Biogeochemistry (2009) 95:231–242
DOI 10.1007/s10533-009-9333-9

Seasonal variation of DOC concentration and annual loss of DOC from an Atlantic blanket bog in South Western Ireland

**Ann-Kristin Koehler · Kilian Murphy ·
Gerard Kiely · Matteo Sottocornola**

Received: 7 March 2008 / Accepted: 14 May 2009 / Published online: 11 June 2009

Abstract This paper represents the first continuous dissolved organic carbon (DOC) record, measured in a stream draining an Atlantic blanket bog in South West Ireland for the calendar year 2007. At 30-min intervals, the DOC concentration was automatically measured using an in-stream spectroanalyser whose variation compared well with laboratory analysed samples taken by a 24-bottle auto-sampler. The concentration of DOC ranged from 2.7 to 11.5 mg L^{-1} with higher values during the summer and lower values during the winter. A simple linear regression model of DOC concentration versus air temperature of the previous day was found, suggesting that temperature more than discharge was controlling the DOC concentration in the stream. The change in DOC concentration with storm events showed two patterns: (1) in the colder period: the DOC concentration seemed to be independent of changes in stream flow; (2) in the warmer period: the DOC concentration was found to rise with increases in stream flow on some occasions and to decrease with increasing stream flow on other occasions. The annual export of DOC for 2007 was 14.1 (±1.5) g C m^{-2}. This value was calculated using stream discharge data that were determined by continuously recorded measurements of stream height. The flux of DOC calculated with the 30-min sampling was compared with that calculated based on lower sampling frequencies. We found that sampling frequency of weekly or monthly were adequate to calculate the annual flux of DOC in our study site in 2007.

Keywords Dissolved organic carbon · Peatland · Seasonal variation of dissolved organic carbon · DOC flux

Introduction

Globally, northern peatlands only account for about 3% of the earth's land area but they have accumulated between 270 and 450 Pg of carbon (C), which represents 20–30% of the world's estimated global soil C pool (Gorham 1991; Turunen et al. 2002). Peatlands in the Republic of Ireland cover 17% of the land area and are estimated to contain between 53 and 62% of the national soil C stock (Tomlinson 2005; Eaton et al. 2007). Atlantic blanket bogs are rare peatland ecosystems, accounting for about 3% of the

---

A.-K. Koehler (✉) · K. Murphy · G. Kiely ·
M. Sottocornola
Centre for Hydrology, Micrometeorology and Climate Change, Department of Civil and Environmental Engineering, University College Cork, Cork, Republic of Ireland
e-mail: a.koehler@student.ucc.ie

Present Address:
M. Sottocornola
IASMA Research and Innovation Centre – Environment and Natural Resources Area, Fondazione Edmund Mach, Loc. Viote del Bondone, Trento 38100, Italy

global peat area. In the Republic of Ireland they cover about 6% of the land area and contain ca. 19% of the nation soil carbon stock (Tomlinson 2005). Blanket bogs are ombrotrophic peatlands that typically develop independently from basins in temperate maritime regions with annual rainfall greater than 1,250 mm (Hammond 1981).

Dissolved organic carbon (DOC) is the carbon contained within organic matter in a solution that passes through a 0.45 µm filter. Organic carbon may derive from plant litter, root exudates, microbial biomass or soil organic matter and is an important component of the global carbon cycle (Meybeck 1993; Worrall et al. 1997). Recent observations have found a rapid rise of DOC concentrations in lakes and streams in the UK (Freeman et al. 2001; Worrall et al. 2004; Evans et al. 2005) and across large areas of Scandinavia and North East North America (Skjelkvåle et al. 2005). This creates concern that stocks of C are beginning to destabilise (Freeman et al. 2001) and may become waterborne and eventually return to the atmosphere. Given the importance of blanket peatlands to Ireland's carbon stock there is a need to measure the magnitude of DOC flux from Irish bogs and to understand the driving factors controlling the DOC concentration in Irish streams.

The mechanisms explaining the DOC concentration in streams are still unclear. Dissolved organic carbon concentrations in organo-mineral catchments seem to depend on stream flow (McDowell and Likens 1988; Hope et al. 1994; Hornberger et al. 1994; Boyer et al. 1997; Dawson et al. 2002), while in temperate peatlands the main driver for seasonal variations in DOC is temperature (Hornberger et al. 1994; Hinton et al. 1997; Dawson et al. 2002). Moreover, since large proportions of the annual DOC flux (36 to >50%) have been shown to occur during short times of peak discharges (Hinton et al. 1997; Buffam et al. 2001; Inamdar et al. 2006; Clark et al. 2007) continuous measurements of DOC concentration over all seasons of the year are needed to reveal the contribution of peak discharges to the total DOC flux. It is further essential to investigate the main environmental controls on the changes in DOC concentration.

The objectives of this study were therefore threefold: (1) to investigate the short term and seasonal variations of DOC concentration in response to changes in stream flow and the influence of other environmental drivers on DOC concentration; (2) to quantify the annual flux of DOC and to estimate it using temperature (as a proxy for biological activity) and (3) to estimate the accuracy of the annual flux of DOC using daily, weekly or monthly observations relative to continuous (30-min) measurements.

To our knowledge this is the first research on quasi-continuous measurements of DOC. Moreover no studies have been published on the riverine loss of carbon as DOC from Irish rivers.

Materials and methods

Site description

The study site is located in an Atlantic blanket bog in Glencar, County Kerry, in South West Ireland (51°55′N, 9°55′W) (Fig. 1). The average annual precipitation over the period 2003–2006 was 2,571 mm year^{-1} (Table 1) while the average number of wet days (i.e. >1 mm day^{-1}) was 208. In the same period the average temperature from May to October was 13.3°C and the average temperature from November to April was 7.7°C giving an annual average of 10.5°C.

The present study was confined to the catchment of a peatland stream whose boundaries are located inside the bog on the west, east and north and is delimited by a small country road on the south (Fig. 1). A water level recorder station is located on the northern end of the catchment (Fig. 1). The catchment area is approximately 73.6 ha, 85% of which is relatively intact bog and 15% is on a hill slope covered by patches of grassland and peaty soils. No drainage and no man-induced erosion were detected inside the catchment.

The slope of the stream as defined by S_{1085} is 22 m km^{-1}, (i.e. the change in elevation between points 10 and 85% of length of the stream). Due to changing stream gradients along the stream length (Fig. 1), there are lengths with pools where the gradients are flat and lengths with riffles where the gradients are steep. The discharge varied from 0.01 to 0.73 m^3 s^{-1} over the calendar year 2007.

The peatland is typical of Atlantic blanket bogs in the maritime regions of North Western Europe in terms of both vegetation and water chemistry (Sottocornola et al. 2009). The vegetation belongs to the phytosociological associations of the *Pleurozio purpureae-*

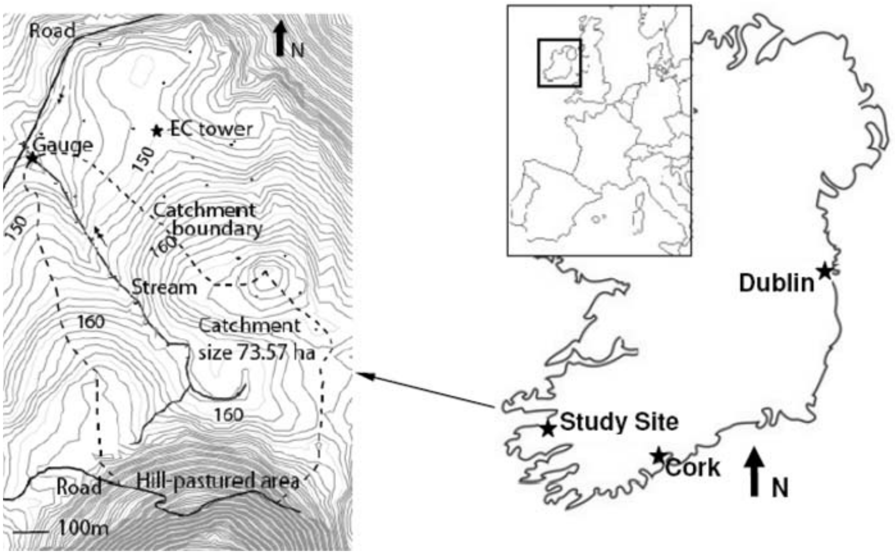

Fig. 1 Site layout and location map. The peatland site is located about 120 km west of Cork City. The catchment boundary is shown with a *dashed line* and the bog stream is shown in a *solid line*. The stream is gauged at the northern side. EC tower = location of an eddy covariance tower

Table 1 Inter-annual variability of the precipitation pattern in Glencar from 2003 to 2007

Year	Total precipitation (mm)	Summer (May–August) (mm)	Autumn (September–November) (mm)
2003	2,510.3	676.6	713.0
2004	2,355.6	547.5	739.5
2005	2,468.3	563.1	794.1
2006	2,951.7	569.3	1,123.0
2007	2,235.3	615.6	396.6

Ericetum tetralicis and *Sphagno tenelli-Rhynchosporetum albae*. The vegetation survey was conducted within an area of about 70 ha in the relatively intact part of the bog (Sottocornola et al. 2009). Vascular plants cover about 30% of the surveyed area with the most common species being *Molinia caerulea* (purple moor-grass), *Calluna vulgaris* (common heather), *Erica tetralix* (cross-leaved heath), *Narthecium ossifragum* (bog asphodel), *Rhynchospora alba* (white beak-sedge), *Eriophorum angustifolium* (common cottongrass), *Schoenus nigricans* (black-top sedge), and *Menyanthes trifoliata* (buckbean). About 25% of the bog surface is covered by bryophytes with the dominant species being a brown moss, *Racomitrium lanuginosum* (woolly-hair moss), and *Sphagnum spp.* (bog mosses). The peat depth ranged from about 0.5 m to over 2 m (Sottocornola et al. 2009) with a carbon concentration of 42.83% in the upper 10 cm and 45.84% in 25–50 cm (unpublished data).

A spectro::lyser^{TM} and a water level recorder station are located at the same point on the northern end of the catchment (gauge site) (Fig. 1).

Spectro::lyser^{TM}

Continuous measurements (30-min interval) of dissolved organic carbon began in January 2007 using an s::can spectro::lyser^{TM} (scan Messtechnik GmbH, Austria). The instrument is constantly immersed in the stream at the gauge site (Fig. 1) and works according to the measuring principle of UV–VIS spectroscopy. The measured spectrum ranges from 200 to 735 nm and the absorbance is determined every 2.5 nm. The calculation of the DOC concentration is based on the inclusion of over 80 wavelengths, some to actually calculate the concentration but most for correction of turbidity.

The spectro::lyser^{TM}'s lenses were automatically cleaned before each 30-min measurement by a blow of pressurised air and manually every 1–2 weeks. Additionally the spectro::lyser^{TM} readings were zeroed using distilled water about every 4 months. These precautions reduced the drifting of the spectro::lyser^{TM} due to environmental conditions. The drifting between two subsequent manual cleaning (usually below 1 mg L^{-1}) and calibration events was corrected assuming a constant linear drift over time. Moreover as the automatic in-stream spectro::lyser^{TM}

is not specifically designed for peatland waters, its measurements were calibrated on a regular basis with results from chemical laboratory analyses. A 24-bottle auto-sampler (6712 portable sampler, Teledyne Isco, Inc., USA) was used about every 6 weeks from April to October 2007 to collect water samples at intervals between 1 and 3 h at the same location as the spectro::lyser$^{\text{TM}}$. The auto-sampler was installed in the stream to monitor a range of flow conditions. Dissolved organic carbon concentration in the water samples were measured in the laboratory using a TOC-V cpH (SHIMADZU Scientific Instruments, USA), which works according to an oxidative combustion-infrared method. Spectro::lyser$^{\text{TM}}$ measurements and laboratory analyses compared well during both dry periods and storm events (Fig. 2) regarding the general trend of DOC concentration, i.e. rise or decrease in concentration. A constant difference between laboratory and field measurements over the sampling time was observed, therefore the spectro::lyser$^{\text{TM}}$ measurements were corrected for linear drifting between following bottle auto-sampler collections. It was noted that the spectro::lyser$^{\text{TM}}$ is less variable than the bottle auto-sampler however the reasons for this are not precisely known.

Missing values of DOC concentration due to instrumentation failure occurred during the first half of January and in December 2007. The concentration of DOC appeared to be independent of stream flow during the colder period (see results: concentration of DOC). Hence the DOC concentrations in the first 2 weeks of January were assumed to equal the mean DOC concentration measured in the last 2 weeks of January. The missing values in December were instead estimated by a linear interpolation based on laboratory analyses of DOC concentration from grab samples taken on December 17th 2007 and January 21st 2008.

Environmental parameters

The stream height was recorded every 30-min at the gauge site using a pressure transducer (1830 Series, Druck Limited, UK). Manual measurements of the instantaneous discharge were carried out at a range of stream heights using an OTT current meter (OTT Messtechnik GmbH and Co KG, Germany). The manual discharge measurements were used to establish a rating curve (Eq. 1), which converted recorded stream height to discharge data for the full year 2007.

$$Q = 0.685 \times s^{1.79}, \quad \text{number of measurements} = 10, \quad r^2 = 0.995, \tag{1}$$

where Q is the discharge in $\mathrm{m}^3\ \mathrm{s}^{-1}$ and s the stream height in m. The total discharge is calculated by

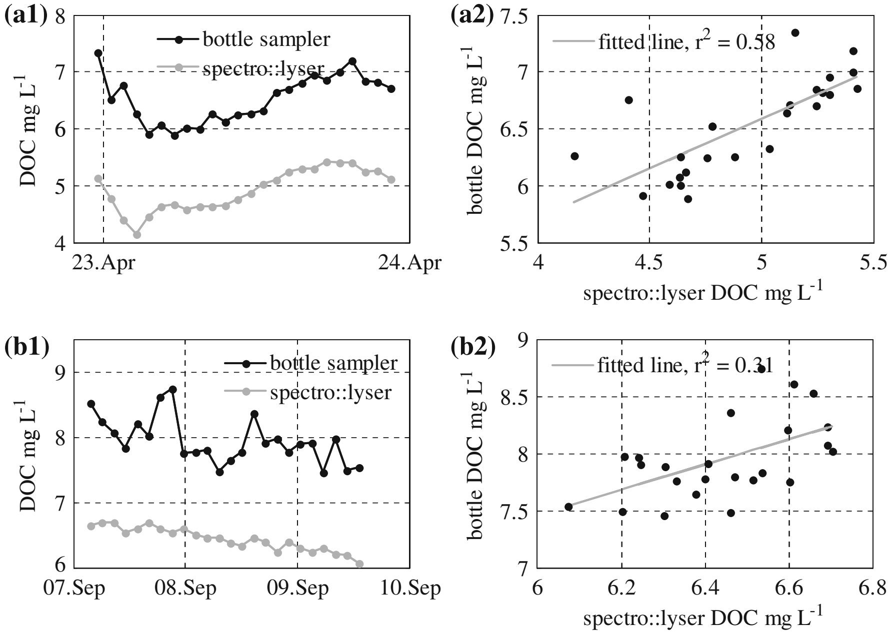

Fig. 2 Comparison of a time series of DOC concentrations measured in the field by the spectro::lyser$^{\text{TM}}$ and laboratory analyses during **a** A storm event and **b** a dry period

integrating the estimated 30-min discharge data. Error analysis for discharge and drainage basin area was done using the approach of Fraser et al. (2001). Discharge error was determined from the standard error of the rating curve (± 0.0080 m), such that minimum and maximum daily discharges were calculated using stages that ranged ±0.0080 m about the best-fit curve. The drainage basin area error was assumed to be ±5% as done by Fraser et al. (2001). The error analysis was included in the calculation of the DOC flux. To calculate the flux of DOC from the catchment, the 30-min DOC concentration data were multiplied by the 30-min discharge data to calculate load, (i.e. mass transported per unit time). The load was converted to flux, (i.e. mass transported per unit catchment area per unit time) by dividing by the catchment area. Integration of the 30-min flux data resulted in the annual flux of DOC.

Precipitation in the study site was measured with two tipping bucket rain gauges (an ARG100, Environmental Measurements Ltd., UK and an Obsermet OMC-200, Observator BV, The Netherlands), while air temperature was measured at 2 m height with a shielded probe (HMP45C, Vaisala, Finland) (see Sottocornola and Kiely 2005). Both parameters were measured at 30-min interval frequency at an eddy-covariance (EC) tower located in the central part of the bog near the North Eastern border of the catchment (Fig. 1).

In order to analyse the DOC data in terms of the relationship to changes in stream flow, the record was considered as a series of events (see approach by Heppell et al. 2002; Worrall et al. 2002). The following parameters were tabulated: absolute increase in discharge, absolute decrease or increase in DOC concentration and time between events. Altogether 130 events were characterised. Pearson correlation analysis was used to investigate the general relationships between stream water DOC concentration and environmental parameters including air temperature, discharge and rainfall.

The influence of infrequent sampling of once a day, once a week and once a month was also examined. For this purpose the 30-min measured DOC concentrations were divided into sub groups of daily, weekly and monthly data, respectively and one random sample was taken from each of those sub groups. The load was estimated using Method 5 (Walling and Webb 1985; Littlewood 1992):

$$F = K \times Q_{\mathrm{r}} \times \left(\frac{\sum_{i=1}^{n} C_i \times Q_i}{\sum_{i=1}^{n} Q_i} \right), \qquad (2)$$

where F is the total solute load carried over a certain time period (here 1 year), K is the conversion factor (here number of seconds in the time period), Q_{r} is the mean discharge from a continuous record, Q_i is the instantaneous discharge, C_i is the instantaneous concentration and n is the number of samples. Dividing by the catchment area converts the load estimate from Eq. (2) to flux. When a record of continuous flow is available Method 5 (Eq. 2) is considered to provide the best estimate of load from the possible integration methods available (Walling and Webb 1985; Littlewood 1992). Standard errors for flux estimates were determined using standard methods described in Hope et al. (1997). This way of determining DOC was run 1,000 times and the mean and standard deviation for the DOC flux was calculated.

Results

Environmental conditions

Compared to the 2003–2006 average, 2007 was slightly warmer (10.9°C), due to warmer temperatures from November to April (average of 8.5°C) while May to October had similar temperatures (average of 13.3°C) as in 2003–2006 (Fig. 3a).

The precipitation in 2007 showed a regular rainfall pattern during the whole year with only few periods of dry weather (Fig. 3b). Dry periods unusually occurred in April and September whereas June to August was rather wet (Fig. 3b). Over the year the total number of wet days was 196, yielding an annual rainfall amount of 2,235 mm, which is less than the average in the previous 4 years (2,571 mm). Our study site showed a high inter-annual variability in the amount of summer and autumn precipitation (Table 1). The summer in 2007 was wetter (615.6 mm of rain) than in the period 2004–2006 (average of 560 mm) but drier than 2003 (676.6 mm). In contrast, the autumn of 2007 (September to November) was extremely dry with about half

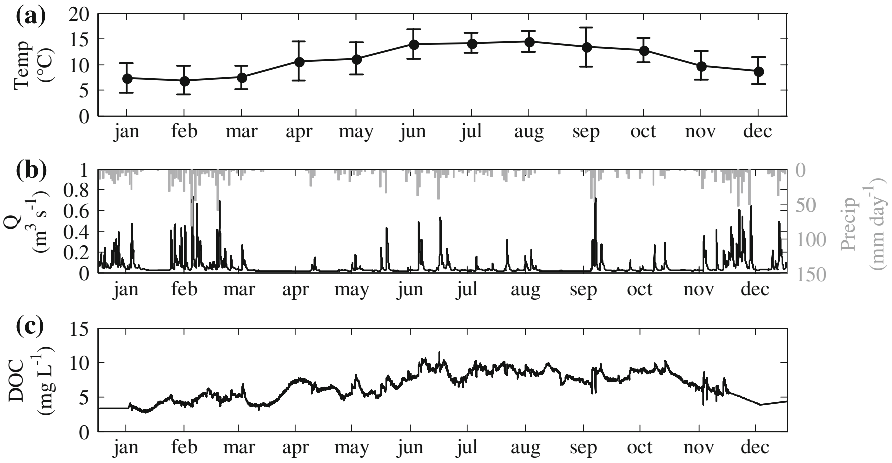

Fig. 3 **a** Mean monthly air temperature for 2007 including standard deviations, **b** half-hourly stream flow (*in black*) and daily precipitation (*in grey*) data during 2007 and **c** half-hourly DOC concentration data. Temp = air temperature, Q = discharge; Precip = precipitation

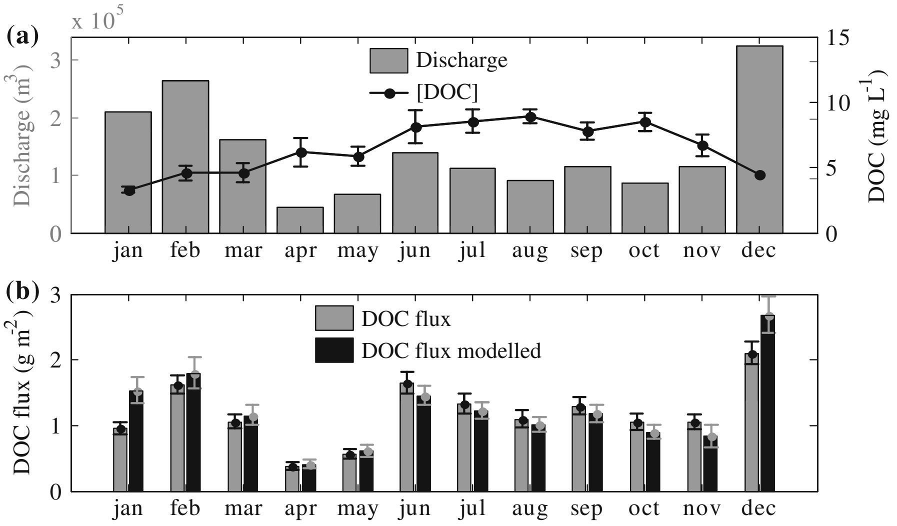

Fig. 4 **a** Monthly stream water discharge and mean monthly DOC concentration and **b** monthly DOC flux calculated from 30-min DOC measurements and modelled monthly DOC flux based on the relationship of DOC concentration and air temperature for 2007. *Error bars* show the combined error of discharge and drainage basin area for the calculated DOC flux. Modelled DOC flux error bars further include the error given by the 95% CI on the model as well as the error for the flux calculation using Method 5 (Eq. 2)

the amount of precipitation of the years 2003–2006 (Table 1).

The stream flow closely followed the precipitation pattern (Fig. 3b). Unit hydrograph studies for Glencar showed that the lag between the centroid of a rainfall event and peak flow was less than 5 h (unpublished data). Due to the regular rainfall pattern, the discharge during May to October of 2007 was high but lower than during the remaining months (Fig. 4a); about 35% of the annual discharge occurred during the months May to October.

Concentration of DOC

Figure 3c shows the half-hour time series data of the DOC concentration in the peatland stream during 2007. No obvious peaks in the concentration of DOC were visible and the average concentration for the month with the lowest concentration, January, and the month with the highest concentration, August, were 3.3 and 8.9 mg L^{-1}, respectively (Fig. 4a) with an annual average of 6.5 mg L^{-1} (Fig. 4a).

To explore the general seasonal relationship between DOC concentration and discharge (*Q*) the DOC time series was subdivided into three periods based on their concentrations (Fig. 3c): from January to March; April to October; November (as December had estimated data). There was no clear increase or decrease in DOC concentration with increasing stream flow for any of these three periods (Fig. 5). Investigation of DOC concentrations versus *Q* gave different results for each individual event, showing increase, decrease or no change in DOC concentration with increasing stream flow. A quantitative analysis was therefore used to investigate the behaviour of DOC concentration with increasing stream flow throughout the year. For each of 130 stream flow events the characteristic of the absolute variation in DOC concentration with increasing *Q* were examined (Table 2). The changes in DOC concentration were rather low during the colder period (November to March) with many storm events not showing any change in DOC concentration over the full storm hydrograph (Table 2). Coinciding with increasing air temperature, a change in DOC concentration to increased flow began in April extending until about October (referred to as warmer period). During the warmer period even many events with a small increase in *Q* resulted in an increase or a decrease in DOC concentration (Table 2). Events not showing any change in DOC concentration during the warmer period were observed for increases in *Q* below 0.05 m^3 s^{-1} without exception (Table 2). Nevertheless none of the events over the full storm hydrograph showed an increase or decrease of more than 3 mg L^{-1}. The time between two subsequent events was not correlated to the absolute change in DOC concentration. Dissolved organic carbon concentration did not correlate with precipitation.

The concentration of DOC was generally higher during the summer and lower during the winter. A relationship to air temperature was established using daily averages of DOC concentration and air temperature. Cross correlation revealed that the concentration of DOC lagged one day behind air temperature. Including the lag of one day, a significant, positive linear relationship with air temperature was found (Fig. 6).

Flux of DOC

In general, the magnitude of the monthly flux of DOC for the Glencar peatland stream was similar from May to October and November to April (Fig. 4b), with 49% of the annual flux of DOC in 2007 occurring in the 6 months from May to October. The flux of DOC during the winter months was high because of high discharge (Fig. 4a), even though the DOC concentrations were low. During May to October, the flux of DOC was high due to higher

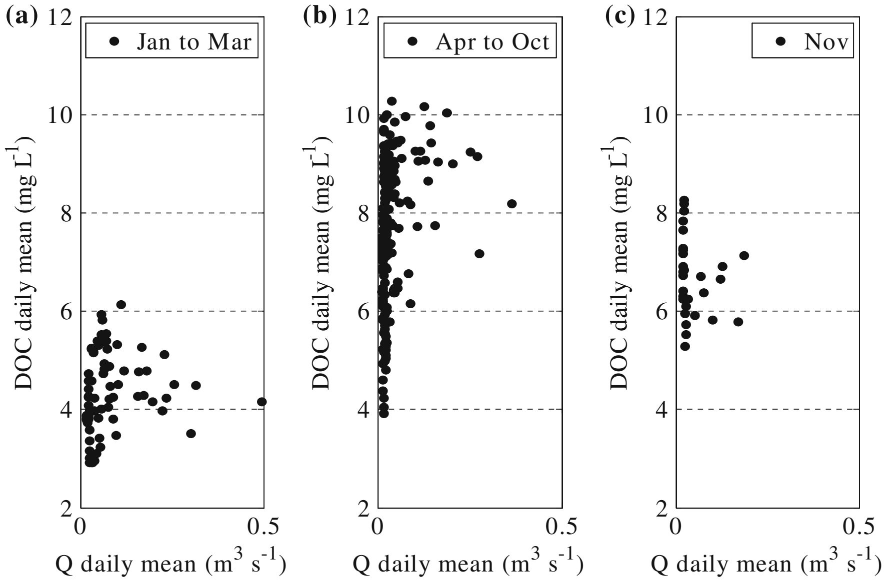

Fig. 5 Daily mean discharge versus daily mean DOC concentration for the three periods January to March (**a**), April to October (**b**) and November (**c**)

Table 2 The results of the event analysis, the number of DOC events in a specified range happening for different increases in *Q* divided between the cold (November to March) and warm period (April to October). The numbers given in brackets are the events with negative change of DOC, without brackets the number of events with positive change in DOC

Change DOC versus rise Q	No change in DOC		DOC < 0.5		0.5 < DOC < 1.5		1.5 < DOC < 2.5		2.5 < DOC < 3.5	
	Cold	Warm	Cold	Warm	Cold	Warm	Cold	Warm	Cold	Warm
Q < 0.05	23	28	3 (1)	12 (5)	1 (–)	9 (5)	–	–	–	–
0.05 < Q < 0.15	2	–	– (3)	–	2 (1)	2 (3)	–	5 (–)	–	–
0.15 < Q < 0.25	1	–	–	–	2 (–)	2 (1)	–	3 (–)	1 (–)	–
0.25 < Q < 0.35		–	–	–	–	– (1)	–	1 (–)	–	–
0.35 < Q < 0.45	2	–	2 (1)	–	– (2)	–	–	1 (–)	–	–
0.45 < Q < 0.55	–	–	–	–	–	–	–	–	–	– (1)
0.55 < Q < 0.65	–	–	– (1)	–	– (1)	–	–	–	–	– (1)
0.65 < