam (2009) on the water samples from Whitelee, more accurate measurements of [P] and [N] can now be made for highly coloured samples – important for future research at these and other peat-dominated catchments. Further to this, using the relationship between DOC and the difference between the non-colour corrected and colour corrected [P] and [N], retrospective colour corrections were carried out on the earlier data from Waldron *et al.* (2009) and the data from October 2007 until September 2008 collected as part of this doctoral research. This allowed for the identification of an accurate magnitude of impact and the use of a longer time series of concentration data in the assessment of impact.

Also related to analytical method development was the examination of sample preservation protocol in terms of filtration on [P] and [N]. This included a comparison between immediate filtration in the field and filtering in the laboratory which concluded that transporting the samples in an iced cool box followed by immediate filtration in the laboratory was a suitable method of preserving and preparing samples for analysis. Filter pore size influence on N and P was also examined due to ambiguity over filter pore size in the literature relating to the methodology for colorimetry. The results of this investigation showed that for water samples from the Whitelee catchments a 0.2 µm filter should be used for determination of concentrations on Technicon Autoanalyser II since this pore size gives clearer, more accurate peak shapes because particles > 0.2 µm interfere in the analysis.

The reduction in [C] observed with a change in analysts in October 2007 was investigated. Differing protocols in the preservation of samples for [C] analysis between analysts was found to influence the C partitioning in samples, with samples which had been stored frozen prior to filtration yielding higher [POC] and lower [DOC] than samples which had been in refrigerated storage. This was thought to be due to the flocculation of particles upon freezing which were consequently filtered out of solution leading to higher [POC]. The [POC] and [DOC] data from Waldron *et al.* (2009) could not be corrected to accommodate for this difference. Additionally, the investigation also found that the [DOC] from October 2007 to June 2010 was under-estimated because of flocculation when the aliquots already filtered for DOC analysis were frozen prior to DOC analysis at a later date. A correction was carried out to account for this underestimate, but for the full time-series [TOC] is used for comparison. This research has shown that in future samples for [C] analysis should not be frozen at any stage.

This research had four aims, building on the pre-disturbance data in Waldron *et al.* (2009). Chapter 4 addressed the first aim which was to identify the impacts which occur on streamwater C, P and N during and after windfarm construction, examine impact magnitude and quantify the recovery time after impact. The [DOC] time series and the harmonic regression of the [TOC] showed that there was a small increase in catchment 13 during 2007-2008, the period of maximum-disturbance in the catchments. [POC] did not show any obvious increases co-incident with windfarm-related disturbance, but there was evidence of occasional increases most likely attributed to point source pollution events from agricultural activity in the N-draining catchments. The most obvious impact was on [SRP] in S-draining catchments 13 and 14 where as much as a tenfold increase was observed from June 2007, which lead to increases in [TP]. The water quality status of these two catchments declined from “good” to “moderate” in terms of the Water Framework Directive (2000) UK Technical Advisory Group Environmental Standards for [SRP] (UKTAG, 2008) and these two catchments have still not shown a full recovery after a further two years. The [NO_3^-] time series did not show the same increases as [P]; however the harmonic regression analysis indicated that there may have been an impact in catchments 13, 15 and 1632 during 2007-2008 because the model of [NO_3^-] does not describe the data well in these catchments during this year.

Chapter 5 dealt with the second and third aims of this research by quantifying annual streamwater exports and comparing the magnitude of streamwater C exports to suggested peatland C sequestration rates. There was no clear inter-annual differences in the annual TOC exports but the greatest annual DOC exports occurred in all catchments in 2008-2009 with the difference attributed to a greater number of high flow events occurring when there was a high DOC availability in the catchments. The greatest annual POC exports also occurred in 2008-2009 with the exception of catchment 13 where the greatest POC export occurred in 2007-2008. The different temporal pattern of POC export for catchment 13 was thought to be caused by the close proximity to extensive clear-felling and mulching. There was no clear pattern in which year the greatest SRP export from the N-draining catchments occurred, but in the S-draining catchments the maximum SRP export occurred in hydrologic year 2008-2009. The greatest annual TP exports during the research period were in 2007-2008 except for catchments 17U and 15 where greatest TP occurred during 2008-2009. The greatest NO_3^- exports occurred generally in 2006-2007, regardless of whether the catchments were N- or S- draining. Streamwater C exports from catchments 13, 15, 1 and 1632 exceeded the only measure that exists of C sequestration rates for the Whitelee peatland (of 18 g C m^{-2} yr^{-1}) for the duration of the research period. Thus for the Whitelee catchments to continue sequestering C, the minimum amount of C fixed has to equal the amount lost via the streamwater pathway plus 18 g C m^{-2} yr^{-1}.

Chapter 6 covered the fourth aim which was to identify the controls on streamwater concentration and export in order to assess if there is impact of windfarm-related disturbance. GIS data was used to describe the physiography of each catchment and to quantify the extent of windfarm-related disturbance. The pre-disturbance streamwater chemistry data determined by Waldron *et al.* (2009) was too short in length to perform a before-and-after impact comparison thus low- and maximum- disturbance phases in the time series were compared to identify potential impacts of windfarm-related disturbance. Best subsets multiple linear regressions were carried out for each parameter with the GIS-derived data and median concentration data during the low- and maximum- disturbance phases for each.

This approach found that flow length per catchment area, the percentage of hydrology of soil type classes 15 and 29, the percentage of coniferous forest and the extent of pasture within the catchment explained the variation in [TOC] during the low-disturbance phase. During the maximum-disturbance phase the HOST classes within the catchment remain controls on streamwater [C] but the percentage of the catchment deforested positively influences [DOC] and [POC] and the access track length negatively controls [POC]. The area of coniferous forest rather than the area deforested exerts a positive control on DOC export, and the distance to the nearest disturbance which exerts a negative control. POC export during the maximum-disturbance phase is influenced by the flow length per catchment area and the percentage of HOST class 24 as well as two windfarm-related disturbances – deforestation and access track length.

During the low-disturbance phase [SRP] was influenced by the two HOST classes and there is a clear change during the maximum-disturbance phase, because the variation in [SRP] in this phase is influenced by three windfarm-related disturbance controls – a positive relationship with the percentage deforested, negative relationships with access track length and distance to nearest disturbance. [TP] was also controlled by the same relationships with deforestation and access track length. Windfarm-related disturbances were not found to influence TP export yet the extent of deforestation and the length of access track were found to control SRP export.

The percentage of the catchment which is pasture and HOST class 24 representing poorly-drained gley soils were found to influence [NO_3^-] during both the low- and maximum- disturbance phases. Similarly, pasture, flow length per catchment area and the proportion of coniferous forest were observed to influence NO_3^- export during both the low- and maximum- disturbance phases. No windfarm-related disturbance was identified as a significant control on either [NO_3^-] or NO_3^- export.

