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Identifying the role of environmental drivers in organic carbon export from a forested peat catchment.

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Highlights:

1. Loads of 9.5 t DOC km^2 year^{-1} and 6.2 t POC km^2 year^{-1} were exported from peatland.
2. Climatic factors explained 59.7% and 58.3% of deviance in stream DOC and POC.
3. Soil temperature, discharge and drought were significant drivers of DOC concentrations.
4. Soil temperature, stream discharge rainfall were significant drivers of POC concentrations.

Key words: Peat catchment, dissolved organic carbon, particulate organic carbon, high resolution monitoring, climate effects.

Abstract

Carbon export in streams draining peat catchments represents a potential loss of carbon from long-term stores to downstream aquatic systems and ultimately, through mineralisation, to the atmosphere. There is now a large body of evidence that dissolved organic carbon (DOC) export has increased significantly in recent decades at many sites, although there is still debate about the drivers of this increase. In this study, DOC export and particulate organic carbon (POC) export were quantified from a forested peatland catchment in the west of Ireland over two years at a fine temporal resolution. The principle drivers of change in stream DOC and POC concentrations were investigated using a general additive modelling (GAM) approach. The study period included drought conditions in early summer 2010 and clearfelling of some commercial forestry in early 2011. The results indicated that annual loads of 9.5 t DOC km^2 year^{-1} and 6.2 t POC km^2 year^{-1} were exported from the catchment in 2010. This combined annual load of 15.7 t C km^2 year^{-1} would represent between 0.01 % and 0.02 % of typical estimates for peat soil carbon storage in the region. Soil temperature, river discharge and drought explained 59.7 % the deviance in DOC concentrations, while soil temperature, river discharge, and rainfall were the significant drivers of variation in POC concentrations, explaining 58.3 % of deviance. Although clearfelling was not a significant factor in either model, large spikes in POC export occurred in 2011 after the first forestry clearance. The results illustrate the complexity of the interactions between climate and land management in driving stream water carbon export. They also highlight the sensitivity of peatland carbon stores to changes in temperature and precipitation, which are projected to be more extreme and variable under future climate scenarios.

1. Introduction

Peatlands are one of the largest global reservoirs of carbon, storing approximately 20-25% of the earth's soil organic carbon (Billett et al., 2010; Montanarella et al., 2006). Carbon is exported in a number of different forms from these systems, including as dissolved inorganic carbon (DIC), dissolved organic carbon (DOC) and particulate organic carbon (POC) in catchment streams, and as gaseous emissions of carbon dioxide (CO_2) and methane (CH_4) from soil carbon stores (Dinsmore et al., 2011). Published estimates of DOC export range from 1.5 t C km^2 $year^{-1}$ to 14.2 t C km^2 $year^{-1}$ (Koehler et al., 2009; Clark et al., 2007; Worrall et al., 2003; Hope et al., 1997) while estimates of POC export range from 0.1 t C km^2 $year^{-1}$ to 31.7 t C km^2 $year^{-1}$ (May et al., 2005; Worrell et al., 2003; Hope et al., 1997). Despite the potential for these two carbon sources to contribute to greenhouse gas emissions when mineralised (Davidson and Janssens, 2006), DOC and POC export from peat stores are often ignored in catchment studies, and are generally not included in national greenhouse gas emissions budgets (e.g. EPA, 2012).

An upward trend in DOC concentrations has been observed in many peat catchments over recent decades (Jennings et al., 2010; Miller and McKnight, 2010; Erlandsson et al., 2008; Monteith et al., 2007; Worrall and Burt, 2007; Evans et al., 2005; Hongve et al., 2004). These increases indicate a potential decrease in the stability of peatland stores (Clark et al., 2007) and have implications for the ecology of downstream rivers and lakes (Bade et al., 2007; Jansson et al., 2007) affecting lake transparency and thermal structure (Keller et al., 2008), drinking water quality (Hongve et al., 2004) and contributing to atmospheric CO_2 (Clark et al., 2007; Freeman et al., 2004; Cole et al., 1994). DOC production and transport are highly sensitive to climatic drivers and the proposed explanations for this long-term increase include changes in the intensity, frequency and seasonal patterns of precipitation and snowmelt (Erlandsson et al., 2008; Hongve et al., 2004), higher temperatures (Preston et al., 2011; Freeman et al., 2001 a), higher frequency of drought events (Clark et al., 2010; Jennings et al., 2010), as well as changes related to the reversal of anthropogenic acidification

(Erlandsson et al., 2008; Monteith et al., 2007). There are, however, also catchment studies where no increase has been found, for example Worrall and Burt (2007).

Step change increases in DOC concentrations following drought conditions have been noted for several catchments (Jennings et al., 2010; Worrall et al., 2003; Watts et al., 2001). Drought can cause a change in both the solubility and export of DOC for several reasons. Lower soil moisture levels can result in decreased soil acidity and an increased dissociation of acid functional groups (Clark et al., 2010). Such decreases in acidity may result in an increase in microbial activity in soils (Andersson et al., 2000). However, an increase in oxygen availability within soil during droughts can also lead to higher rates of aerobic decomposition (Fenner and Freeman, 2011; Yallop et al., 2009; Mitchell and McDonald, 1992), and may also trigger an enzymic latch mechanism as described by Freeman et al. (2001 b), where phenolic oxidase activity is switched on in the soil porewaters, reducing the concentration of inhibitory phenolic compounds.

The particulate load in a river is influenced by soil type and catchment characteristics. Peat soils are sensitive to erosion owing to their low density (McHugh, 2007). Other factors affecting erosion include steep topography, thin soils, sparse vegetation cover and the presence of bare peat (Grayson et al., 2012; Marttila and Klove, 2010). Wetter winters and warmer summers also have an erosive effect on the peat surface, with droughts leading to cracking and disintegration of surface and lower peat layers (Evans et al., 2005). POC is principally transported during periods of high precipitation, which open up flow pathways and increase the washout to surface waters.

Land use changes, such as the intensification of farming and afforestation, have also been linked to increases in both DOC and POC concentrations (Rodgers et al., 2011; Worrall and Burt, 2007; Cummins and Farrell, 2003). In Ireland, the main land use change in peatland catchments has been the establishment of commercial forestry and subsequent clearfelling. Currently 10.15 % or

7000 km^2 of land area in Ireland are under commercial plantation forestry (National Forest Inventory, 2007). It is estimated that 3000 km^2 of this is located on peatland in the west of the country (Rodgers et al., 2011; EEA, 2004). Forestry clearfelling and extraction of timber can result in an increase in particulate matter in streams (Rodgers et al., 2011). Other causes of accelerated peat erosion include overgrazing by sheep and other livestock (Grayson et al., 2012; Marttila and Klove, 2010; Stott and Mount, 2004).

Climate projections for catchments in western Europe point to drier summers, more episodic precipitation and wetter winters (Fealy et al., 2010; Samuelsson, 2010). Given the sensitivity of carbon export to climatic factors, these changes may affect the export of DOC and POC through washout, changes in flow rates and pathways, and changes in rates of decomposition (Clark et al., 2010; Jennings et al., 2010; Clark et al., 2007; Evans et al., 2006;). Naden et al. (2010) modelled changes in DOC concentrations under future climate scenarios and projected a 20 % increase in DOC export from the Glenamong sub-catchment, the focus of the current study, with the annual median DOC concentration projected to increase from 8.7 mg C L^{-1} to 10.5 mg C L^{-1}.

The aim of this current study was to quantify carbon export from a peatland catchment in the west of Ireland and identify the principle drivers of variability in stream DOC and POC concentrations. The study used high resolution monitoring data to estimate DOC and POC export over a two year period which included a period of summer drought, and forestry clearfelling. The study assessed the importance of a range of drivers using a general additive modelling (GAM) approach. The results give an insight into the effect of climate on carbon dynamics in such systems and have relevance for our understanding of the global carbon cycle. Accurate estimates of carbon exports can also help inform catchment management and national carbon budgets.

2. Material and Method

2.1 Site Description

The Glenamong sub-catchment (18.21 km^2) is located in the Burrishoole catchment in the west of Ireland (53^0 56’50” N, 9^0 34’30” W) (Fig. 1). The sub-catchment is comprised of 77 % upland peat, 23 % forestry (dominant species include Sitka spruce (*Pinus sitchensis*) and lodgepole pine (*P. contorta*)) and small pockets of transitional woodlands and scrub. The main land use in the sub-catchment is extensive sheep grazing on commonage. The steep slopes result in a hydrological system with a quick reaction time to precipitation events (Müller, 2000). The sub-catchment experiences a moderate climate due to its close proximity to the Atlantic Ocean. The air temperature rarely goes above 25^{o}C in the summer or below -5^{o}C in the winter (Fealy et al., 2010) and snowfall is occasional. The ten year average precipitation measured at the Glenamong rain-gauge situated within the sub-catchment was 2022 mm year^{-1} (Fig. 1, Table 1). Forestry clearfelling took place in the Glenamong sub-catchment during two short periods commencing on 8th February 2011 (0.15 km^2) and 1st July 2011 (0.09 km^2).

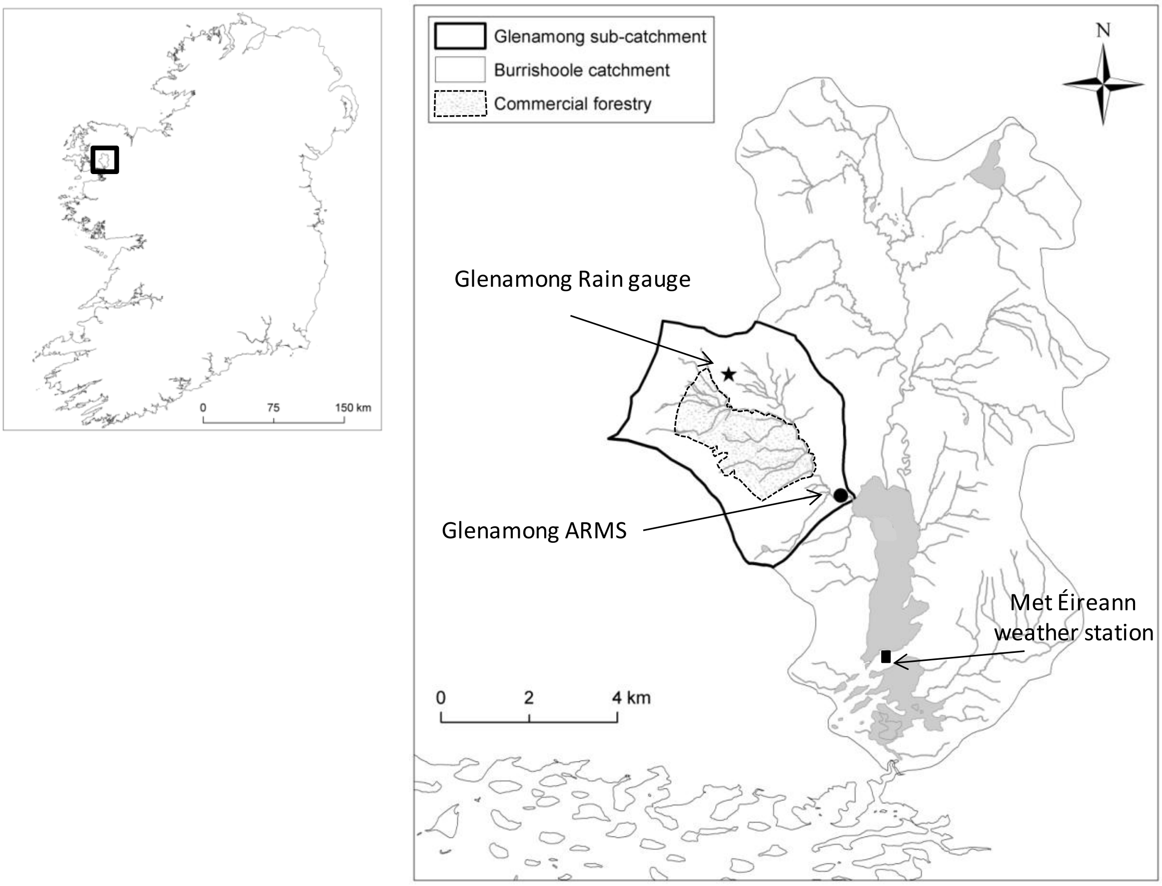

Figure 1: Location of the Burrishoole catchment in Ireland, an outline of the study site, the Glenamong River automatic river monitoring station (ARMS), the Glenamong sub-catchment rain gauge and the location of the monitoring equipment including the Met Éireann weather station in the Burrishoole catchment. The gray shading represents lakes located in the Burrishoole catchment.

Table 1: Site description.

Parameters	**Met Éireann weather station**	**Parameters**	**Glenamong River**
Maximum air temperature (°C)	27	Geology	Schist, gneiss, granite
Minimum air temperature (°C)	-9	Catchment area (km^2)	18.21
Mean air temperature (°C)	10.2	River length (m)	38016
Precipitation (mm)		Catchment start altitude (m)	13
Glenamong rain-gauge 10 year average	2022	Catchment finish altitude (m)	375
Met Eireann weather station 2010	1258	% forested	23
Met Eireann weather station 2011	1755	*pH range	3.8-6.9
Glenamong rain-gauge 2010	1911	*Colour (mg PtCo mg L^{-1})	91.9
Glenamong rain-gauge 2011	2683	*DOC (mg L^{-1})	9.3
Mean daily wind speed (m sec^{-1})	2.4		
Predominant wind direction	South/west		

*(Represents mean measurement from spot water samples taken in 2010 and 2011; pH ranges are taking from two minute high frequency sensor data for the same period).

2.2 In-situ monitoring of stream parameters

Estimates of DOC and POC export were made using data from in-situ high frequency sensors as proxies for concentration, together with flow data for the site. Chromophoric dissolved organic carbon (CDOM) fluorescence was used as a proxy measurement for DOC concentration, while nephelometric turbidity units were used as a proxy for POC. Data were collated from an automatic river monitoring station (ARMS) located in the Glenamong (Rouen et al., 2005) (Fig. 1).The ARMS was instrumented with a SeaPoint CDOM UV Fluorometer (SeaPoint Sensors, Inc., Exeter, NH, USA), a Hydrolab Quanta measuring pH, conductivity, dissolved oxygen and temperature (Hydrolab Corporation 8700 Cameron Road, Suite 100 Austin, Texas 78754 USA), and a Chelsea minitracka II nephelometer (Chelsea Technology Group (CTG) Sensor Technology, UK). All sensors were continuously submerged and measured water parameters every two minutes throughout the year. Data were logged and stored by a Campbell Scientific CR1000 data logger (www.campbellsci.com).

