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**Organic carbon and  
nutrient export from  
disturbed peatlands**

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# The significance of organic carbon and nutrient export from peatland-dominated landscapes subject to disturbance

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## Abstract

The terrestrial-aquatic interface is a crucial environment in which to consider the fate of exported terrestrial carbon in the aquatic system. To a large extent the fate of dissolved organic carbon (DOC) may be controlled by nutrient availability. However, peat-dominated headwater catchments are normally considered of low nutrient status and thus there is little data on the interaction of DOC and nutrients. Here we present nutrient and DOC data exported from two UK catchments, both dominated by peat headwaters, but of differing land-use. Glen Dye is a moorland with no trees; Whitelee has partially forested peats and peaty podzols, and is now undergoing development to host Europe's largest on-shore windfarm, the Whitelee Windfarm. There are significant linear relationships between DOC and soluble reactive phosphorus and nitrate concentrations in the drainage waters, but inter-catchment differences exist. Changes in the pattern of nutrient and carbon export in Whitelee suggest that disturbance of peatlands soils can impact the receiving water and that nutrient export does not increase in a stoichiometric manner that will promote increase in biomass. As such the changes are more likely to cause increased aquatic respiration, and thus lead to higher dissolved CO<sub>2</sub> concentrations (and therefore CO<sub>2</sub> efflux). Hence disturbance of terrestrial carbon stores may also impact the gaseous carbon cycle. Confirming the source of carbon and nutrients in these study sites is not possible. However, nearby <sup>14</sup>C measurements are in keeping with other published literature values from similar sites which show C in DOM exported from peatlands is predominantly modern, and thus supports an interpretation that nutrients, additional to carbon, are derived from shallow soils. Estimates of organic carbon loss from Whitelee catchments to the drainage waters suggest a system where losses are approaching likely sequestration rates. We suggest such sequestration assessment should inform the decision-making tools required prior to development of terrestrial carbon stores.

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## 1 Introduction

Small order systems at the terrestrial-aquatic interface represent the first aquatic environment in which terrestrially-exported carbon can be recycled and are particularly interesting as they tend to be more hydrologically responsive, and less well buffered chemically than larger systems. Increasing dissolved organic carbon (DOC) export in freshwater drainage systems has been observed by several groups (Roulet and Moore, 2006), the cause of which has been subject to debate (e.g., Evans et al., 2002), but globally is strongly correlated with a decrease in atmospheric acid deposition (Monteith et al., 2007).

Freshwater bodies connect terrestrial C losses with the atmospheric carbon cycle through CO<sub>2</sub> production from heterotrophic respiration (e.g., Lennon, 2004) and uv-oxidation (e.g., Osburn et al., 2001) of exported DOC, resulting in CO<sub>2(aq)</sub> oversaturation and thus CO<sub>2</sub> efflux (Cole et al., 2007). Contemporaneous nutrient availability will influence that connectivity: availability of nutrients will support DOC fixation through bacterial and primary producer biomass production; without such nutrients, maintenance respiration is more likely the norm. Few studies of DOC export have considered contemporaneous nutrient availability. Our first aim here is to assess if there are relationships between DOC and nutrient export. We have chosen two contrasting Scottish field sites draining soils rich in carbon: Whitelee, a partially-forested peat and peaty-podzol ridge, now undergoing development to host Europe's largest on-shore windfarm (status at planning approval in summer 2006), the Whitelee Windfarm; for comparison, Glen Dye, a peaty-podzol dominated moorland with no trees, and comparatively little landscape management.

These are two interesting sites to compare nutrient status in receiving waters: in Whitelee the peatland is in the headwater of the catchments and thus can be quite far from sampling locations; in Glen Dye catchment sampling points are more intimately placed in the peatland and peaty podzols and attenuation of headwater imports should be less. Whitelee is additionally interesting as soil disturbance and extensive

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and on-going deforestation are required as part of the windfarm development. Whilst immediate and localised impacts can arise from the necessary development activities e.g., deforestation (Neal et al., 2004a, 2004b; Kortelainen et al., 2006), how far these impacts propagate to the larger catchment scale is unknown. Thus a second aim of this research is to assess whether impact of disturbance of the terrestrial carbon and nutrient stores can be detected outwith the immediate area of disturbance. In assessing this, budgets for organic carbon export from terrestrial carbon stores can be constructed, necessary to consider the sensitivity of landscapes, important in carbon sequestration, to disturbance.

## 2 Materials and methods

### 2.1 Study sites and sampling strategy

The following description of the Whitelee wind farm has been sourced from the environmental impact statement (EIS) prepared by Scottish Power for planning consent for the windfarm (CRE Energy, 2002). The wind farm will comprise 140 turbines erected over a 176 km<sup>2</sup> partially-forested moorland plateau (55°40'24 N, 4°16'00 W), in the central belt of Scotland, 22.5 km south of Glasgow (Fig. 1). The turbines should generate 322 MW of power, estimated to provide electricity for 150,000 to 20 0000 homes, and have an approved lifespan of 25 years. Predominant land use in this area is currently forestry, with rough grazing on the areas of open moorland, and more areas of improved pasture and arable land on the lower slopes north of the east-west drainage divide. The windfarm is mostly located in appreciable areas of peat, underlain by a clay seal and weakly permeable igneous or moderately permeable sedimentary rocks. Peat depth, measured at 161 locations across the site ranges from five to over 500 cm, mean depth of 190 cm ( $\pm 1$  S.D. 134.7 cm).

All of the peatlands within the development area are classified as blanket bog. There are no raised bogs, but in several locations the blanket bog displays features that

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are associated with intermediate bogs. Here the peat deposit is comparatively deep (>4.5 m) and there are a number of large *sphagnum*-dominated pools and lawns, which contain several species of *Sphagna*, in contrast with the surrounding drier, heather-dominated, less species rich *Calluna vulgaris*-*Eriophorum vaginatum* vegetation.

5 Only 35 ha (3.5%) of the unforested blanket bog can be classified as primary natural bog. The remainder has been impacted, mostly due to plantation of the Whitelee forest, a first rotation plantation of 5917 ha of mainly Sitka spruce, established between 1962–1992 and ranging in altitude from 220 to 376 m. Within the forest, most of the bog exhibits varying degrees of surface drying and damage to the bog surface. In areas  
10 where tree growth has closed the forest canopy, the original bog vegetation has generally been highly modified or lost completely. The bog surface is dry from the dewatering effect of forestry drainage and there is often evidence of oxidative wastage. For the windfarm, deforestation of 1042 ha and changes to the management of 1999 ha (e.g., short rotation planting) of forestry is required, thus deeper soils would be expected to  
15 become exposed and subject to run-off loss of nutrients.

Outwith the forest and unmodified peatland, acid grassland habitat and rush pastures are found. Acid grassland habitat is one of the most common British upland semi-natural habitats, and comprises of several vegetation communities and transitional groups including those dominated by wavy-hair grass (*Deschampsia flexuosa*),  
20 mat grass (*Nardus stricta*) and purple moor grass (*Molinia caerulea*). There are several NVC communities of marshy grassland present within the site; collectively they can be termed 'rush pasture', again a common habitat in the UK, occurring on poorly drained, usually acidic soils in lowland areas that receive high rainfall.

25 Planning was approved in May 2006. Construction of 140 turbines on peat deposits up to 5 m deep, will require excavation of 300 000 m<sup>3</sup> of peat, road construction (and thus drainage) and felling of 3041 ha of forest. In October 2006 construction of the spine road to connect the site E-W started. Deforestation commenced in winter 2006, but in adherence to Forest and Water guidelines for best practice (Forestry Commission, 1993), will be undertaken as isolated coups. Deforestation required for immediate

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turbine operation is scheduled until the end of 2007, with continued management of the forest (to avoid air flow impedance) and non-windfarm related deforestation beyond the end of construction. Quarrying on-site for hardcore created borrow pits in which peat excavated during construction activities will be stored until later landscaping. The windfarm is proposed to be operational in November 2008, and at present, there is a scoping exercise being undertaken prior to a second planning application to extend the windfarm by 78 turbines (218 in total). Thus this terrestrial carbon store will continue to be managed beyond the immediate period of first phase windfarm construction.