7.3. Overall Impact of Windfarm-Related Disturbance on Streamwater Chemistry

This research found that the greatest impact on streamwater chemistry was through the enrichment of [P] and that there was a smaller increase on [C], with consequent impacts of SRP and POC export. The source of this additional C and P resulted most likely from forestry operations, namely, clear-felling large areas of catchment and extensive brash mulching associated with the windfarm HMP, with new organic material available for decomposition and the potential for erosion of the newly-exposed soil surface. The remains of fertilisers used to establish the conifer trees, reduced vegetation uptake of soil P and P release from the roots of the felled trees are three further sources of P in streamwater.

This research has shown that windfarm-related infrastructure can also influence streamwater chemistry, although exerting a less obvious impact, with increasing access track length decreasing [POC], [SRP] and [TP] causing subsequent decreases in POC and SRP export. This is likely to be caused by the effective use of settlement ponds, flocculation blocks and ditch blocking to reduce the amount of particulate matter reaching the stream network; and potentially through the adsorption of P by the access track construction material. Although it is encouraging that there are no large increases detrimental to streamwater quality due to the construction of the windfarm infrastructure, this more subtle relationship between streamwater chemistry and windfarm access track infrastructure has the potential to impact on in-stream ecology by changing the energy budgets of streams and the availability of organic matter for consumption.

7.4. Recommendations for Future Windfarm Developments

Based on the summary of findings of Chapter 7.3 and to address aim 5, the following two recommendations for best practice at future windfarm developments on peatland are suggested:

7.4.1. Recommendation 1

- Monitor C, P and N in streamwater in all catchments draining a windfarm on C rich soils before, during and after construction to allow the identification of impact

Using an approximately bi-monthly water sampling regime at sampling points outwith the immediate area of disturbance, an impact on streamwater [C] was observed at Whitelee. Although there was only a small increase in streamwater [C] and POC export, development at the Braes of Doune windfarm showed a more significant impact on streamwater [C] (Grieve and Gilvear, 2008). This variation in response between windfarm developments highlights the need for a site-by-site assessment of impact on streamwater [C]. Additionally, streamwater [C] data from monitoring could be used to improve the accuracy of C payback time estimates in the “C calculator” (Nayak *et al.*, 2010), which is being adopted readily by windfarm developers and anti-wind campaign groups to show whether the C footprint of a development is appropriate.

This research has shown there is a significant increase in [P] in catchments 13 and 14 and a significant increase in SRP export in catchment 13, both due to windfarm-related deforestation, underpinning the need for establishing a long pre-disturbance baseline to allow the identification of impact as well as monitoring during and after windfarm construction until a full recovery from any impact is observed. Although no windfarm-related impact on streamwater [NO_3^-] was observed at Whitelee, studies of other disturbed catchments have shown significant increases in [NO_3^-] (Reynolds *et al.,* 1994, Neal *et al.,* 2003a, Tetzlaff *et al.,* 2007). The lack of impact at Whitelee does not necessarily mean that an impact will not occur at other peatland-based catchments therefore [N] should be included in any monitoring programme.

Windfarm EIAs often mention a possible impact on water quality, in terms of eutrophication of lochs and reservoirs, maintaining public and private water supply or fish stocks but at present nutrient export in streamwater draining windfarm developments is not considered as likely (CRE Energy, 2002). The incorporation of long-term monitoring for impact on streamwater [P] and [N] can supplement the hydrological studies already carried out at windfarm developments in order to ensure that water quality is maintained in rivers as well as in lochs, reservoirs and drinking water supplies. The focus should not be on maintaining drinking water supplies only, because environmental regulators will also be concerned about the change in trophic status observed in the two usually low nutrient status catchments in light of the Water Framework Directive (2000). This raises questions about whether discharges from forest management such as mulching on peatland, should require to be licensed.

Further studies at catchments subject to windfarm-related disturbance should include an undisturbed control catchment and a long (approximately a year) pre-disturbance baseline to understand the seasonality of the river system. Including these two suggestions in future catchment studies will assist in the clear identification of any impact on streamwater chemistry. Ideally both bi-monthly and event sampling should be carried out, but if this is not feasible then a monthly sampling frequency will allow the identification of, at the very least, large impacts on streamwater chemistry. The distance downstream the sampling points should be from disturbance depends on the catchment size and the scale of the disturbance in each catchment, as there will always be a localised impact on streamwater chemistry. A catchment study of multiple, longitudinal sampling points in the same stream at increasing distance from disturbance should allow the identification of the most appropriate sampling point location for a catchment and determine at what distance no impact is observed. Sampling points should certainly be upstream of any reservoirs or lochs which may act as a buffer and attenuate impact, and upstream of any other sources of C, P and N within the catchment such as dairy farming, to allow the clear identification of any impact. Along with the monitoring of concentration, the volume of water passing thought the catchment should also be gauged to allow the calculation of export.

7.4.2. Recommendation 2

- Minimise potential for P impact of brash mulching on streamwater chemistry

Adhering to the Forests and Water Guidelines (Forestry Commission, 2003) appears to have limited the impact of forestry operations on streamwater C, P and N dynamics in the Whitelee catchments but the tenfold increase in streamwater [P] in S-draining catchments 13 and 14 indicates that windfarm-related forestry operations have had a significant impact on streamwater quality. Three further mitigation strategies are suggested to minimise the potential for P impact from brash mulching.

7.4.2.1. Recommendation 2 – Mitigation Strategy 1

Large areas of the impacted catchments were not only clear-felled but extensive areas were also subject to brash mulching. Dense layers of brash can hinder natural regeneration of vegetation (Moffat *et al.,* 2006) and this management was chosen undoubtedly because mulching means the breakdown of brash occurs over a shorter timescale, therefore the re-establishment of bog forming vegetation occurs more quickly (Fahley *et al.,* 1991). However, brash is an important source of leachable nutrients and, although mulching would have been understandably desirable for rapid restoration of bog, the large scale (3 km^2) at which this was carried out within an extended timeframe (14 months) appears to have been to the detriment of water quality lasting more than 2 years after mulching was completed. The clear-felling of small blocks of forest relative to catchment size, called phased felling, mitigates impacts which are observable at the larger scale (Harriman *et al.,* 2003; Neal *et al.,* 2004; Soulsby *et al.,* 2006). The first recommended mitigation strategy is to phase the brash mulching in order to reduce the proportion of a catchment with P available for transportation into streams, mitigating the impact. However, it is noted that this strategy does not reduce the total P load leaving the harvested area, it simply spreads the load reaching the stream network over time.

7.4.2.2. Recommendation 2 – Mitigation Strategy 2

The second recommended mitigation strategy involves reducing the P availability after clear-felling by clearing much of the brash from the felled area in order to minimise downstream P losses. Forest residues can be a source of woodfuel energy generation, and brash can be subdivided into the amount necessary for soil protection in the form of brash mats and the remainder used for biofuel (Moffat *et al.,* 2006). In catchments where the main objective of felling is restoration of peatland habitat, the harvesting of forest residues may make a positive contribution to this restoration process and brash removal through brash bundling can be used to reduce P enrichment by removing a large proportion of the nutrient store from the catchment (pers. comm. Andrew Heald, Head of Assurance with UPM Tilhill).

7.4.2.3. Recommendation 2 – Mitigation Strategy 3

The final recommended mitigation strategy is based on increasing the retention capacity of the catchment. Buffer zones, which can filter runoff before it reaches streamwater, are effective in removing particulate P but are far less efficient in removing SRP (Uusi-Kämppä, 2005; Stutter *et al.,* 2009) and the creation of buffer zones in peatland can be challenging (Ryder *et al.,* 2010). Natural re-vegetation is too slow to mitigate against P release from mulching, however, seeding clear-felled areas with suitable fast-growing native grasses immediately after tree harvesting can reduce P release from blanket peatlands compared to clear-fell only control areas (O'Driscoll *et al.,* 2011). The P contents of the above-ground vegetation biomass were significantly higher than those of the control areas and the water extractable P in the seeded areas was significantly lower than in the control areas (O'Driscoll *et al.,* 2011). It is therefore recommended that at future windfarm developments, and also at other forestry operations on peatland, where large areas of clear-felling and mulching are required, the immediate seeding with fast growing grass should be employed as a mitigation measure for P release.

7.5. Ideas for Further Research

Based on the findings of this research the following seven ideas for further research into streamwater chemistry at windfarm developments hosted on peatlands are proposed:

1) The mitigation measures recommended in this research warrant some additional research. Plot studies should be carried out to determine the best practice mitigation measures for P release in peatland catchments. By comparing the effect on streamwater [P] of brash mulching with bailing a proportion of brash for the biomass market, and with the seeding of clear-felled areas immediately after tree harvesting with suitable fast-growing native grasses, the best practice to minimise

P enrichment of receiving watercourses can be determined.

2) Multiple, longitudinal sampling points in the same stream at increasing distance from disturbance are recommended in future catchment studies to clearly determine impact. As an increase in [P] was only observed in the two Whitelee catchments where the sampling points were < 2 km away from the nearest disturbance, whereas no response was observed in the other catchments where the sampling points were > 4 km away from the nearest disturbance, the lack of an increase in [NO_3^-] may also have been due to the distance downstream to the sampling point. Further to this, Chapter 6 showed that the distance to disturbance was an important control on streamwater [SRP] and DOC export, highlighting the issue of scale when implementing a water sampling regime. It is not yet clear at what distance downstream there is no observable impact therefore longitudinal catchment studies in the most impacted catchments are suggested because it would help determine how great the impact is on water quality in the immediate area of disturbance and at what point impact is no longer detected.

3) Further research is required into the relationship between access track construction material and streamwater dynamics. Although the EIA states that sources of site-won and imported material were checked to ensure inertness in relation to its place of use in order to prevent any potential reaction with water (CRE Energy, 2002), there is evidence that it reduces streamwater [POC], [SRP] and [TP] which subsequently impacts on exports. Studies could be carried out to see if the material could be used as a flocculent treatment, for example, in the original forest plough furrows which may be acting as a conduit to the stream network, as a measure to treat P mobilised by forestry operations on peat soils.

4) Although the bi-monthly sampling used in this research is a greater frequency than is employed by regulatory bodies and was frequent enough to detect impact in the catchments, some of the detail of concentrations and exports during high flow events are likely to have been missed. The installation of in-stream continuous monitoring equipment such as the SCA:N spectrolyser which can provide an output of DOC-equivalents and is now successfully generating data from catchment 13 as part of the NERC KE CLAD network (www.clad.ac.uk). This would yield higher resolution data with more accuracy and enable the identification of more detailed impacts. Along with a sampling regime which targets high flow

events where there are often large transfers of C and P, this would add to our understanding of streamwater chemistry dynamics and processes in a disturbed peat-dominated catchment.

5) The main focus of this research was to indentify the impacts and controls of streamwater C, P and N, however, the changing stiochiometry of the streamwater has yet to be examined for the latest data, building on the findings of Waldron *et al.* (2009). The interaction of C, P and N in streamwaters is complex but the potential for DOC to be respired to CO_2 is ultimately influenced by the availability of P and N, connecting the terrestrial C cycle to the atmospheric C cycle. Examining the changes in stiochiometry would add to our understanding of the interaction of C with P and N and ultimately the fate of C in streamwater, whether it is used to increase in-stream microbial biomass or used to support aquatic respiration where greater CO_2 evasion may prevail – important when considering that windfarms are built with the particular purpose of offsetting CO_2 emissions. This could be supplemented with a laboratory-based incubation study of water samples from streams draining windfarm-related disturbance designed to investigate how changing C, N and P ratios may impact the cycling of C, with particular reference to CO_2 and CH_4 evasion.

6) This research is one of the first studies to examine the impacts of windfarm development on peatland and the sole focus was streamwater C, P and N dynamics; and in terms of C, examined the DOC and POC only. Further research could take a similar approach to Dawson *et al.* (2004), Billett *et al.* (2004) and Dinsmore *et al.* (2010) by also studying inorganic C and gaseous forms of C to include the whole aquatic C cycle.

7) Streamwater C exports from Whitelee were compared to C sequestration rates for the nearest peatland, so further research should contextualise streamwater exports with an understanding of catchment C sequestration rates.

7.6. Postscript

Two extensions to the Whitelee windfarm have been consented and will be constructed by July 2012. The Phase 1 extension will comprise 36 turbines generating 130 MW and Phase 2 will add a further 39 turbines with a capacity to generate 141 MW. These additional turbines will be in catchments 14, 15 and 1, southwest of the original development. The extensions will require the construction of 40 km of access track and the extraction of construction material from 4 new and 2 existing borrow pits. The monitoring of streamwater quality is ongoing throughout the construction of the extensions.

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Appendices

A.1 Photographs of Windfarm-Related Disturbance

Figure A1. Borrow pit (onsite quarry) where stone has been removed and then backfilled with peat.

Figure A2. Floating road design access track with cable trenches parallel to road lines.

Figure A3. Excavation for installation of turbine foundation. Photo courtesy of Scottish Power.

Figure A4. Sediment settling ponds as a water quality mitigation measure.

Figure A5. Whole tree mulching in practice where trees were not viable for harvest.

A.2 Sampling Point Photographs

A.2.1 Sampling Points in North Draining Catchments

Figure A6. Sampling point 17. Looking downstream in summer 2007. Photo courtesy of Kate Heal.

Figure A7. Sampling point 17U. Looking upstream in spring 2010.

Figure A8. Sampling point 9A. Looking upstream during event flow in winter 2008.

Figure A9. Sampling point 9D. Looking upstream in summer 2007. Photo courtesy of Kate Heal.

Figure A10. Sampling point 456. Looking upstream.

A.2.2 Sampling Points in South Draining Catchments

Figure A11. Sampling point 13. Looking upstream during event flow in winter 2008.

Figure A12. Sampling point 14. Looking upstream in winter 2010.

Figure A13. Sampling point 15. Looking upstream in winter 2010.

Figure A14. Sampling point 1. Looking upstream during event flow in winter 2007.

Figure A15. Sampling point 1632. Looking upstream in winter 2010.

A.3 Reagents for Analysis on Technicon Autoanalyser

Reagents were made using AnalaR® grade chemicals and helium de-gassed de-ionised water. Standard stock solutions and working standards were stored below 4 °C between analyses.

A.3.1 SRP and TP Analysis

A.3.1.1 Reagents for SRP and TP Analysis

The same reagents were required for SRP and TP analysis.

- Acid molybdate solution

120 mL concentrated sulphuric acid was added to 700 mL de-ionised water in a 1 L glass amber bottle and the solution was allowed to cool. 10.4 g ammonium molybdate was added whilst stirring. 0.2 g antimony potassium tartrate was dissolved in 50 mL de-ionised water and added to the acid solution with gentle mixing to avoid the formation of a precipitate and made up to 1 L with de-ionised water. This solution was stored in the dark.

- Ascorbic acid solution

1.5 g ascorbic acid was dissolved in 90 mL de-ionised water in a 100 mL volumetric flask. 1.25 mL of 20 % sodium dodecyl sulphate (SDS) wetting agent was added, and the volume made up to the mark with de-ionised water. This reagent is unstable upon long-term storage so was freshly prepared on the day of analysis.

A.3.1.2 Standard Solutions for SRP and TP Analysis

A 1000 mg L^{-1} phosphate-phosphorous standard stock solution was made using potassium dihydrogen phosphate, dried at 105 °C for 1 hour and allowed to cool in a desiccator. 4.394 g of the dry potassium dihydrogen phosphate was dissolved in approximately 900 mL de-ionised water in a 1 L volumetric flask and made up to the volume with de-ionised water. A working standard of 0.1 mg L^{-1} was prepared for SRP from this using the appropriate dilution. A working standard of 0.1 mg L^{-1} was prepared for TP analysis from the same stock solution and, to keep the matrix the same as the samples, 1 mL 30 % H_2SO_4 plus 0.3 g K_2SO_4 was added to 100 mL of standard. 1 mL of 30 % H_2SO_4 plus 0.3 g K_2SO_4 was added to 100 mL de-ionised water and used as a zero standard.

A.3.2 TON Analysis

A.3.2.1 Reagents for TON Analysis

- Buffer solution

22.5 g sodium tetraborate and 2.5 g sodium hydroxide were dissolved in 900 mL of de-ionised water and the solution was made up to 1 L.

- Griess Reagent

100 mL concentrated hydrochloric acid was added to 800 mL de-ionised water in a 1 L volumetric flask. 10.0 g sulphanilamide and 0.5 g n-1-napthylenediamine dihydrochloride were weighed into a 1 L beaker and a quantity of the acid solution was added with stirring. This solution was then added to the remaining hydrochloric acid and made up to 1 L using de-ionised water.

- Reducing agent

0.3 g hydrazine sulphate was added to 800 mL of de-ionised water and the solution made up to the mark without shaking. The mixture was stirred gently with a magnetic stirrer avoiding the formation of a vortex to prevent the entry of oxygen.

- Catalyst solution

1 mL of 2.47 % copper sulphate solution and 1 mL of Brij-35 15 % solution were added to 100 mL de-ionised water and the resulting solution was gently stirred.

A.3.2.2 Standard Solution for TON Analysis

A 1000 mg L^{-1} nitrate-nitrogen standard stock solution was made using sodium nitrate, dried at 105 °C for an hour and allowed to cool in a desiccator. 6.068 g of the dry sodium nitrate was dissolved in approximately 900 mL de-ionised water in a 1 L volumetric flask and made up to the volume with de-ionised water. A working standard was prepared by dilution to produce a 1 mg L^{-1} solution.

A.3.3 NO_2^- Analysis

A.3.3.1 Reagents for NO_2^- Analysis

- Griess Reagent

As prepared in A3.2.1.

- Wetting agent solution

8 mL of 15 % Brij-35 solution was added to 1 L of de-ionised water with gentle mixing.

A.3.3.2 Standard Solution for NO_2^- Analysis

A 1000 mg L^{-1} nitrite-nitrogen standard stock solution was made by drying sodium nitrite at 105 °C for an hour and allowing it to cool in a desiccator. 4.926 g of the dry sodium nitrite was dissolved in approximately 900 mL de-ionised water in 1 L volumetric flask and made up to volume with de-ionised water. A working standard of 0.1 mg L^{-1} was prepared from this using the appropriate dilution.

A.4 Background Colour Correction

Background colour correction for highly coloured samples is not mentioned for the automated analysis of SRP, NO_3^- and NO_2^- (MEWAM, 1981b; MEWAM, 1992). Eaton *et al.* (2005) states that automated analysis for SRP and NO_3^-, sample colour that absorbs in the photometric range used will interfere, but does not advise of a method for addressing this interference. Manual SRP methods do mention that a correction for colour may be required, recommending that the absorbance of a blank, prepared by adding all reagents except ascorbic acid or antimony potassium tartrate to a sample, should be subtracted from the absorbance of each sample (Eaton *et al.*, 2005). In the SRP by vanadomolybdophosphoric acid method that excess colour is removed by shaking 50 mL of sample with 200 mg activated carbon in an Erlenmeyer flask. However Sarirullah *et al.* (1990) found that even charcoals sold specifically as low in phosphate, have high phosphorus content and are only suitable for de-colourising in the concentration range expected in soil extracts and sewage effluents but not for low level water analysis.