The CDOM fluorometer uses UV light emitting diodes (LEDs) as the CDOM excitation source (Ex 370 nm CWL, 12 nm FWHM; Em 440 nm CWL, 40 nm FWHM, where CWL is the centre wavelength and FWHM is the full width at half maximum wave height). The gain was set to 1 for all measurements. The instrument output was in mV and is referred to as relative fluorescence units (RFU). Assessment of instrument performance was carried out using a quinine sulphate standard as recommended by the manufacturers (1 QSU = 1 µg quinine sulphate L^{-1}). An instrument specific temperature correction coefficient was applied to the raw CDOM fluorescence data, (Ryder et al., 2012) providing temperature corrected CDOM fluorescence data ($CDOM_{cor}$). A relationship between the high resolution $CDOM_{cor}$ fluorescence and DOC concentration (mg L^{-1}) was established by collecting 24 water samples over one day every month at the Glenamong ARMS site from July 2010 to June 2011 (r^2=0.59, p≤0.001, n = 178). DOC was measured in the filtered water samples (GF/C) using a Sievers TOC Analyser model 5310 (range 4 ppb to 50 ppm, accuracy ±2% or 5% ppb).

A Chelsea nephelometer optical sensor was used to measure turbidity. The nephelometer was calibrated in January 2011, using a formazin turbidity standard and raw data (mV) was then expressed in formazin turbidity units (FTU). Subsequently, a linear relationship between FTU units and suspended sediment (mg L^{-1}) was established (r^2=0.70, p≤0.001, n=186), which allowed the FTU data from the nephelometer to be expressed in terms of mg L^{-1} of suspended sediment. When very high spikes in the raw nephelometer data were recorded (>500 mV or 11 FTU), the corresponding estimate of suspended sediment was capped at 94.3 mg L^{-1} due to uncertainties in the suspended sediment (SS) and FTU rating curve at the upper limits (Pierson et al., 2008). These occasions represented 1.3 % of nephelometer data measured over the monitoring period. The organic content of the sediment transported in the Glenamong River was calculated using loss on ignition values for sediment samples (n =196). The LOI data for 2010 and 2011 had a median organic matter content of 83 % LOI, with an interquartile range of 50 % (25 %ile) to 100 % (75 %ile). Organic sediment was converted to POC based on the measured carbon content of the organic fraction of suspended sediment for the Burrishoole catchment (44.7 %) (Sparber, 2012).

Continuous monitoring of the water level was carried out at the Glenamong ARMS every fifteen minutes using an OTT Hydrometry Orpheus Mini (www.ott.com). These data were converted to discharge ($m^3 sec^{-1}$) using a rating curve for the study site ($r^2 = 0.98$, Marine Institute unpublished data). Precipitation was measured using a Davis rain collector II and a HOBO event logger (www.onsetcomp.com) within the sub-catchment (Fig. 1). Air temperature, soil temperature at 5 cm and 10 cm and sunshine hours were collected from the Met Éireann weather station (Newport) located 4 km from the Glenamong sub-catchment.

2.3 Data analysis

The Standardised Precipitation Index (SPI) (Lloyd-Hughes and Sanders, 2002) was used to assess relative changes in rainfall and to establish the occurrence of extreme dry periods (drought events). Seasons were defined as spring (March, April and May), summer (June, July and August), autumn (September, October and November) and winter (December, January and February). The output of the index is split into 7 categories: extremely wet >2, severely wet 1.5 to 2, moderately wet 1 to 1.5, near normal -1 to 1, moderately dry -1 to -1.5, severely dry -1.5 to -2 and extremely dry < -2. Daily rainfall data from the Glenamong rain gauge over 10 years (2002-2011) was used for this analysis. The occurrence of any significant step changes in estimated DOC and POC concentrations were checked using the method of Rodionov (2006) (Shift Detection V 3.2, www.beringclimate.noaa.gov/regimes). Data were normally distributed, and the influence of serial correlation was eliminated prior to analysis through pre-whitening. Soil moisture deficit (SMD) was calculated using the daily precipitation from the Glenamong rain-gauge and daily potential evaportranspiration. Evaportranspiration was calculated using the method of Priestly-Taylor (Priestly and Taylor, 1972).

General Additive Modelling with a cubic smoothing regression spline and cross-validation was used to identify the main drivers of estimated DOC and POC concentrations. Analysis was carried out using the mgcv package (Woods, 2006; Woods, 2004) in R (version 2.15.2, R development Core Team, 2011). The spreads of the residuals was relatively homogenous, indicating that a Gaussian distribution was appropriate for the model (Zuur et al., 2009). Separate additive models were developed for the DOC and POC response variables. The DOC model was based upon daily data stripped to every fifth day over the study period (12th January 2010 - 26th November 2011) in order to remove serial correlation in the data. The POC model was based on log transformed POC daily data stripped to every third day over the study period (12th January 2010 - 22nd September 2011). Potential explanatory variables included in the analysis were drought and felling (as factors) and climatic and hydrological data (as continuous variables). The latter included daily measurements of maximum, minimum and mean air temperature (^{o}C), soil temperature at 5 cm, rainfall (mm day^{-1}), water temperature (^{o}C), discharge (m^{3} sec^{-1}), stream pH, SMD (mm day^{-1}) and actual evapotranspiration (mm day^{-1}). Additional variables were constructed by accumulating data for rainfall and discharge over 5, 10, 15, 20, 30 days. In the model output, a smoother line based on the cubic smoothing regression spline summarises the trend due to a given response variable. The data sets were checked visually for any breaches of assumptions prior to analysis. To find the best DOC and POC GAM models, the explanatory variables were selected using a stepwise procedure. The optimal or best fit models were selected using the Akaike's Information criterion (AIC) (Zuur et al., 2009; Akaike, 1974).

3. Results

3.1 Hydro-meteorological conditions 2010-2011

The two study years, 2010 and 2011, differed in their weather conditions, with 2010 being both drier, particularly earlier in the year, and having a greater temperature range. The annual and mean daily precipitation values for 2010 were 1911 mm year^{-1} and 5.2 mm day^{-1} respectively, while the equivalent values for 2011 were 2683 mm year^{-1} and 7.4 mm day^{-1} (Table 1, Fig. 2 a). There were also fewer rain days (defined as days with >1 mm) in 2010 (229 days) compared to 2011 (263 days). For perspective, the 10 year-average annual precipitation value for the site was 2022 mm year^{-1}. The maximum and minimum air temperatures in 2010 were 24.2^{o}C in May 2010 and -8.3^{o}C in December 2010. This low December temperature occurred during a period when extreme cold temperatures were recorded across Western Europe in the winter of 2010/2011. The maximum air temperature in 2011 was 21^{o}C in July, with a minimum of -2.9^{o}C recorded in January 2011.

Water discharge in the Glenamong River responded quickly to precipitation (Fig. 2 a). Although the highest flows were recorded in September in both years (7.27 m^{3} sec^{-1} on the 8th of September 2010 and 7.34 m^{3} sec^{-1} on 11th of September 2011), high flow events of a similar magnitude occurred throughout most of the study period, with the exception of the early part of 2010. Low flow (defined as flow <0.2 m^{3} sec^{-1}) occurred on 29 % of days during 2010 and 20 % in 2011. High flow (defined as flow >0.9 m^{3} sec^{-1}), occurred on 20 % of the days in 2010 and 34 % in 2011.

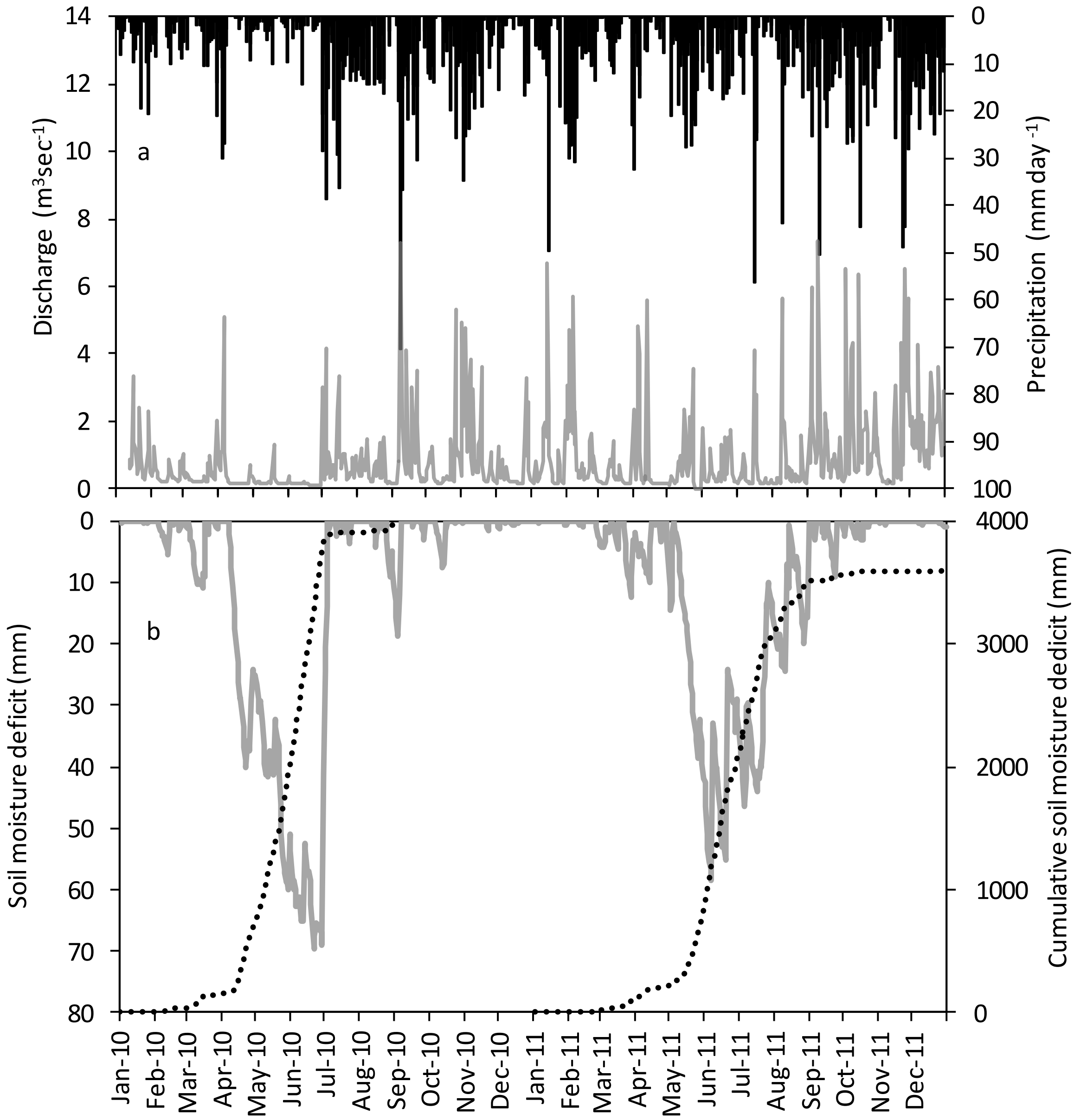

Figure 2: a) Mean daily precipitation (black line) and mean daily discharge (gray line) and b) daily soil moisture deficit (SMD) (gray line) and cumulative SMD (dotted line) for the Glenamong sub-catchment for 2010 and 2011.

The pattern in SMD also differed between the two years, reflecting the differences in precipitation patterns (Fig. 2 b). The soil was below field capacity from the beginning of April to the beginning of July in 2010, with an average daily SMD of 21.0 mm day^{-1} for spring (March, April, May) 2010. In that year, the cumulative SMD reached a maximum of 69.6 mm day^{-1} on 21st June but returned to zero within two weeks following high precipitation and stayed in or around zero for the remainder of the summer. In 2011, a persistent SMD did not begin to develop until the beginning of

May, and was then constantly positive from the 8th of May to 15th August 2011, and reached a maximum value of 58.5 mm day^{-1}. The average daily SMD for spring in 2011 was 9.8 mm day^{-1}, less than half of the value for 2010. The average daily actual evapotranspiration value for spring 2010 was 2.0 mm day^{-1}, while that for the same period in 2011 was 1.9 mm day^{-1}, showing that low levels of precipitation were the main contributing factor to the differences in SMD levels in the two years.

An assessment of the precipitation for the two years based on the seasonal SPI values, showed that, when compared to the previous 10 years data, the winter of 2010 (December, January, February) was classified as moderately dry, and was then followed by extremely dry (drought) conditions in spring (March, April, May 2010), a three month period when only 271 mm of rainfall was recorded at the sub-catchment rain gauge (Fig. 3). All other seasons in the two year period were classified as wet or moderately wet based on the index, with the exception of winter 2010 and summer 2011 which were classified as near normal.