We commenced sampling of the receiving waters from Whitelee windfarm after planning approval had been announced. Thus the data presented in Figs. 3 to 7 comprises a period of collection prior to disturbance of surface soils associated with Whitelee construction. We divided the Whitelee ridge into nine drainage catchments (Fig. 1, catchment sizes given in the legend), with only two catchments nested (WL9D and WL9A are nested in WL17). A topographic ridge splits these drainage catchments into north- and south-draining catchments (hereafter termed N-draining and S-draining respectively). We know localised impact associated with felling may occur (Neal et al., 2004a, 2004b), but given the scale of this development we wished to assess how far downstream such impact, if occurring, may propagate. Hence the catchment sampling points were outwith the site development boundaries. All catchments were sampled in one day, approximately every three weeks. We do not yet know what diatom or algal communities are present in the Whitelee drainage systems, but unlike Glen Dye, negligible colonisation by algal communities was observed during sampling trips. A contributory factor here may be the high colouration of the water limiting light penetration.

Glen Dye (56°56'27 N, 2°36'00 W), a headwater sub-catchment of the River Dee in NE Scotland, is predominantly upland in character, with an altitude range from 100–580 m. Detailed diagrams of topography and sampling points, soil coverage, geology and landuse of the Glen Dye catchment are available (Waldron et al., 2007b). The climate is cool and wet, with an estimated mean annual precipitation of 1130 mm which

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mainly falls as rain, though snow does occur during the winter months (generally <10% of annual precipitation) and snow pack accumulation can occur in cold years. Water balance estimates suggest annual evaporation rates of ca. 300 mm.

The Water of Dye drains a granite-dominated area, although there is a small outcrop of schist in its headwaters. The catchment is characterised by extensive plateau areas on the interfluvies above 450 m that are dominated by peats (up to 5 m deep) and peaty podzols (<1 m deep). Only on the more incised catchment slopes do the most freely-draining humus iron podzols (<1 m deep) occur and the main river valley bottoms generally have freely draining alluvial deposits and soils.

Land use is largely restricted to sheep grazing, and grouse (*Lagopus lagopus*) and Red deer (*Cervus elaphus*) shooting on heather moorland in the upper reaches of the basins. The moorlands are managed by regular burning to retain the mosaic of habitats required by grouse. The long history of burning may have contributed to peat erosion, as the peat is degraded and hagged in some places (Thompson et al., 2001). This results in a high density of ephemeral drainage channels covering the peat, connecting it to the perennial stream channel network. In some places erosion extends to the organo-mineral interface, allowing seepage into the underlying parent material and bedrock.

Data presented are for samples collected from two nested catchment scales within the Water of Dye: at 1.3 km<sup>2</sup> from Brocky Burn, a second order river system draining the hillslope peats and at 41.7 km<sup>2</sup> on the Water of Dye. Brocky Burn, approximately 2.7 km long and a maximum of 1 m wide, is a tributary of the Water of Dye (Dawson et al., 2001). The stream slopes are seasonally densely vegetated, predominantly with bracken (*Pteridium aquilinum*). The Water of Dye at Charr flume is a 4th order channel with extensive riffles and pool habitats and is circa 10 m wide. Bracken co-exists with heather at Charr, and there is little riparian vegetation. The catchment at Charr comprises peatland and alluvial deposits.

At low flows the depth of water at the sampling sites is usually no greater than 50 cm, and water can be coloured, but the particulate load is low (Waldron, unpublished data).

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Light penetration supports diatom and algal community growth on bedrock and boulders in the river channel, with species typically present including the diatoms *Hantzschia arcus* and *Navicula/Nitzschia* (common at 41.7 km<sup>2</sup>); *Tabellaria* and *Meridion* in 1.3 km<sup>2</sup>; and filamentous algae such as *Microspora* and *Stigeoclonium* at all sites.

## 5 2.2 Stoichiometric and isotopic characterisation of [DOC] and [POC]

One litre water samples were collected in polyethylene bottles, and stored cool until they could be frozen (usually within 24 h) to await analysis. When ready for analysis (usually within one week), the sample was defrosted, filtered through a pre-combusted GF/F filter (0.7 µm), and reduced to a concentrate by rotary evaporation (at 50°C, and 50 mbar). Where carbonate was likely to be present in the samples, the filtrate was acidified to pH 4 with 0.1M H<sub>2</sub>SO<sub>4</sub> prior to rotary evaporation. The concentrate was subsequently freeze-dried to a powder. δ<sup>13</sup>C, wt.% C and wt.% N were assayed by analysis of circa 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). With the volume of sample filtered, and mass of solid residue and the wt% C and N known, the DOC and total dissolved nitrogen concentrations, [DOC] and [TDN], could be calculated. [POC] was calculated by assuming 60% of the loss on ignition that occurred after ashing of oven-dried (105°C) filter papers at 375°C for 16 h was carbon.

## 20 2.3 Nutrient analysis

Upon return from the field all samples were stored at 4°C until and during analyses. Samples were analysed for three phosphate fractions: reactive orthophosphate, acid-hydrolysable phosphate and total phosphate (TP). Additionally from the Whitelee samples only, nitrate, nitrite and ammonium were characterised. Soluble reactive phosphorus (SRP) was the priority analyte on return from the field. N species were measured immediately afterwards (usually the next day). As total P required digest of all sample

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and vapour losses are not an issue, this was carried out at a convenient time later (for some samples up to one year after collection). Gaps exist in the data set for other than [TP] due to a number of reasons e.g., logistical difficulties in analyzing the samples quickly enough on return from the field to be confident that the measured concentration accurately represented field concentrations.

Prior to the measurement of SRP, nitrate-N, nitrite-N and ammonium-N samples were filtered through a 0.2  $\mu\text{m}$  Supor membrane filter. Samples for total hydrolysable P (THP) and TP were digested without filtration. All analyses were carried out colorimetrically using a Technicon Autoanalyser II system using a method adapted for low level analysis. SRP was measured using an ammonium molybdate-ascorbic acid method with a limit of quantification of 1  $\mu\text{g P/litre}$ . Samples for hydrolysable P and TP were digested with sulphuric-nitric acid and potassium persulphate-sulphuric acid mixtures, respectively, in an autoclave at 121°C for 30 min (Clesceri et al., 1998) prior to analysis by the method used for SRP.

Total oxidised nitrogen was analysed using a Cu-Hydrazine reduction method to reduce nitrate to nitrite, subsequently measured by the Griess Ilosvay method. Nitrite was measured directly using the Griess Ilosvay reaction and nitrate calculated by subtraction. Limits of quantification for nitrate and nitrite were 10  $\mu\text{g N per litre}$  and 1  $\mu\text{g N per litre}$  respectively. Nitrite data is not presented here.

Contemporaneous water samples for nutrient analysis were collected from Whitelee. However, the significance of nutrients to the fate of exported DOC was not considered at the time of Glen Dye sample collection, and thus for Glen Dye samples, nutrient analyses were carried out on waters of known [DOC] by redissolution of the freeze-dried sample residue in distilled water.

The Whitelee catchments are currently ungauged. However, a Scottish Environment Protection Agency gauging station records discharge on the River Irvine at the town of Newmilns (circa 3 km west of WL1). The area of the Whitelee site is sufficiently small that the flow regimes of the ungauged catchments will be broadly similar to the River Irvine and thus we have used this as a proxy for sub-catchment discharge. Comparison

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of sampling dates with specific discharge from the R. Irvine shows that sampling was carried out during both base flow and wetter periods (Fig. 2). Hydrological events were not targeted. The hydrographic profile for Brocky for the sampling period can be found in Waldron et al., 2007b. The DOM powder aliquots used for nutrient analyses were chosen to span the range of flow conditions.

Statistical analyses were carried using Minitab V 15, based on general linear models, under the assumption of normality, which was tested.

### 3 Results

Whitelee [DOC] ranges from 3.5 mg C/L (WL9A on 5 February 2007) to 40.1 mg C/L (WL15 on 17 July 2007) (Fig. 3a). Brocky [DOC] ranges from 7 to 29.9 mg C/L (Fig. 5A) for the samples from which nutrient concentrations have also been shown, although it can be higher than this (unpublished data, Waldron; Dawson et al., 2004). Whilst each sample is a “snapshot” of DOC export and there may be considerable variation between samples depending on hydrological conditions (Grieve, 1994), this seasonal pattern of changing concentrations is observed elsewhere (e.g., Billett et al., 2004; Worrall et al., 2006), with highest concentrations in catchment outflow at the end of summer, after peak terrestrial productivity and strongly influenced by increased hydrological export (Tipping et al., 2007). Early summer 2007 was particularly wet in the UK (Fig. 2) and thus increased [DOC] commences earlier. For all sampling occasions, [DOC] in S-draining Whitelee catchments is greater than the N-draining catchments. In Whitelee we are not sampling headwater drainage systems or targeting event export, yet [DOC] is significantly higher than many other non-headwater UK drainage systems (e.g., Worrall et al., 2004; Evans et al., 2007; Baker et al., 2007). [DOC] in S-draining catchments is comparable to that observed in smaller headwater catchments intimately connected with the peat landscape (e.g., the Brocky data; Dawson et al., 2004; Worrall et al., 2006; Dawson and Smith, 2007), but not as high as [DOC] in drainage waters from Auchencorth Moss: mean of 38.6 mg C/L<sup>-1</sup> (Billett et al., 2004). Auchencorth

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is a 3.5 km<sup>2</sup> lowland ombrotrophic raised bog only 25 km ENE from Whitelee. The catchment is smaller than the Whitelee catchments and slope gradient is shallower, thus water residence time may be longer. Both these differences may result in higher [C] in drainage waters. However, Auchencorth Moss is also subject to disturbance: peat harvest occurs in 8% of the catchment and the extent to which this influences [DOC] export is unknown (Billett et al., 2004). Notably, further disturbance will occur if the planning application under consideration to mount a 45 MW windfarm (submitted February 2006) on this site is approved.

Whitelee [POC] ranges from 0.41 mg C/L (WL15 on 19 February 2007) to 23.66 mg C/L (WL15 on 4 September 2007) (Fig. 3b). [POC] shows similar seasonality with enhanced export at times of high [DOC] export likely reflecting a hydrological control. Until June 2007, [POC] is comparable between N- and S-draining catchments. After June 2007, there is separation between N- and S-draining catchments, with [POC] higher in the S-draining catchments than the N-draining catchments.

[TP] ranges from 2 µg P/L (WL9D on 23 March 2007) to 165 µg P/L (WL17 on 5 September 2006) (Fig. 4). Whitelee [TP] shows a similar pattern as [DOC], with higher concentration in the summer months, but an offset in [TP] between N- and S-draining catchments occurs less often. As defined by [TP], the trophic status of the Whitelee drainage waters shows variation from mesotrophic (10–≤35 µg/L), to eutrophic (>35–≤100 µg/L) or hypertrophic (>100 µg/L). [TP] for the Brocky samples is generally in the oligotrophic range: 4.0 to 12.7 µg P/L, with median [TP] of 7.4 µg P/L. However, unlike Whitelee, [TP] has been measured from 0.7 µm filtered sample residues. If a similar field relationship exists between filtered and non-filtered samples as observed in Whitelee, Brocky field [TP] may be up to 50% greater, and thus of trophic status straddling the oligotrophic-mesotrophic boundary.

[SRP] is not given as a time series, but shown in relation to [DOC]. For all field sites there are statistically significant relationships between [DOC] and [SRP] (Fig. 5a). These relationships are also catchment specific, with more SRP exported for a given [DOC] in N-draining Whitelee, than S-draining Whitelee than Brocky (the slope of

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the line decreases). As with [SRP], statistically significant relationships exist between [DOC] and [TP] for Whitelee (a similar comparison is not undertaken for Brocky given the difference in sample matrix): Whitelee north:  $[TP]=3.35[DOC]+3.98$ ,  $R^2=0.219$ ,  $F_{1,82}=24.26$ ,  $p<0.0001$ ; Whitelee south:  $[TP]=1.77[DOC]-0.03$ ,  $R^2=0.298$ ,  $F_{1,105}=46.03$ ,  $p<0.0001$ . These relationships may be statistically less significant than observed with [DOC]–[SRP] as the TP pool includes a particulate contribution, and thus different sources influence the concentrations of the two pools.

Whilst Whitelee data exists for nitrite and ammonium, interpretation of these export profiles is the subject of another study and will not be discussed here. Rather we focus on the quantitatively most important inorganic nitrogen pool nitrate, ( $\text{NO}_3^{2-}$ ). Whitelee  $[\text{NO}_3^{2-}]$  ranges from 0.1 mg N/L (multiple sites on multiple dates) to 1.9 mg N/L (WL9A on 5 February 2007) (Fig. 5b).  $[\text{NO}_3^{2-}]$  export data does not exist for Brocky.  $[\text{NO}_3^{2-}]$  mostly remains distinct between Whitelee N- and S-draining catchments, but the trend is reversed in comparison to [DOC], with  $[\text{NO}_3^{2-}]$  greater in N- than S-draining catchments. The statistically significant relationships between [DOC] and  $[\text{NO}_3^{2-}]$  show inverse correlation, i.e. increased [DOC] is associated with decreased  $[\text{NO}_3^{2-}]$ , and vice versa (Fig. 5).

Figure 6 shows molar C:P (calculated using TOC and TP) and molar C:N (calculated using TP and TDN) for the N- and S-draining Whitelee catchments. Whilst nitrate, nitrite and ammonium and SRP are the nutrient forms immediately available to bacteria without any extracellular processing, when orthophosphate is limiting, all osmotrophic organisms can supplement their P uptake by efficient hydrolysis of DOP compounds (Lovdal et al., 2007) and similarly organic nitrogen can be used as a metabolic source (Lennon and Pfaff, 2005). For these reasons, our stoichiometric ratios are shown as carbon vs. TP and TDN, pools which include both biologically available inorganic and organic components.

There is considerable temporal variability with molar C:P ranging from 227 (WL9A, 20 February 2007) to 6678 (WL1, 4 April 2007), and molar C:N ranging from 3 (mul-

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5 tiple sites, multiple dates) to 50 (WL15, 12 October 2006). Spatial variability between  
the N- and S-draining Whitelee catchments is less marked, although the S-draining  
catchments generally have lower molar C:P than the N-draining. These stoichiomet-  
ric ratios are similar to ranges previously observed by Kortelainen et al. (2006) from  
10 a range of Finnish catchments also with varying % peatland. The seasonal export  
pattern apparent with [DOC] and to a lesser extent [TP] is not discernible. Catchment  
specific differences are maintained with C:N; the S-draining catchments have always  
greater C:N and, whilst there is variation between catchments, there is a suggestion  
that C:N is higher in summer and autumn, than spring. Both molar C:P and molar  
15 C:N are shown relative to these estimated molar ratios of microbial biomass (Cross et  
al., 2005). We have chosen this stoichiometric yardstick rather than the Redfield ratio  
as primary production over the year of sampling appeared insignificant. Whilst there  
may be a trend for a gradual rise in C:P from June 2006 until May 2007, this seems to  
reverse afterwards to produce compositions that are more similar to microbial stioichio-  
metric requirements. In comparison, there is a sustained difference in C:N between N  
and S draining catchments, with N draining catchments having compositions compara-  
ble to bacterial stioichiometry .

## 4 Discussion

20 This discussion will focus on the Whitelee catchments, with reference to the Brocky  
catchment when comparison with a more pristine peat moorland is required. Recent  
publications successfully document landscape controls on aquatic carbon and nutrient  
export (e.g., Smart et al., 2005; Kortelainen et al., 2006). However, a Geographic In-  
formation System based analysis of landscape controls on carbon and nutrient export  
from Whitelee currently forms part of recently-started doctoral research programme  
25 and is thus not included here. Rather we focus this discussion on our previously  
outlined aims:

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i) The interaction between DOC and nutrient export: The statistically significant relationships between [P] and [DOC] suggests that the source of P is closely linked to the DOC source, and/or they share the same export mechanism. The inverse linear relationship between [DOC] and  $[\text{NO}_3^{2-}]$  suggests that the same is not true for nitrate.

5 Increased rock outcrop and steeper slope can positively influence nitrate concentrations in stream waters (Smart et al., 2005). These landscape characteristics are not conducive to peat formation, which positively influences [DOC] in drainage waters (e.g., Kortelainen et al., 2006), thus an inverse linear relationship between nitrate and [DOC] is unsurprising. A limited supply of nitrate (as controlled by these landscape characteristics) diluted by run-off with higher [DOC] during higher flow, could give rise to negative linear relationships. However, the N-draining catchments, which have less peat and more farm- than forested-land, have consistently higher  $[\text{NO}_3^{2-}]$  in drainage waters (Fig. 5b), suggesting this negative relationship reflects catchment specific differences in baseline  $[\text{NO}_3^{2-}]$  rather than dilution of a fixed source.

15 The linear relationships between [DOC] and [P] indicate that as DOC export increases, so too does P export, although inter-catchment differences exists: for a given amount of C, Brocky, the headwater catchment (most intimately connected in the peat landscape) exports least P, whilst in the Whitelee N-draining catchments, where there is least peatland, more P is exported. Observing nutrient-DOC interaction across three different geographic regions suggests similar responses may be found elsewhere, indeed Kortelainen et al. (2006) also observed highly significant relationships between TOC and TP and TN (particularly TON) export, but not the inverse relationship with N that we document. Thus new catchment studies should be approached with the view that the stoichiometric composition of DOM cannot be assumed from existing work and will require individual catchment assessment.

25 Catchment drainage systems are important sources of atmospheric  $\text{CO}_2$  (Cole et al., 2007) and greater [DOC] can fuel higher  $\text{CO}_2$  efflux. For example, respiration from freshwater microbial communities over a 3 to  $16.8 \text{ mg C l}^{-1}$  DOC gradient (less than the Whitelee range), increased linearly with increased [DOC] regardless of differences in

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the source (and thus inferred quality) of the DOM (Lennon and Pfaff, 2005). Despite the complexity of carbon and nutrient interaction in surface waters – for example, in addition to the quality of source input, bacterial production will be influenced by community structure and environmental conditions, such as temperature (Lennon and Pfaff, 2005) – ecological stoichiometrical theory would predict that potential for the DOC load to be respired to  $\text{CO}_2$  will be strongly influenced by the availability of P and N, as the latter are requisite for biomass production. Although trophic status of the Whitelee receiving waters is high (Fig. 4), DOC is in excess to microbial requirements (Fig. 6) and thus excess C and increases in [DOC] may allow and enhance respiration respectively. Temporal variation in the stoichiometric composition of Whitelee may similarly cause temporal variation in  $\text{CO}_2$  efflux. For example, in the S-draining catchments increase in [TP] but decrease in [DOC] (reflected by a decrease in molar C:P) since 17 June 2007 may result in lower  $\text{CO}_2$  efflux. For Whitelee the inferred stoichiometric influence on  $\text{CO}_2$  efflux suggests larger intra-catchment variation than exists between the pooled N- and S-draining catchments.

Understanding the mechanism for significant linear relationships between [DOC] and [P] and [N] would be greatly enhanced by an ability to identify the source of nutrients. Primary production can convert atmospheric inorganic C to organic C. Bacterial atmospheric nitrogen fixation is possible, but not likely important in Whitelee. Thus the only mechanisms for P and N transfer to the receiving waters are from catchment runoff, or directly by aerial deposition, and Whitelee is sufficiently small to assume that aerial deposition will be broadly similar across the catchments. Flow pathways from terrestrial reservoirs to drainage waters have complexities of scale (from micropores to peatland piping (e.g., Holden, 2005), thus in catchment scale studies, pin-pointing the exact source of an allochthonous analyte is challenging. The positive correlations with [DOC] and [P] and the negative correlation with  $[\text{NO}_3^{2-}]$  provide circumstantial evidence that DOC and P share a common source, but not DOC and  $\text{NO}_3^{2-}$ . P has no naturally occurring isotopes. However, isotopic characterisation of DOC allows an assessment of whether primary production produces sufficient DOC to significantly alter

the allochthonous terrestrial DOC signal, and if not, whether the DOC pool is young, particularly meaningful for a site subject to disturbance such as Whitelee, as it may indicate C export from older deeper terrestrial stores.

$\delta^{13}\text{C}_{\text{DOC}}$  showed little intra-site variation in composition (all Whitelee data:  $-29.1 \pm 0.3$ ,  $n=208$ , all Brocky data:  $-27.7 \pm 0.3$ ,  $n=21$ ), but inter-site differences are apparent. The more  $^{13}\text{C}$ -enriched DOC in Glen Dye drainage water may reflect a peat source material with a higher degree of humification (Kalbitz and Geyer, 2002), or simply differences in source material isotopic composition e.g., in Whitelee conifer litter will contribute to the DOM pool. However,  $\delta^{13}\text{C}_{\text{DOC}}$  from both sites is within the range typical of terrestrially-derived carbon. Thus either autochthonous carbon (if such a pool can be isolated from a river) has a similar isotopic signature, or  $\delta^{13}\text{C}_{\text{DOC}}$  primarily represents DOC of dominantly allochthonous origin. With little evidence of primary production in the Whitelee catchments during the year of sampling, the latter seems most probable. We do not have  $\Delta^{14}\text{C}_{\text{DOC}}$  for the Whitelee or Glen Dye sites for which there exists accompanying nutrient data. However, previously published measurements of Brocky (Glen Dye)  $\Delta^{14}\text{C}_{\text{DOC}}$  sampled on two different occasions in 1998 show the stream DOC to be dominated by young carbon (Palmer et al., 2001). Sampling of the Water of Dye, into which Brocky drains circa one km downstream, in 2004 on the falling limb of a hydrological event also shows the DOC exported is young (Table 1):  $\Delta^{14}\text{C}_{\text{DOC}}$  indicates the composition to be modern either from DOC produced from organic material deposited circa 1996, or from mixing of significantly older carbon with post-1950s' carbon, such that by mass balance, the pool signature is still modern. DOC from other peat drainage streams under non-baseflow conditions also shares a "modern" signature (Evans et al., 2007; Billett et al., 2007), with a similar range in age observed between low and high flow samples as we observed between Brocky sampled in 1998 (Palmer et al., 2001) and its receiving stream under high flow in 2004. Indeed it has been noted that DOC exported from C-rich landscapes appears younger than the soil C itself, much of it comprising C assimilated post-1950s (Evans et al., 2007). Thus whilst we do not have  $\Delta^{14}\text{C}_{\text{DOC}}$  of the samples which were analysed for nutrients, the sim-

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ilarity of  $\Delta^{14}\text{C}_{\text{DOC}}$  between different UK peatland streams sampled over considerable temporal and spatial scales may offer a more generic interpretation as to the source of DOC: although translocation of DOC within peatlands can give rise to young DOM in pores of older peats (Chasar et al., 2000), the DOM pool largely derives from younger and shallower peats.

Given this, and as there exists a linear relationship between P and DOC export for all sites, we infer that the source of riverine P and DOC is also from shallow soils. Thus disturbance to the soil may be expected to change concentrations of carbon and nutrient export (as a larger surface area may be exposed). However, unless older layers are disturbed which may contain more recalcitrant C and have stoichiometrically higher C:P (or C:N), there may not be much change in the quality of the DOM.

ii) is the impact of disturbance of the terrestrial carbon and nutrient stores detectable outwith the immediate area of disturbance? Despite best practice (Forestry Commission, 1993), clear-felling of forest and the peat disturbance, compaction and dewatering arising from turbine and road construction would be predicted to impact run-off and nutrient dynamics (e.g., Neal et al., 2004b). For example, timber-felling on peaty-mineral soils generally leads to an increase in streamwater [DOC] which may persist for a few years, especially at a local scale (Neal, 2004; Neal et al., 2004a, 2004b); when clear-felled (vs. phased felling), nitrate concentration can be significantly higher in run-off for several years after deforestation (Neal et al., 2004b); increases in phosphorus appear more localised (Neal, 2004), except where, as with the some Whitelee catchments, gley soils are present (Neal et al., 2004a). In Whitelee, the N-draining catchments have proportionally less disturbance scheduled than the S-draining catchments. We hypothesise that an offset in [DOC], [POC] and [P, N] in the run-off waters exists between N- and S-draining catchments due to differences in catchment characteristics and thus, if all remained equal between catchments, then the catchment offset should also remain broadly equal with time. This hypothesis is not supported by our observations.  $\Delta[\text{DOC}]$  between N- and S-draining catchments appears to increase circa April

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2007 (Fig. 3a); a similar response is observed in  $\Delta[\text{POC}]$  from July 2007 (Fig. 3b). Additionally, although both N- and S-draining Whitelee catchments periodically exhibit hypertrophic P status, the trend since June 2007 when S-draining now surpassed N-draining catchments in  $[\text{TP}]$  (and  $[\text{SRP}]$ , time series data not shown), is consistent with a projected steady increase in  $[\text{TP}]$ . We do not observe the same switch in relative export with nitrate. The stoichiometry of the export waters suggests the DOM pool is more limited in P than N, thus consumption of  $\text{NO}_3^{2-}$  is not likely the primary cause for lack of concomitant increase in  $[\text{NO}_3^{2-}]$ . Rather lack of change in catchment drainage  $[\text{NO}_3^{2-}]$  further supports an interpretation that soil profiles disturbed by development and/or new flow pathways accessed that promote the increase in C and P export, are less important to nitrate delivery.

Spine road construction across the peatland commenced in late autumn 2006. Deforestation for construction of turbine foundations or for clearance to overcome wind impedance began in early 2007 and is-ongoing. Whilst the time series we present here spanning before and after the start of the disturbance are short, these time series do not support the null hypothesis of no detectable changes in export patterns between catchments, and thus suggest changes in flow pathways through soil horizons previously less accessible, such as would occur after deforestation/peat disturbance. These changes are detectable downstream of the zone of disturbance. The lag in impact on the receiving waters with respect to the Whitelee development may reflect continued disturbance propagating downstream with time as buffering capacity upstream decreases or simply greater hydrological connectivity with wetter conditions. As with the Whitelee development, this research programme is on-going and thus will allow us to assess the validity of this inference.

iii) to investigate, through construction of budgets for organic carbon export from terrestrial carbon stores, how sensitive landscape carbon sequestration is to disturbance. As carbon trading markets grow, carbon sequestered naturally – “carbon landscapes” – will become more important such that the scientific discipline of carbon geomorphology

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is predicted to emerge from cross-disciplinary research to form a coherent subject in its own right (Kelly, 2007). Aquatic C loss from undisturbed peatland systems can be as large as net gaseous C loss to the atmosphere (Rivers et al., 1998; Waddington and Roulet, 2000; Billett et al., 2004) and is likely to be exacerbated by the activities associated with peatland development. Ultimately, anthropogenic activity such as this may shift the “delicate” (Rivers et al., 1998) C balance in the peatland to one of net carbon loss rather than gain. We must assess how easily this balance is tipped. Research initiatives that allow the sensitivity of a natural carbon store to be assessed have value, particularly for supporting decision-making processes that involve disturbance of these often slow-forming terrestrial C stores. From almost bi-monthly time series of nutrient export we are able to estimate total fluxes for DOC, POC and TP for each Whitelee catchment (Table 2). To do this we have made the following assumptions:

1. that mean specific discharge (Fig. 2) for the nearest gauging station scaled for each catchment, appropriately describes discharge in each of the study catchments;
2. that the change in the determinant of interest between sampling periods is linear.

Assuming linear change may over-estimate concentration, but this will be somewhat balanced by missing detail of enhanced concentrations that are associated with event flow (e.g., Jordan et al., 2007). Further, preliminary spatial survey of WL1632 and WL1 showed either constancy in [DOC] (under high flow), or a decrease by 5 to 40 mg C/L from close to the head of the catchment to sampling (Ross, 2008). Thus, using the lower catchment outlet concentration to be representative of losses throughout the catchment will generally under-estimate loss and whilst the above assumptions are unlikely to hold completely, particularly the latter, our approach is conservative and sufficiently robust for preliminary estimates of flux (which can be revisited as the Whitelee catchments are gauged as part of our on-going research programme).

We have no evidence to support the interpretation that a significant component of the DOC is autochthonous in origin,  $\delta^{13}\text{C}_{\text{DOC}}$  shows little variation and is typical of al-

lochthonous OM), thus assuming Whitelee OC export primarily represent loss from the terrestrial catchment is reasonable. From this perspective, between 11.7 and 25.5 g C m<sup>2</sup>yr<sup>-1</sup> is lost to the receiving waters, similar to smaller peat-dominated headwater catchments (Fig. 7). There is little data for catchments the size of Whitelee; we tend to focus as a community on headwaters catchments or large river basins, and study few meso-scale basins. For similar sized catchments for which there is data, only Moorhouse in the Pennine Hills of northern England and with 90% peat cover exports more carbon than the Whitelee sites. [DOC] is documented to increase with % peat coverage (e.g., Kortelainen et al., 2006), and thus we may infer that the smaller OC export from Whitelee reflects proportionally less peat in the catchment, an interpretation further supported by the offset in C export between N and S draining catchments.

Little data exists on C sequestration rates in UK peatlands. That which does shows a range of approx 5–50 g C m<sup>2</sup>yr<sup>-1</sup> (e.g., Dawson and Smith, 2007), but with median values of closer to 25 g C m<sup>2</sup>yr<sup>-1</sup> (Hargreaves et al., 2003). A preliminary estimate of C sequestration from <sup>210</sup>Pb dating of three cores within peatland just outside the Whitelee development suggests C sequestration rates of 18.7 g C m<sup>2</sup>yr<sup>-1</sup> (MacKenzie personal communication), close to the median estimate for UK peatland. If this is representative of the larger Whitelee site, then aquatic export alone approaches suggested sequestration rates. If gaseous emissions and aquatic inorganic carbon export are included (the latter requires differentiation of C derived from respiration of organic matter and export from minerogenic sources, Waldron et al., 2007a), it is possible that the Whitelee sites no longer offer a net carbon sink, and thus considered from the perspective of preserving a terrestrial carbon store, these catchments have little buffering capacity to disturbance. Further, our estimates of C loss are constructed from budgets that only latterly suggest an increase in OC export from disturbance. The projected impact of increased disturbance is to increase OC (and possibly inorganic carbon) export thus moving these sites closer to net loss of carbon.

Whitelee is being developed for windpower. The EIS undertaken for such developments assume complete oxidation of the peatland disturbed for turbine and road

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construction, and still calculate that carbon lost will be offset within a few years of renewable energy generation. However, such EIS do not generally consider the impact that occurs if deforestation is additionally required. Accommodating the impact this may have on carbon sequestration in the calculations of the viability of peatland development seems required for a more accurate assessment of the contribution of such developments to reducing carbon emissions. Additionally, at the scoping stage for renewable energy developments long-term monitoring is often required e.g., ecological surveys spanning one year are undertaken to characterise bird populations. We suggest that future EIS should incorporate estimates of C sequestration and pre-development losses prior to planning decisions.

Average annual TP export for Whitelee catchments is  $28.8 \pm 5.5 \text{ kg P km}^2 \text{ yr}^{-1}$ , approximately 6 times higher than calculated for Finnish catchments (Kortelainen et al., 2006); Whitelee DOC export is almost three times higher than the Finnish catchments. Assessing DOC flux contemporaneously with nutrient stoichiometry enables estimation of the proportion of DOC export in excess of biomass production and available for respiration, and hence, dependent on the  $\text{CO}_2$  equilibria, potentially effluxed. Again certain assumptions have been necessary:

1. that all C in excess of the microbial biomass stoichiometric composition is available for conversion to  $\text{CO}_2$ ;
2. that the concentrations of both N and P are sufficiently high that the system is not likely to be nutrient limited.
3. that whilst only the N-draining catchments have excess N, these systems are P-more than N-limited and thus calculations of excess C are on the basis of excess C:P.

Subject to the same uncertainties in flux estimate calculation as defined previously, these assumptions predict maximum  $\text{CO}_{2(\text{aq})}$  production for each catchment at the catchment outflow (Table 2). Such approaches are useful for testing assumptions re

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field measurements or for modelling that requires the extremities of the system to be defined.

## 5 Conclusions

Carbon and nutrient interaction in surface freshwaters is complex. For example, labile C will allow heterotrophic bacteria to increase size and optimise their competitive abilities (Lovdal et al., 2007); higher DOP may allow bacterial consumption of recalcitrant organic molecules (Lennon and Pfaff, 2005); aquatic organisms also impact the stoichiometry of their environment: heterotrophic biofilm bacteria recycle phosphorus and nitrogen making them available to algae and invertebrate consumers (Rubin and Leff, 2007). Clearly, both the lability of the organic material and the concentration and form of key nutrients influence DOM quality, and in turn CO<sub>2</sub> efflux.

However, the systematic interaction of C export with other ecologically important elements such as N and P observed here, suggests that the terrestrial carbon cycle can be stoichiometrically linked to the atmospheric carbon cycle through aquatic biogeochemical cycling. Characterisation of the carbon and nutrient budgets is useful as it allows the rate at which carbon is being exported from terrestrial reservoirs to be quantified, and the link between terrestrial export of DOC to the atmospheric carbon cycle to be explored through assessing the potential for respiration. Our knowledge of the capacity for smaller catchments to emit CO<sub>2</sub> is poor (Cole et al., 2007) and thus even qualitative approaches such as this currently have value in shaping future research direction. Future aquatic CO<sub>2</sub> efflux studies may wish to incorporate a stoichiometric perspective to deepen the resolution such an approach can offer, with greatest interpretative power offered by linked DOC-nutrient-aquatic respiration studies.

Whilst we are aware that immediate and localised impacts can arise from the necessary development activities (e.g., deforestation, Neal et al., 2004b), that these impacts can propagate to the larger catchment scale has been little documented. The consequence of changing nutrient stoichiometry of receiving waters on riverine carbon efflux

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is an aspect that does not appear from the EIS for the windfarm development (e.g. CRE Energy, 2002) to require significant consideration. We suggest this is due to paucity of data rather than knowledge that such changes may not be of biogeochemical significance. The preliminary data we present here of the temporal and spatial changes in stoichiometry of the receiving waters, with additional data from an undisturbed system for comparison, will contribute to the framework of data required to develop such understanding and thus assess the impact on stoichiometry of receiving waters.

As the political importance of carbon geomorphology gathers momentum, flux estimates should be more prevalent in assessments of impact development on terrestrial carbon stores. However, prior to using that knowledge in a decision-making capacity to offer guidance upon the viability of development on terrestrial carbon stores, we have an important question to address: Is it better to disturb a landscape where net balance approaches carbon loss, or it is better to disturb a site that has a high capacity to sequester carbon as here the buffering capacity of the site to disturbance will be greater, and the site may continue to sequester carbon? Answering this is not possible without more data on the natural variation in carbon fluxes and sequestration rates of terrestrial carbon stores, and the impact of disturbance.

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**Table 1.**  $\Delta^{14}\text{C}_{\text{DOC}}$  from the Water of Charr, the mainstem river into which Brocky Burn discharges, collected during event flow. The average age of the DOC of approximately 8 years (110% modern is equivalent to 1996, Levin and Kromer 2004) although the 09.15 a.m. sample is significantly different and indicates carbon with an average age of 11 years.

Date and time collected	Publ. code	$^{14}\text{C}$ enrichment (Absolute % modern)	$\delta^{13}\text{C}_{\text{DOC}}\text{‰}$
Charr 24 June 2004 12:55	SUERC 7242	110.05±0.34	−28.1
Charr 24 June 2004 17:30	SUERC 7243	110.25±0.30	−28.2
Charr 24 June 2004 22:40	SUERC 7244	110.05±0.45	−28.3
Charr 25 June 2004 02:25	SUERC 7245	110.38±0.34	−28.2
Charr 25 June 2004 09:15	SUERC 7246	112.57±0.34	−28.3
Charr 25 June 2004 12:40	SUERC 7248	111.04±0.30	−28.3
	Mean (±1 S.D.)	110.72±0.97	−28.2±0.1

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**Table 2.** Annual flux estimates of DOC, POC and TP export for one calendar year beginning 3 July 2006. The potential contribution to CO<sub>2(aq)</sub> through respiration of DOC and POC in stoichiometric excess of P consumption can be calculated. \*WL17 does not include the nested catchments of 9D and 9A, thus total flux at sampling point 17 is the sum of 9A, 9D and 17.

	WL13	WL14	WL15	WL1	WL1632	WL456	WL9A	WL9D	WL17*
Area (km <sup>2</sup> )	9.4	14.4	13.4	29.4	30.0	11.7	7.9	11.6	15.1
Σ DOC (Mg)	183	246	300	431	541	120	82	86	120
Σ POC (Mg)	51	88	71	213	178	69	43	54	71
Export g C m <sup>2</sup> yr <sup>-1</sup>	23.1	21.5	25.5	20.3	22.1	14.9	14.8	11.2	11.7
Σ TP (kg)	257	484	319	1018	701	453	226	359	597
Export mg P m <sup>2</sup> yr <sup>-1</sup>	25.2	31.2	21.9	32.0	21.6	35.7	26.6	28.7	36.6
Potential CO <sub>2(aq)</sub> (Mg)	177	234	292	408	525	110	77	78	106

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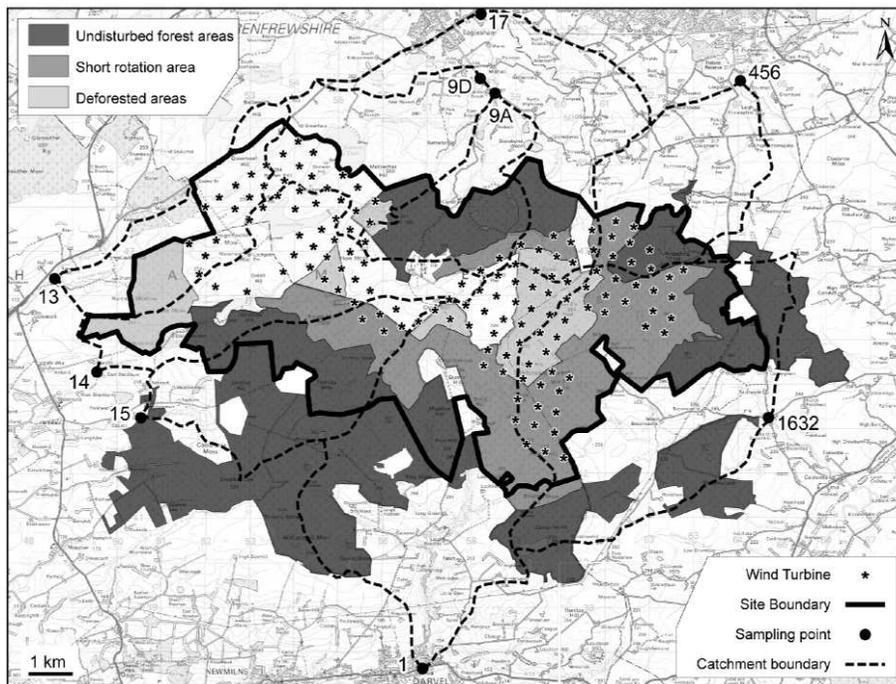
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**Fig. 1.** The Whitelee site showing proposed turbine location, planned deforestation and the nine-subcatchments sampled. The area of each catchment is as follows: WL13: 9.4 km<sup>2</sup>; WL14: 14.4 km<sup>2</sup>, WL15: 13.4 km<sup>2</sup>, WL1: 29.4 km<sup>2</sup>; WL1632: 30.0 km<sup>2</sup>; WL456: 11.7 km<sup>2</sup>; WL9A: 7.9 km<sup>2</sup>; WL9D: 11.6 km<sup>2</sup>; WL17: 34.5 km<sup>2</sup>.

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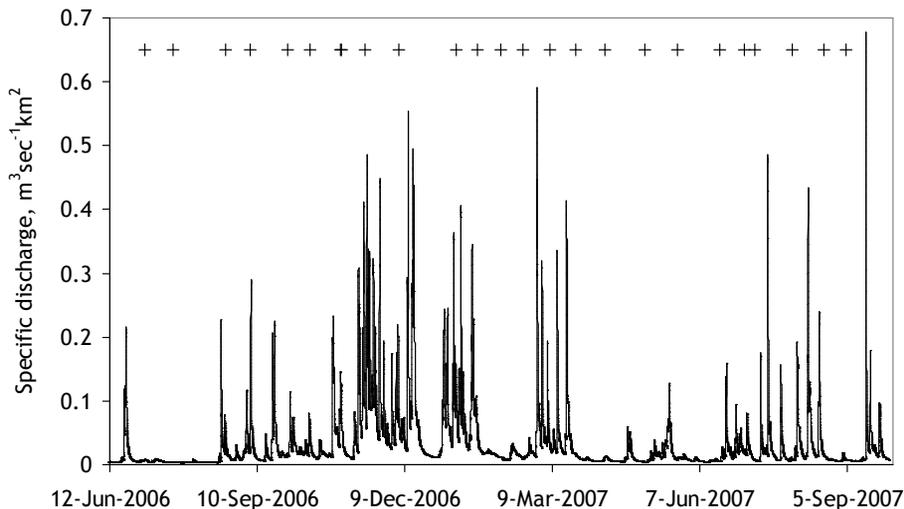
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**Fig. 2.** Specific discharge from the nearest catchment to the Whitelee development currently gauged, the River Irvine at Newmilns, catchment area 72.8 km<sup>2</sup>. Sampling dates are indicated by the crosses.

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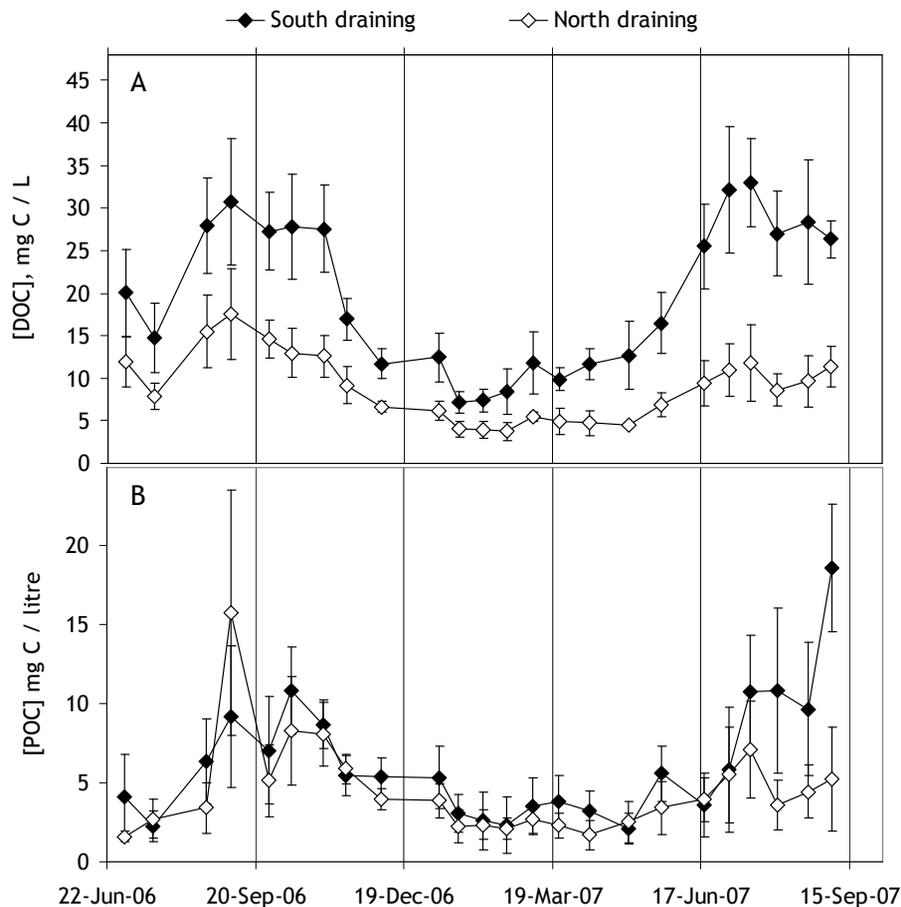
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**Fig. 3.** [DOC] (panel A) and [POC] (panel B) in Whitelee N- and S-draining catchment waters. Each sample point is the mean  $\pm$  1 S.D. of the four N- or five S-draining catchments sampled on the same day.

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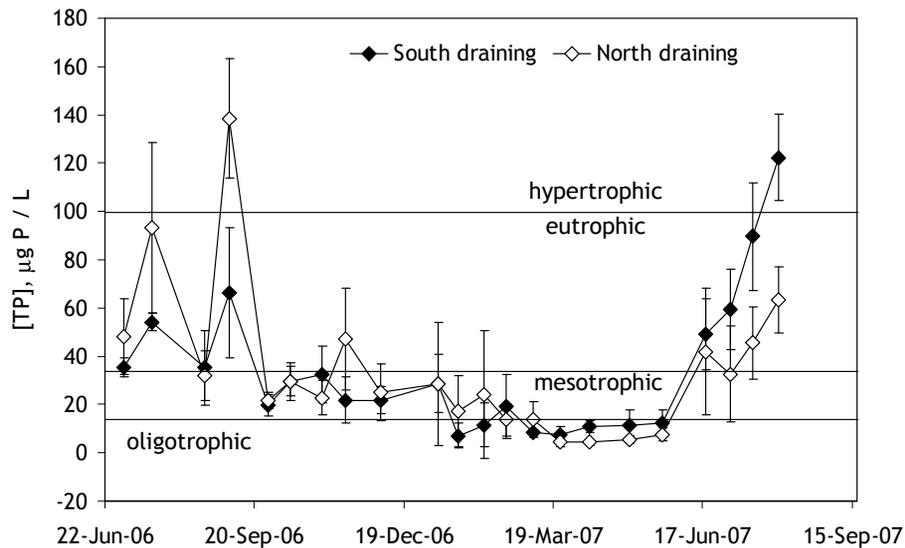
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**Fig. 4.** [TP], µg P/L, in Whitelee drainage waters. Each sample point is the mean ± 1 S.D. of the four N- or five S-draining catchments sampled on the same day.

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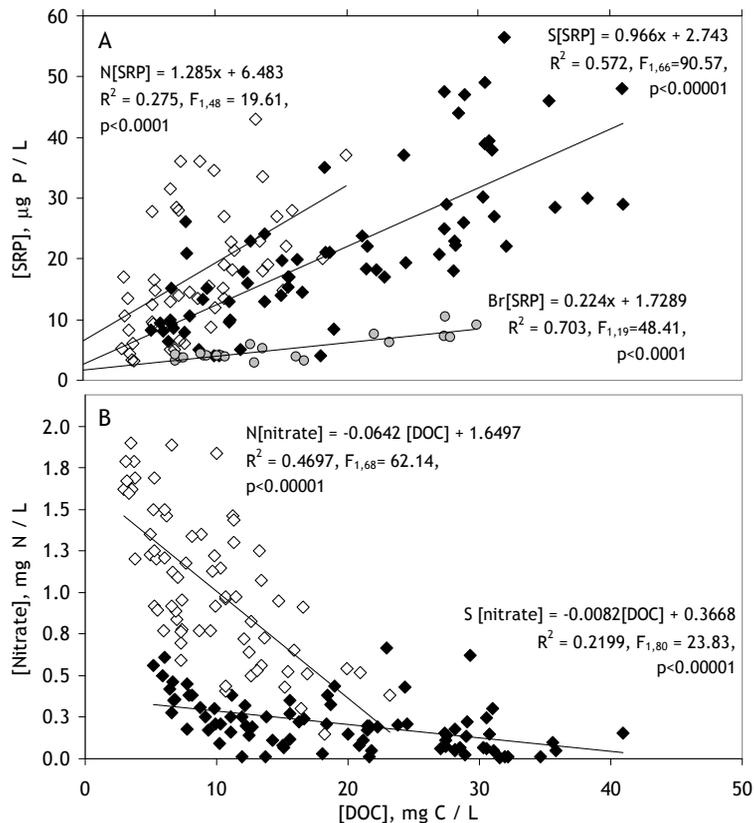
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**Fig. 5.** Interaction between [DOC] (mg C/L) and [SRP] (panel A,  $\mu\text{g P/L}$ ) and  $[\text{NO}_3^-]$  (panel B,  $\text{mg N/L}$ ). The legend for the N- and S-draining catchments is the same in Fig. 4; in panel A Brocby samples are represented by the shaded grey circles.

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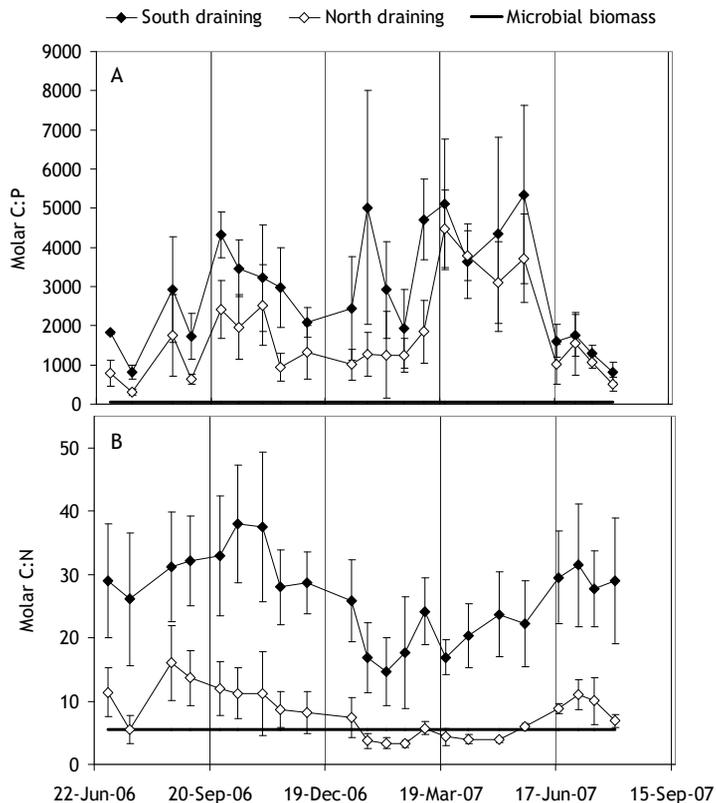
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**Fig. 6.** Molar C:P (panel A) and molar C:N (panel B) for the N- and S-draining Whitelee catchments. Each sample point is the mean $\pm$ 1 S.D. of the four N- or five S-draining catchments sampled on the same day. Molar C:P was calculated from combined DOC and POC, with respect to TP. It was assumed that, as insufficient P is available to meet microbial requirements that particulate P may be used, and thus particulate C would also be available. TDN is from the dissolved pool only, thus molar C:N was calculated using only DOC.

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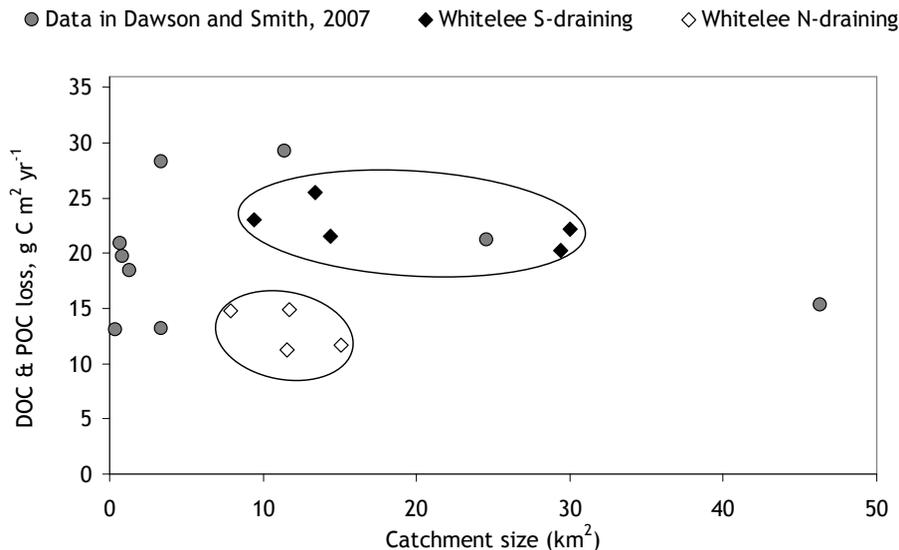
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**Fig. 7.** Organic carbon export in catchment drainage waters, as a function of catchment area. All data for comparison with Whitelee are from Dawson and Smith, 2007, Table 3, where if a range is given the average value has been plotted. The exception to this is Moorhouse, where the POC range was significantly larger than other sites, thus values considered most representative by the authors (Worrall et al., 2003) were used instead.

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