A.4.1 Methodology for Colour Correction

As there is no method reported in the literature for colour correction, modified reagents which do not cause a colour reaction had to be developed for SRP and NO_2^- analysis. The following methodology was developed by Adams (2009) in an unpublished Honours Dissertation. Using the same manifold, for each system it involved removing one constituent at a time from the reagent while leaving the conditions (pH, viscosity, ionic environment) of the new, non-reacting reagents as similar as possible to the original reagents. A series of standards and samples were then run to see if peaks were measured. If a peak was observed for a standard then a colour reaction must have taken place and another reagent was made removing a further constituent. This procedure was continued until no peaks occurred for the standards, but peaks were still observed in the samples.

A.4.2 Reagents for Colour Correction

- Colour Correction Reagent for SRP

250 mL of the background colour correction reagent was made by adding 30 mL concentrated sulphuric acid to approximately 200 mL helium de-gassed de-ionised water in a 250 mL volumetric flask. This was allowed to cool and then 1.67g ammonium sulphate was dissolved in the solution by stirring gently. The reagent was then made up to 250 mL with helium de-gassed de-ionised water and mixed gently.

The colour correction reagent was made with ammonium sulphate instead of ammonium molybdate and antimony potassium tartrate. This reagent replaced the acid molybdate reagent, with the ascorbic acid solution kept the same as the standard set-up.

- Colour Correction Reagent for NO_2^-

A 250 mL solution was made by adding 25 mL concentrated HCl to approximately 200 mL of helium de-gassed de-ionised water in a 250 mL volumetric flask and mixed gently before making up to volume with helium de-gassed de-ionised water. This colour correction reagent replaces the Griess reagent and does not contain sulphanilamide and n-1-napthylenediamine dihydrochloride.

A.5 Summary of Concentrations from Time Series

Table A1. Summary of mean, median and range of concentrations in N-draining catchments.

Parameter	Catchment	Mean	Median	Range
TOC (mg L^{-1})	456	17.9	15.3	4.8 – 47.5
	9A	13.2	11.4	4.2 – 30.3
	9D	11.0	10.0	5.4 – 24.4
	17	11.0	10.5	4.3 – 27.4
	17U	14.1	11.1	5.6 – 32.2
DOC (mg L^{-1})	456	13.3	12.0	3.7 – 41.4
	9A	11.4	10.7	3.5 – 28.5
	9D	8.7	8.0	2.9 – 22.4
	17	8.7	8.2	3.1 – 26.3
	17U	11.9	9.8	5.0 – 29.9
POC (mg L^{-1})	456	3.59	1.82	0.49 – 23.38
	9A	1.15	0.93	0.31 – 7.23
	9D	1.52	1.03	0.34 – 17.78
	17	1.19	1.07	0.46 – 1.86
	17U	2.22	1.24	0.50 – 16.56
Alkalinity (mg $CaCO_3$ L^{-1})	456	55.9	55.0	26.4 – 103.2
	9A	37.4	36.9	5.4 – 79.3
	9D	37.2	41.2	9.8 – 53.4
	17	N/A	N/A	N/A
	17U	52.4	53.4	15.5 – 100.7
TP (μg L^{-1})	456	70	62	6 – 255
	9A	34	24	3 – 152
	9D	35	25	3 – 155
	17	49	36	4 – 165
	17U	61	47	14 – 198
SRP (μg L^{-1})	456	27	20	3 – 149
	9A	13	12	1 – 41
	9D	13	10	2 – 68
	17	22	22	4 – 41
	17U	22	18	9 – 91
NO_3^- (mg L^{-1})	456	1.02	0.97	0.27 – 2.44
	9A	0.97	0.71	0.14 – 8.44
	9D	0.82	0.82	0.13 – 1.79
	17	1.12	1.04	0.52 – 1.82
	17U	0.80	0.79	0.31 – 1.55
NO_2^- (μg L^{-1})	456	19.2	14.4	0.2 – 91.6
	9A	7.4	5.6	0.7 – 61.4
	9D	4.6	3.9	0.1 – 26.7
	17	10.0	9.7	1.1 – 26.3
	17U	8.5	5.7	2.0 – 28.0

Table A2. Summary of mean, median and range of concentrations in S-draining catchments.

Parameter	Catchment	Mean	Median	Range
TOC (mg L^{-1})	13	31.1	28.3	13.5 – 59.1
	14	24.3	21.9	9.5 – 50.8
	15	29.8	27.5	9.9 – 55.5
	1	21.6	18.9	7.8 – 47.8
	1632	23.9	19.8	9.8 – 58.6
DOC (mg L^{-1})	13	27.3	25.6	7.7 – 57.1
	14	21.2	20.2	6.7 – 47.4
	15	26.9	25.5	6.6 – 50.3
	1	8.9	18.1	5.2 – 42.6
	1632	21.3	18.9	6.5 – 51.8
POC (mg L^{-1})	13	2.03	1.71	0.09 – 8.85
	14	1.65	1.22	0.44 – 6.45
	15	1.62	1.09	0.38 – 10.67
	1	1.60	1.25	0.34 – 8.95
	1632	1.63	1.06	0.38 – 8.03
Alkalinity (mg $CaCO_3$ L^{-1})	13	33.3	24.3	5.0 – 99.3
	14	26 2	24.8	6.9 – 50.4
	15	13.1	8.7	0.4 – 47.5
	1	36.6	31.4	1.7 – 84.3
	1632	28.1	23.6	7.0 – 70.3
TP (µg L^{-1})	13	101	96	6 – 328
	14	82	70	7 – 296
	15	45	40	3 – 128
	1	50	40	4 – 171
	1632	48	38	4 – 133
SRP (µg L^{-1})	13	59	53	3 – 164
	14	49	36	3 – 289
	15	27	22	1 – 122
	1	22	20	4 – 51
	1632	23	22	3 – 59
NO_3^- (mg L^{-1})	13	0.11	0.09	0.003 – 0.27
	14	0.21	0.19	0.02 – 0.61
	15	0.07	0.06	0.002 – 0.28
	1	0.28	0.26	0.05 – 0.63
	1632	0.19	0.18	0.01 – 0.88
NO_2^- (µg L^{-1})	13	5.9	5.1	0.1 – 18.6
	1	6.2	4.5	0.3 – 42.9
	15	4.8	3.4	0.3 – 16.4
	1	5.7	4.7	0.8 – 27.0
	1632	4.8	4.0	0.1 – 12.3

A.6 Uncertainties in [DOC] Calibration

A.6.1 Calculation of Standard Deviation of Unknown [DOC]

s_0, the standard deviation of an unknown [DOC], was calculated for each calibration of the Thermolux TOC analyser using the three equations below (*c.f.* Miller, 2006). From this the 95 % confidence interval could be calculated for x_0, the [DOC].

$$s_0 = \frac{s_{y/x}}{b}\left\{\frac{1}{m}+\frac{1}{n}+\frac{(y_0-\bar{y})^2}{b^2\sum_i (x_i-\bar{x})^2}\right\}^{\frac{1}{2}}$$

Equation A1. Calculation for s_0, the standard deviation of an unknown [DOC]. The term $s_{y/x}$ is defined by Equation A2. b is the gradient of the calibration line. m is the number of times the test material was measured. n is the number of points on the calibration graph. y_0 is the unknown [DOC] response as peak area. $\bar{y}$ is the mean calibration response in peak area. x_i is the [DOC] of the calibration standards. $\bar{x}$ is the mean [DOC] .

$$s_{y/x} = \left\{\sum_i \frac{(y_i-\hat{y}_i)^2}{n-2}\right\}^{\frac{1}{2}}$$

Equation A2. The term $s_{y/x}$ for Equation A1 is defined by this equation. y_i is the peak area of the calibration standards. $\hat{y}_i$ is the fitted y values.

$$\frac{t^2 s^2{}_{y/x}}{b^2\sum_i (x_i-\bar{x})^2} \le 0.05$$

Equation A3. Equation A1 is only valid if Equation A3 is true. t is t value taken at the required probability level and (n-2) degrees of freedom.

A.6.2 Worked Example

The following is a worked example of the calculation of s_0 using the calibration of the Thermolux TOC analyser for the batch of samples analysed on the 6th July 2009. 51 samples were run on this calibration and the calibration standards were in the 10 – 60 mg L^{-1} range. The data from this calibration are in Table A3 and Figure A16.

Table A3. Data of calibration graph for the Thermolux TOC analyser for 6th July 2009. $\hat{y}$ was generated in Minitab v.16 using the "predict" subcommand.

x_i, [DOC], mg L^{-1}	y_i, peak area	$\hat{y}$, fitted peak area
10	10432	9753
20	19480	21537
30	34546	33321
40	45640	45105
50	56977	56888
60	68201	68672

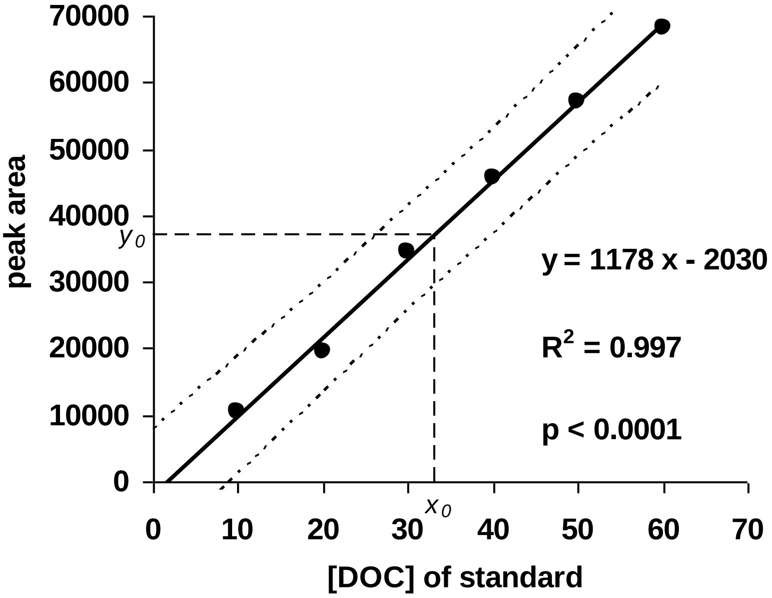

Figure A16. Calibration line of the Thermolux TOC analyser for 6th July 2009.

A.6.2.1 Equation A2 for Example Calibration

In order to carry out Equation 1, the term $s_{y/x}$ needed to be calculated (Equation). $s_{y/x}$ for this sample run is 1295.2.

$$s_{y/x} = \left\{ \frac{6709673.7}{6-2} \right\}^{\frac{1}{2}}$$

Equation A4. Equation A2 for calibration of Thermolux TOC analyser from 6th July 2009. y_i was the peak area of the calibration standards and $\hat{y}_i$ was the fitted y values as shown in Table A3.

A.6.2.2 Equation A1 for Example Calibration

Using $s_{y/x}$ as defined by Equation A4, s_0, the standard deviation of an unknown [DOC] could be calculated using Equation A1 (Equation A5). For example, an unknown [DOC] y_0 had a peak area recorded using this calibration was 37092, which has an s_0 of 1.19. The 95 % confidence limits for x_0 are thus 33.2 ± 3.3 mg L^{-1}.

$$s_0 = \frac{1295.2}{1178.4^2} \left\{ \frac{1}{1} + \frac{1}{6} + \frac{4497227}{1178.4^2 * 1750.0} \right\}^{\frac{1}{2}}$$

Equation A5. Calculation of s_0, the standard deviation of a peak area of 6336, the lowest recorded peak area on the sample run on the Thermolux TOC analyser on 6th July 2009.

A.6.2.3 Equation A3 for Example Calibration

$$\frac{2.78^2 * 1295.15^2}{1178.4^2 * 1750.0} \leq 0.05$$

Equation A6. Equation A3 for calibration of Thermolux TOC analyser from 6th July 2009 using the 2-tailed t-value for p = 0.05 and 4 degrees of freedom of 2.78.

The function in Equation A6 has the value 0.005, which is less than 0.05 which means that the approximation is valid and that the 95 % confidence intervals are good approximations.

A.7 Summary of Annual Exports

Table A4. Summary of annual exports for the N-draining catchments. Estimates of Q by Method 1 were used in the calculation of exports from catchments 456, 9A and 17. Estimates of Q by Method 2 were used in the calculation of exports from catchments 9D and 17U. Due to the differing storage methods of samples on return to the laboratory, the DOC and POC exports could only be calculated for three years from the hydrological year 2007. As sampling was discontinued at catchment 17 due to the construction upstream of a flood storage facility and 17U was added as an alternative to the discontinued sampling point in 2008, exports for these two catchments were calculated for two years only.

Parameter	Catchment	Year			
		2006-07	2007-08	2008-09	2009-10
TOC	456	17.8	14.4	19.0	17.9
(g C m^{-2} yr^{-1})	9A	18.0	11.7	16.0	11.2
	9D	12.6	13.1	13.9	12.1
	17	13.5	10.9	N/A	N/A
	17U	N/A	N/A	15.0	10.7
DOC	456	N/A	12.8	16.4	15.1
(g C m^{-2} yr^{-1})	9A	N/A	12.1	16.1	11.5
	9D	N/A	11.3	12.5	9.8
	17	N/A	9.8	N/A	N/A
	17U	N/A	N/A	13.0	9.0
POC	456	N/A	3.15	3.93	3.69
(g C m^{-2} yr^{-1})	9A	N/A	1.12	1.31	0.91
	9D	N/A	1.16	1.30	1.09
	17	N/A	1.12	N/A	N/A
	17U	N/A	N/A	1.92	1.73
TP	456	46.1	89.5	89.3	63.6
(mg P m^{-2} yr^{-1})	9A	32.6	44.7	41.4	25.1
	9D	38.5	60.9	36.6	28.7
	17	40.3	63.5	N/A	N/A
	17U	N/A	N/A	67.7	36.6
SRP	456	25.5	21.6	28.7	42.1
(mg P m^{-2} yr^{-1})	9A	27.4	23.2	29.9	20.7
	9D	20.1	19.2	14.0	12.3
	17	23.4	17.3	N/A	N/A
	17U	N/A	N/A	20.0	20.0
NO_3^-	456	1.64	1.50	0.88	0.94
(g N m^{-2} yr^{-1})	9A	1.08	0.97	0.89	0.74
	9D	1.51	0.97	0.89	0.81
	17	1.63	1.37	N/A	N/A
	17U	N/A	N/A	0.78	0.61

Table A5. Summary of annual exports for the S-draining catchments. Estimates of Q by Method 1 were used in the calculation of exports from catchments 15 and 1. Estimates of Q by Method 2 were used in the calculation of exports from catchments 13, 14 and 1632. Due to the differing storage methods of samples on return to the laboratory, the DOC and POC exports could only be calculated for three years from the hydrological year 2007.

Parameter	Catchment	Year			
		2006-07	2007-08	2008-09	2009-10
TOC (g C $m^{-2} yr^{-1}$)	13	38.5	44.0	44.9	35.3
	14	17.7	15.1	17.0	13.0
	15	34.2	29.3	36.5	28.3
	1	26.7	20.8	24.9	20.2
	1632	33.2	28.1	33.9	26.9
DOC (g C $m^{-2} yr^{-1}$)	13	N/A	40.6	42.3	33.7
	14	N/A	14.4	16.3	12.6
	15	N/A	28.1	34.7	26.9
	1	N/A	20.0	23.8	19.5
	1632	N/A	27.3	31.9	26.3
POC (g C $m^{-2} yr^{-1}$)	13	N/A	2.95	2.59	1.67
	14	N/A	0.98	1.05	0.80
	15	N/A	1.20	1.80	1.46
	1	N/A	1.58	1.89	1.45
	1632	N/A	1.87	2.59	1.46
TP (mg P $m^{-2} yr^{-1}$)	13	62.5	206.4	171.7	89.9
	14	47.8	69.2	50.7	29.8
	15	41.4	47.2	57.1	39.1
	1	49.3	77.7	58.7	40.7
	1632	52.1	80.2	70.7	45.2
SRP (mg P $m^{-2} yr^{-1}$)	13	32.9	100.7	104.4	56.6
	14	15.7	27.4	29.8	17.3
	15	30.5	30.5	51.7	39.0
	1	20.1	24.7	27.8	19.9
	1632	18.8	32.5	36.2	25.6
NO_3^- (g N $m^{-2} yr^{-1}$)	13	0.18	0.17	0.16	0.18
	14	0.21	0.09	0.13	0.11
	15	0.22	0.08	0.07	0.07
	1	0.45	0.42	0.28	0.25
	1632	0.36	0.40	0.23	0.23

A.8 Comparison of Annual Export Discharge Estimation Methods

Table A6. Comparison of annual exports for catchments 13, 14, 1632, 9D and 17U using the two different methods to estimate Q used in the calculation of export. Estimates of export calculated using Q from Method 1, scaling SEPA Q for catchment size, are the column labelled M1. Estimates of export calculated using Q from Method 2, using the relationship between SEPA Q and Isco Q, are in the column labelled M2. Due to the differing storage methods of samples on return to the laboratory, the DOC and POC exports could only be calculated for three years from the hydrological year 2007. 17U was added as an alternative to the discontinued sampling point 17 in 2008, so exports for this catchments were calculated for two years only.

Parameter	Catchment	Year							
		2006-07		2007-08		2008-09		2009-10	
		M1	M2	M1	M2	M1	M2	M1	M2
TOC (g C m^{-2} yr^{-1})	13	30.1	38.5	32.1	44.0	34.1	44.9	25.3	35.3
	14	28.5	17.7	24.4	15.1	27.3	17.0	21.3	13.0
	1632	28.2	33.2	23.3	28.1	29.2	33.9	21.3	26.9
	9D	12.1	12.6	10.0	13.1	11.4	13.9	9.1	12.1
	17U	N/A	N/A	N/A	N/A	16.6	12.4	10.1	10.7
DOC (g C m^{-2} yr^{-1})	13	N/A	N/A	30.1	40.6	32.2	42.3	24.5	33.7
	14	N/A	N/A	23.4	14.4	26.2	16.3	20.6	12.6
	1632	N/A	N/A	22.6	27.3	27.5	31.9	20.8	26.3
	9D	N/A	N/A	10.5	11.3	11.8	12.5	8.5	9.8
	17U	N/A	N/A	N/A	N/A	13.8	11.3	10.0	9.0
POC (g C m^{-2} yr^{-1})	13	N/A	N/A	2.13	2.95	1.92	2.59	1.18	1.67
	14	N/A	N/A	1.59	0.98	1.71	1.05	1.31	0.80
	1632	N/A	N/A	1.50	1.87	2.19	2.59	1.13	1.46
	9D	N/A	N/A	1.16	1.38	1.30	1.42	1.09	1.27
	17U	N/A	N/A	N/A	N/A	2.22	1.92	1.96	1.73
TP (mg P m^{-2} yr^{-1})	13	49	63	151	206	129	172	64	90
	14	77	48	113	69	82	51	50	30
	1632	43	52	65	80	57	71	34	45
	9D	38	39	54	61	34	37	24	29
	17U	N/A	N/A	N/A	N/A	73	68	42	37
SRP (mg P m^{-2} yr^{-1})	13	25	33	77	101	82	104	42	57
	14	25	16	45	27	49	30	30	17
	1632	16	19	27	33	31	36	20	26
	9D	16	20	16	19	13	14	11	12
	17U	N/A	N/A	N/A	N/A	22	20	18	16
NO_3^- (g N m^{-2} yr^{-1})	13	0.14	0.18	0.14	0.17	0.13	0.16	0.14	0.18
	14	0.34	0.21	0.14	0.09	0.21	0.13	0.18	0.11
	1632	0.30	0.36	0.35	0.40	0.20	0.23	0.19	0.23
	9D	1.36	1.51	0.89	0.97	0.81	0.89	0.67	0.81
	17U	N/A	N/A	N/A	N/A	0.84	0.78	0.69	0.61

A.9 Lists of GIS Files

Table A7. Raw data GIS files from external sources, grouped into catchment physiography and windfarm-related disturbance, including file type and a brief description of what data each file contains. ### indicates file name is followed by a unique file ID based on map tile numbering.

File	Type	Description	Source
Catchment Physiography			
Catchment Area			
asciito_ns###	raster	OS Landform DTM tiles (1:10,000)	www.digimap.com
Soil Type and HOST			
WhiteleeSoil	shapefile	polygons of the 13 soil type and the 13 HOST classes	Macaulay Land Use Research Institute
Land Use			
LandUse	shapefile	polygons of 11 land use classes covering all catchments	
Forestry	shapefile	polygons of forested areas	
ShortRotation	shapefile	polygons of short rotation forest areas	
Windfarm-Related Disturbance			
TurbineLocations	shapefile	pointfile of turbine locations, including peat depth and elevation	Scottish Power Renewables
BorrowPits	shapefile	polygons of borrow pit locations	Scottish Power Renewables
DevelopmentBoundary	shapefile	polyline indicating windfarm boundary	Scottish Power Renewables
AccessTracks	shapefile	polylines of windfarm access tracks (as-built)	Scottish Power Renewables
FelledAreasWindfarm	shapefile	polygons of clear-felled areas	Forestry Commission

Table A8. GIS data files created to derive catchment areas. # indicates file name is followed by a unique file ID based on catchment number.

File	Type	Description
dtmraster	raster	Digital terrain model covering Whitelee catchment areas
dtmfill	raster	Hydrologically correct topographic surface with sinks in DTM filled
flowdirofdtm	raster	Layer to determine direction of flow through each cell
flowaccum	raster	Layer to calculate the amount of water that flows into every cell from the uphill cells that drain through it
setnullflow	raster	Layer where accumulation values < 722.4 converted into no data, and the cells with the accumulated flow of > 722.4 assigned a value of one
strmnet	raster	Layer of stream network but all cells have the same value
strmlnk	raster	Each stream segment assigned a unique ID and short segments in this layer that did not connect other segments together were removed
strmorder	raster	Stream order assigned to segments using Strahler method
streamshape	shapefile	Polylines of stream network
strmgrp	raster	Layer with unique basin identifiers assigned to the streams
zonflowmax	raster	Layer of maximum accumulated flow within each basin
GPSlocations	shapefile	Point file of all sampling locations from GPS-derived grid coordinates supplemented with elevation data
WL#	shapefile	Point file showing an individual sampling point, required to define the catchments
catchment#	raster	Layer showing sampling point location so watershed tool could be used to delineate the catchment area
catch#	raster	Delineated catchment area
areacatch#	shapefile	Polygon feature containing the area of the catchment, flow length to the sampling point and grid co-ordinate of the sampling point

Table A9. Derived data GIS files, grouped into catchment physiography and windfarm-related disturbance, including file type and a brief description of what data each file contains. # indicates file name is followed by a unique file ID based on catchment number.

File	Type	Description
Catchment Physiography		
Soil Type and HOST	shapefile	Polygon feature of geometry of the catchment area with soil type and HOST in attribute table
Whitelee_soil_#		
Land Use	shapefile	Polygon feature of geometry of the catchment area with land class data in attribute table
LandUse_#		
Slope		
slope#	raster	DTM clipped to shape of Whitelee catchment areas
Reclass of slope #	layer	Standardised scale of slope classification to allow comparison between catchments
Windfarm-Related Disturbance		
AccessTracks_#	shapefile	Polylines of access track length in all catchments
#deforest	shapefile	Polygons of area deforested in all catchments

A.10 Dependent Variables for Multiple Linear Regression Analysis

Table A10. Median concentration and export used in multiple linear regression for low-disturbance phase. For the low-disturbance phase data from 23 sampling occasions used to calculate median concentrations and data from 14 months was used to calculate median export.

Catchment	TOC		SRP		TP		NO_3^-	
	Conc. mg L^{-1}	Export g m^{-2}	Conc. μg L^{-1}	Export mg m^{-2}	Conc. μg L^{-1}	Export mg m^{-2}	Conc. mg L^{-1}	Export g m^{-2}
13	23.5	2.23	16.2	1.20	21	2.94	0.08	0.01
14	20.2	1.32	15.5	1.50	28	3.16	0.23	0.01
1	25.9	3.80	20.2	1.32	22	2.66	0.10	0.02
1	19.4	1.66	14.4	1.05	27	1.95	0.26	0.02
1632	21.4	2.44	13.6	1.23	15	2.46	0.16	0.02
456	14.8	1.28	18.3	1.50	36	2.87	1.14	0.06
9A	13.2	1.89	12.4	1.53	19	3.15	0.55	0.07
9D	8.8	0.82	8.2	0.59	16	4.19	0.90	0.02

Table A11. Median concentration and export used in multiple linear regression for maximum-disturbance phase. For the maximum-disturbance phase data from 34 sampling occasions used to calculate median concentrations and data from 21 months was used to calculate median export.

Catchment	DOC		POC		TOC		SRP		TP		NO_3^-	
	Conc. mg L^{-1}	Export g m^{-2}	Conc. mg L^{-1}	Export g m^{-2}	Conc. mg L^{-1}	Export g m^{-2}	Conc. μg L^{-1}	Export mg m^{-2}	Conc. μg L^{-1}	Export mg m^{-2}	Conc. mg L^{-1}	Export g m^{-2}
13	25.9	2.01	1.85	0.12	27.9	2.18	73.3	5.24	127.7	14.9	0.13	0.01
14	23.0	1.99	1.17	0.07	21.4	1.17	50.7	2.15	92.0	4.82	0.16	0.01
15	23.4	3.02	1.03	0.16	27.4	3.08	21.6	3.17	50.6	6.00	0.08	0.01
1	16.5	1.40	1.25	0.11	18.9	1.42	23.6	1.97	63.0	4.04	0.28	0.02
1632	19.4	2.08	1.10	0.12	20.4	2.15	23.1	2.83	50.9	4.89	0.19	0.03
456	11.2	1.01	1.70	0.16	15.3	1.16	18.9	1.67	78.1	6.85	0.94	0.08
9A	10.7	1.64	0.93	0.14	11.9	1.74	11.2	1.64	39.1	4.55	0.79	0.13
9D	8.7	0.82	0.93	0.11	9.6	0.97	9.3	0.88	32.7	9.76	0.79	0.01