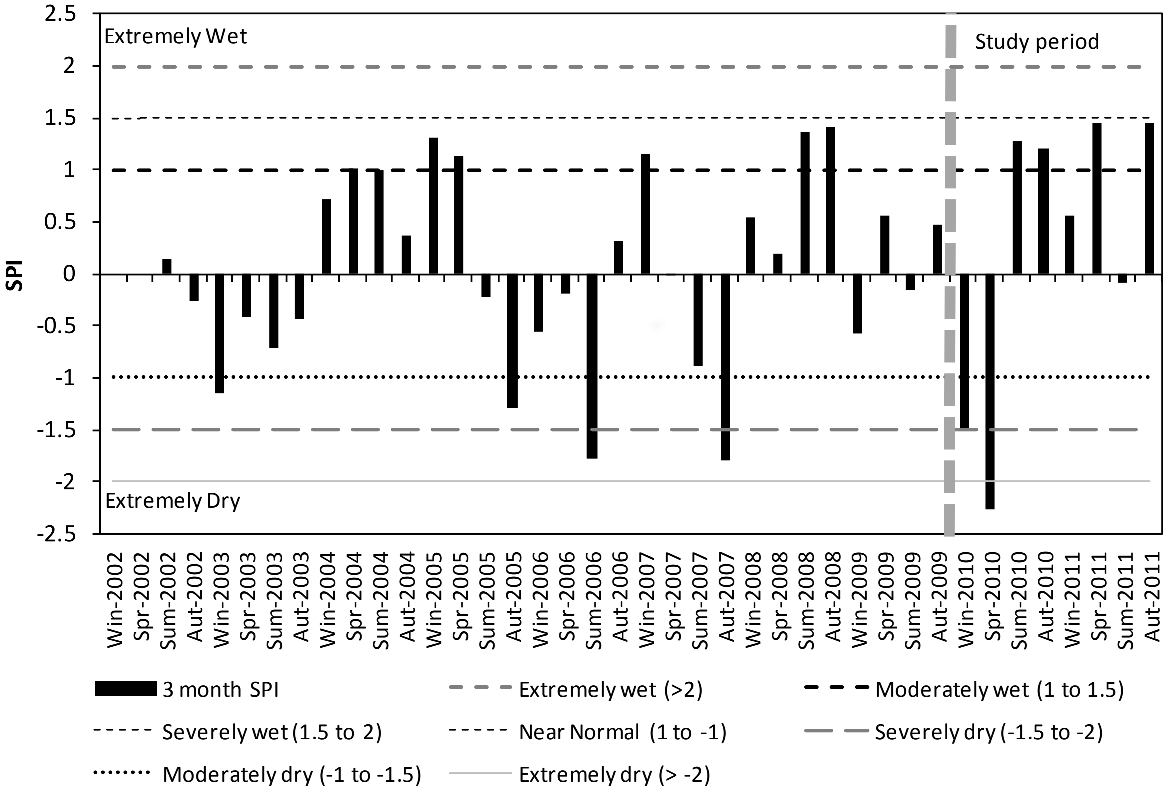

Figure 3: The three month Standardised Precipitation Index (SPI) calculated using data from the Glenamong rain gauge from 2002 to 2011. The SDI, standard deviations > 2 or > -2 representing extremely wet and extremely dry conditions respectively, denoted by the black dashed lines. The gray dashed line indicated the study period. Spring (March, April, May), summer (June, July, August), autumn (September, October, November) and winter (December, January, February).

3.2 Estimation of the annual export of DOC and POC

There were two contrasting annual patterns in estimated DOC concentrations in the Glenamong River and in DOC export in the two years (Fig. 4). Estimated DOC concentrations were low in early 2010, during the dry winter and spring, and reached a minimum of 2.7 mg C L^{-1} day^{-1} in June. They increased rapidly to a high of 14.1 mg C L^{-1} day^{-1} at the beginning of July following the high rainfall at that time. Estimated concentrations then gradually dropped again until December 2010. The mean monthly minimum and maximum DOC concentrations (for 24 samples taken over 24 hours) were 3.9 mg C L^{-1} in April and 12.4 mg C L^{-1} in July. In 2011, DOC estimate concentrations increased over the summer, although with some fluctuation, with a peak of 12.1 mg C L^{-1} day^{-1} in August and a subsequent low of 4.9 mg C L^{-1} day^{-1} in September. The mean monthly minimum and maximum DOC concentrations were 7.0 mg C L^{-1} in April and 11.1 mg C L^{-1} in August (Fig. 4). The mean daily estimated DOC concentration for 2010 was 7.8 mg C L^{-1} day^{-1} while that for 2011 was slightly higher at 8.1 mg C L^{-1} day^{-1}. The highest export of DOC occurred in mid-summer in 2010, but in mid-autumn in 2011. The peak monthly load in 2010 was exported to the lake in July (1.7 t C km^2) while the peak in 2011 occurred in October (1.8 t C km^2), a time of decreasing concentrations but with high rainfall and flows.

The increase in estimated DOC concentrations at the end of June 2010 represented the start of a statistically significant step change in DOC concentrations which began on the 9th of June and persisted until the 5th of November, after which there was a significant downward step change (Fig.

4). The first upward step change occurred after the first precipitation of 9.9 mm day^{-1} following the extreme dry period identified in early summer 2010. After November 2010, estimated DOC concentrations remained higher than concentrations recorded before the June 2010 step change. The mean DOC concentrations for the three regimes were 6.5 mg C L^{-1} day^{-1}, 9.5 mg C L^{-1} day^{-1} and 7.9 mg C L^{-1} day^{-1} respectively.

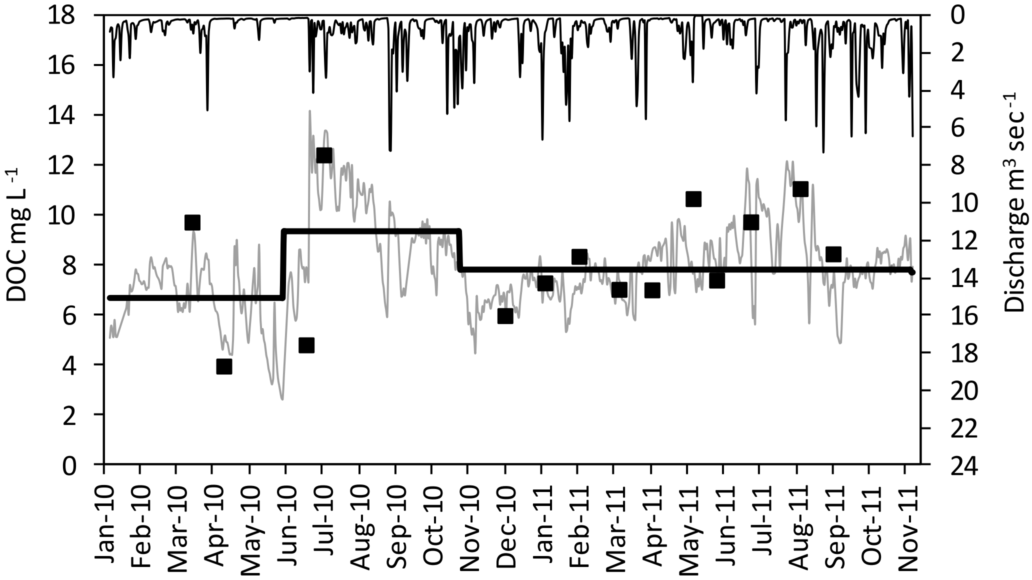

Figure 4: Mean daily DOC$_{est}$ (gray line), mean daily DOC (black squares) and discharge (thin black line) from the Glenamong River. Thick black line represents the weighted mean for each significant regime as defined by Rodionov (2006).

The largest increases in the cumulative daily DOC load were generally in response to higher precipitation and discharge events. The highest increase occurred on the 7th of September 2010 when the cumulative load rose from 91359 kg to 97825 kg (Fig. 5 a). The total DOC export in 2010, the year for which a full set of data were available, was 171.4 t C (9.5 t C km^{2} year^{1}). In contrast, carbon export was higher in 2011, when 223.4 t C (12.4 t C km^{2}) was exported between 1st January and 26th November, and 248.1 t C (13.7 t C km^{2} year^{-1}) from November 2010 to October 2011. There were no apparent pulses of DOC concentration associated with the forestry clearfelling events.

The POC load in the Glenamong River in 2010 (12th January to 31st December) had a maximum POC load of 52.4 kg C day^{-1}, with an average daily load of 1.8 kg C day^{-1}. In 2011 (1st January to 22nd September) the average daily POC load was 4.6 kg C day^{-1} and the maximum and minimum POC export occurred in April 2011 with an export rate of 4.7 t C km^{2} and March 2010 with 0.13 t C km^{2} respectively. The maximum daily POC export of 149.8 kg day^{-1} and a maximum mean daily discharge of 4.7 m^{3} sec^{-1} occurred on the 5th April 2011. This high flow event was the first large flood event following the clearfelling of 0.15 km^{2} of forestry upstream from the Glenamong ARMS monitoring station in February 2011. The peaks in export that followed the second, less extensive clearfelling (0.09 km^{2}) in July 2011 were lower with 102.6 C kg day^{-1} with 5.6 m^{3} sec^{-1} on the 10th of August 2011. The mean annual loading of POC in the Glenamong River was estimated to be 6.2 t C km^{2} year^{1} in 2010 but was over twice this figure for the year from October 2010 to September 2011 (12 months^{-1}) at 13.6 t C km^{2} year $^{-1}$ (Fig. 5 b and c).

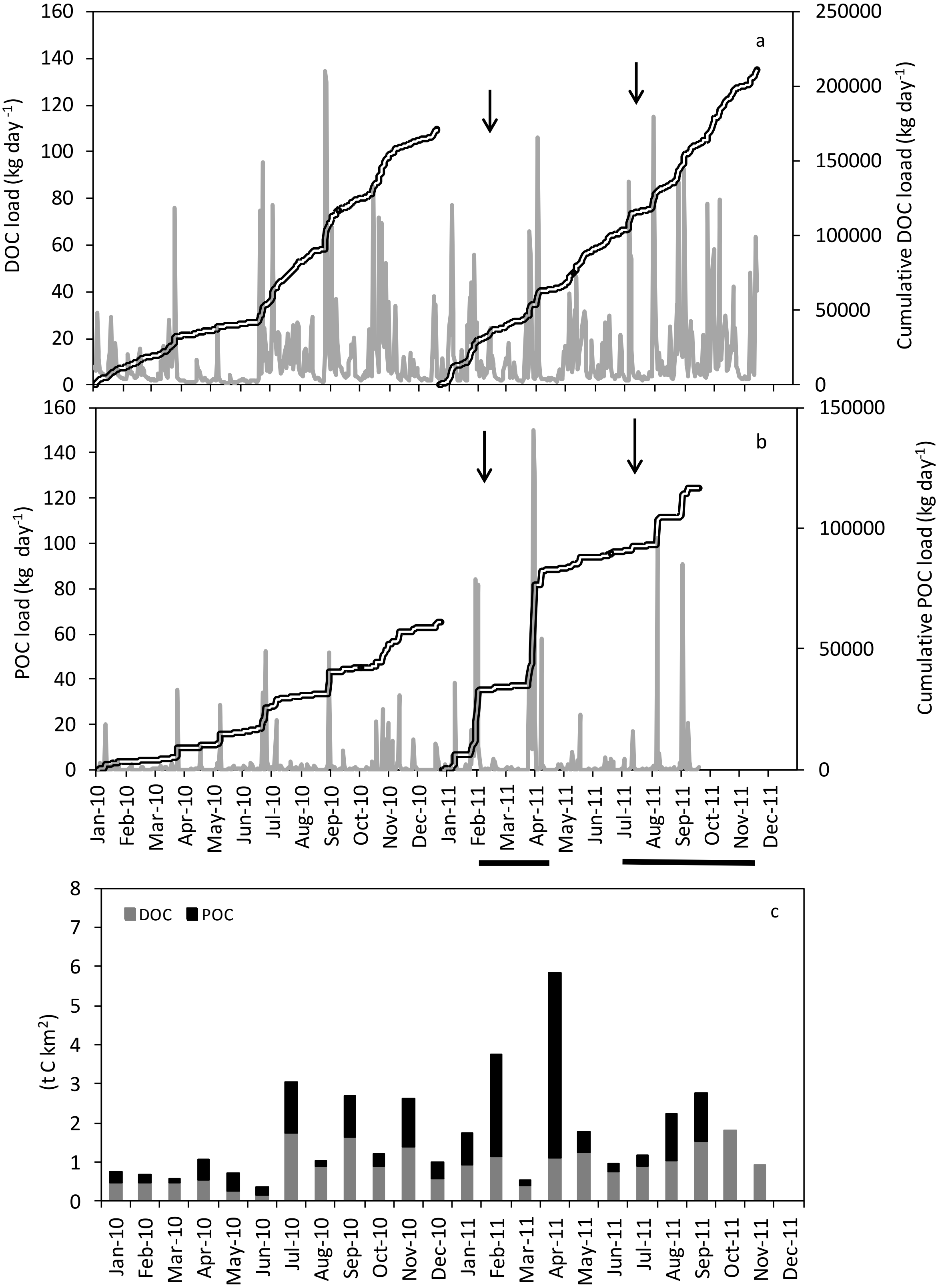

Figure 5: a) Mean daily DOC load (gray line) and the cumulative daily DOC load (black double line) exported for the period 12th January 2010 to the 26th of November 2011. b) POC export (gray line) and cumulative POC load (double black line), c) Monthly sum of DOC and POC exported from the

Glenamong River. Arrows indicate the commencement of clearfelling, the thick black lines under the x axis in graph b indicate duration of clearfelling activity in the Glenamong sub-catchment.

3.3 Drivers of DOC and POC

The optimum generalised additive model for DOC concentration included two smoothers (cumulative soil temperature at 5 cm for the preceding 10-day period and stream discharge for that day) and one factor (drought), and explained 59.7 % of variance in concentrations (Fig. 6 and Table 2). Other factors which were examined but which were not significant included stream water pH, cumulative or daily precipitation and SMD. The optimum generalised additive model for log transformed POC concentration included three smoothers, (cumulative soil temperature at 5 cm for the preceding 10-day period, cumulative rainfall for the preceding 20-day period and log transformed water discharge for that day) and explained 58.3 % of the variance (Fig. 7 and Table 2). It should be noted that log transformed discharge alone explained 50.5 % of the variance when a single factor model was used. Neither change in landuse (pre- and post-felling) nor drought were significant factors in the model for POC.

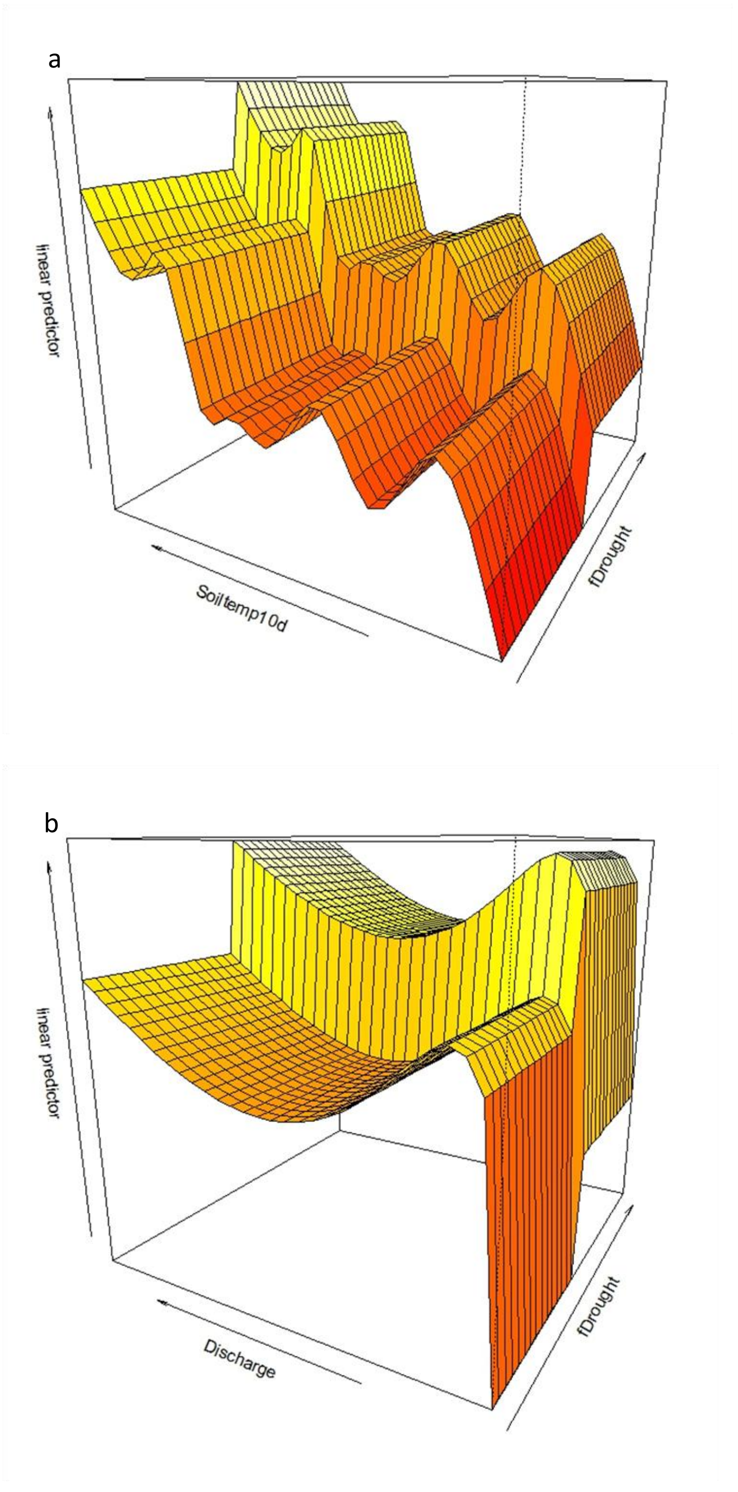

Figure 6: Three-dimensional graph showing the fitted values for the generalised additive model with DOC concentration as the response variable. The graph shows the effect of the drought event on the DOC concentrations in response to a) cumulative soil temperature at 5 cm for the preceding ten days and b) discharge from the Glenamong River over the study period 2010 to 2011.

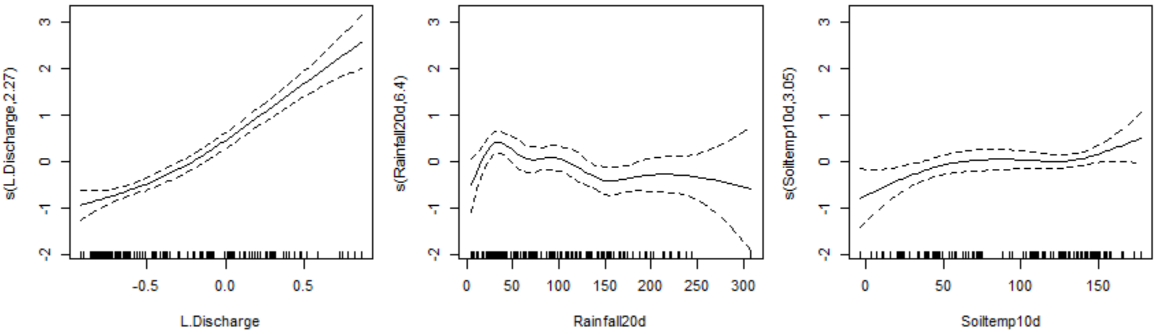

Figure 7: Smoothers for the contribution that each explanatory variables, (log transformed water discharge for that day (L.Discharge), cumulative rainfall for the preceding 20-day period (rainfall20d) and cumulative soil temperature at 5 cm for the preceding 10-day period (soil temperature 10d)) to the optimal GAM explaining POC export. The solid line is the smoother and the dotted lines are 95 % confidence bands.

Table 2: Results of general additive models applied to DOC export (top) and POC (log transformed) export (bottom) for the Glenamong sub-catchment in 2010 and 2011. Soiltemp10d refers to cumulative soil temperature at 5 cm for the preceding ten days and Rainfall 20d refers to cumulative rainfall for the proceeding twenty days.

DOC:

	Estimate	Std. Error	t value	Pr (>|t|)
Intercept	7.49	0.25	29.95	<0.001
Drought	0.99	0.29	3.39	<0.001

Approximate significance of smooth terms:

	edf	Ref.df	F	p-value
Soiltemp10d	8.07	8.70	8.55	<0.001
Discharge	7.11	7.61	6.89	<0.001

R-sq.(adj) = 0.54 Deviance explained = 59.7 %.

GCV score = 1.59 Scale est. = 1.38 n=130

Log POC:

	Estimate	Std. Error	t value	Pr (>|t|)
Intercept	-0.48	0.06	-8.25	<0.001

Approximate significance of smooth terms:

	edf	Ref.df	F	p-value
Log Discharge	2.27	2.82	57.37	<0.001
Rainfall20d	6.41	7.33	2.62	0.013
Soiltemp10d	3.05	3.79	2.61	0.041

R-sq. (adj) = 0.55 Deviance explained = 58.3 %.

GCV score = 0.56 Scale est. = 0.51 n=154.

4. Discussion

The results of this paper highlight the sensitivity of aquatic carbon export from peat catchments to variability in climate. For DOC concentration, these climatic drivers included soil temperatures and the influence of local rainfall patterns, through both their effect on stream discharge and soil moisture levels. The response to soil temperature was generally positive, although the smoother did contain several peaks and troughs. Increased rates of decomposition would be expected at higher temperatures. These relationships are often bell-shaped, and decline after an optimum temperature has been reached (Davidson and Janssens, 2006; Byrne et al., 2001). The presence of multiple peaks may indicate temperature optima for more than one decomposer population, or substrate (Hartley et al., 2007). In contrast to soil temperature, the relationship to stream discharge was highest at both very low flows when there would have been minimal dilution, and conversely, at very high flow when additional flow pathways become active and the critical source area is extended (Raymond and Saiers, 2010; Saraceno et al., 2009).

Both the step change analyses and the modelling approach confirmed the presence of a significant step change in DOC concentrations in June 2010 following an extreme dry period. This period was classified as extreme relative to average conditions in this high rainfall catchment. The estimated soil moisture deficit for that time period nevertheless confirmed that soil water levels were extremely low, and that conditions in the upper layers would have been oxic. The lowest estimated DOC concentration over the study period (2.7 mg C L^{-1}) occurred during this extreme dry period. Scott et al. (1998) reported low DOC production in soils during drought and attributed this to a decrease in microbial activity due to increased acidity following oxidation of organic sulphur to sulphate when oxygen availability increased in the soil. The step change analysis indicated that the initial step continued until November 2010, but that elevated DOC concentrations persisted into 2011, and did not return to the low levels recorded before the drought. Watts et al., (2001) reported that step changes in DOC concentrations following drought in a UK peatland catchment could persist for 3-5 years.

The mechanisms behind the effect of water table fluctuations on peat decomposition are still not fully understood. An enzyme latch mechanism has been identified (Fenner and Freeman, 2011; Freeman, 2001 b) as a possible explanation, where drought stimulates bacterial growth and phenol oxidase activity, reducing the concentration of inhibitory phenolic compounds in the peat and stimulating microbial growth. However, rewetting will also stimulate decomposition. Ryan et al. (1998) noted an immediate increase in soil pH and ammonium levels upon initial rewetting in experimental plots, suggesting increases in microbial activity. It is likely that the step changes reported in this paper reflected both drought effects on soil biogeochemistry, including effects on soil pH and the oxidation of organic sulphur as described by Scott et al. (1998), and changes in enzyme activity, coupled with washout of high levels of available DOC in soil stores during the subsequent wet conditions (Fenner and Freeman, 2011).

However, identification of any persistence of the step change in DOC levels into 2011 was complicated by the two phases of forestry clearfelling in the second year. In contrast to studies from other peat rich regions and felling operations over a larger area (Schelker et al. 2012; Nieminen, 2004), our results indicated that clearfelling was not a significant factor in the DOC model. Cummins and Farrell (2003) found that a gradual increase in DOC concentrations occurred following clearfelling in another west of Ireland catchment. Drinan et al. (2012) also reported a single high value for DOC concentration in a stream draining a recently clearfelled forestry coup in the same study sub-catchment as used in the current study. While it is highly likely that such spikes in DOC occur as a result of clearfelling, our results show that these events need to be viewed in the context of the annual cycle in DOC concentrations to correctly assess their relative importance.

The estimated export of the two carbon fractions for 2010, 9.5 t C km^2 year^{-1} for DOC and 6.2 t C km^2 year $^{-1}$ for POC, are within the range reported in other studies from peatland catchments (Naden et al*.,* 2010; Koehler et al., 2009; Agren et al., 2007; Clark et al., 2007; May et al., 2005; Worrall et al., 2003; Hope et al., 1997). On an annual basis, the POC load was estimated to represent just under 40 % of the combined POC and DOC load. While the use of high frequency data gives a greater confidence in these estimated export rates, POC export was based on both high frequency measurements of the suspended sediment load, and on less frequent measurements of the organic matter content of this load. There will, therefore, be greater uncertainty in the estimates of POC export than in the DOC estimates due to this additional calculation step. The contribution of organic particles to the overall suspended sediment load in a river is catchment specific (Dawson et al., 2011), but as expected for a peat catchment was high in the Glenamong River. While acknowledging this uncertainty, the results presented nevertheless provide insight into the relative contribution of POC to carbon export in streams draining upland peat systems. The overall export in 2010 was 15.7 t C km^2 year^{-1}. Peatlands represent 17.36 % of the land area in Ireland, storing between 53 % and 62 % of national soil organic carbon stores (Eaton et al., 2008; Tomlinson, 2005). The storage in the Glenamong sub-catchment in unknown, however, Wellock et al. (2011) estimated that the carbon stored in high-level blanket bog at two sites in County Mayo was 72,700 t C km^2 and 162,000 t C km^2 respectively. Based on these estimates, the total carbon export from the Glenamong would represent between 0.01 % and 0.02 % of the soil carbon store.

The assessment of the main factors contributing to variability in suspended sediment and therefore POC concentrations in the Glenamong River also highlighted the sensitivity of carbon export to climatic factors. Flow, cumulative rainfall over the preceding twenty days, and cumulative soil temperature in the previous ten-day period accounted for 58.3 % of deviance in concentrations. As might be expected, while the optimal model indicated that rainfall and soil temperature were significant, stream discharge was the most important explanatory factor, with an almost linear relationship between the log of flow and the log of POC concentration. The role of stream discharge in the transport of particulate material is well recognised (Strohmeier et al., 2010; Pierson et al., 2008) and has been previously highlighted in studies in the Glenamong sub-catchment (Rodgers et al., 2011). In contrast, the smoothing curve for the effect of cumulative rainfall on POC concentrations showed an initial increase, but then a gradual decline in influence of this driver. This supports the results of an earlier study in the catchment (May et al., 2005), which reported that discharge alone did not adequately explain sediment export, as antecedent conditions also played a significant role. The decline in suspended sediment levels at higher antecedent cumulative rainfall suggests that prolonged wet periods may result in a washout of erodible material on exposed soils and in the stream network. The relationship of particulate concentrations to preceding periods of warmer weather is less intuitive, but may be the result of the peat soils drying out and fracturing, and hence exposing more particles to erosion (Evans et al., 2006).

Surprisingly, forestry clearfelling was not a significant driver of POC concentrations over the study period when included in the model as a factor. However, there were two large pulses in POC export in February and April 2011, and two smaller pulses in August and September 2011, which were coincidental with high flows soon after the forestry operations. As with DOC, longer term monitoring of the catchment as clearfelling continues may allow separation of climatic and land use factors. It should also be noted that this sub-catchment is being clearfelled in a pro-active manner, in order to minimise prolonged disturbance of sensitive aquatic environments, and therefore only small coupes are being cleared each year. The results presented here indicate that even though clearfelling has in the past been related to high levels of suspended sediment export (Rodgers et al., 2011), a management regime that includes felling in small increments may reduce the impact on downstream systems.

The current directional trends in the global carbon cycle and global climate give added relevance to the results presented in this paper. Based on future climate scenarios that projected higher temperatures and decreased precipitation during summer, with higher rainfall in autumn and winter, Naden et al. (2010) forecast higher DOC export from the study catchment for the mid to late 21st century. The positive feedback that exists between the water table level and peat decomposition may further increases the sensitivity of decomposition to temperature (Mäkiranta et al., 2009; Ise et al., 2008). The current study indicates that particulate carbon export (POC) may be equally sensitive to these projected changes in climatic factors, namely higher soil temperatures, precipitation and flow. Both carbon sources (DOC and POC) have the potential to be subsequently mineralised within downstream aquatic systems, thus further contributing to atmospheric carbon dioxide levels (Davison and Janssens, 2006). Taken together, the results presented here along with the work described in Naden et al. (2010) should leave little doubt that carbon export from peatland catchments is particularly sensitive to climatic factors and must be considered as a significant component of carbon cycles in regions with peat rich soils. Long-term monitoring of dissolved and particulate carbon in aquatic systems, along with advances in the estimation of gaseous carbon emissions from rivers and lakes, will be crucial in the quantification of carbon budgets in the future.

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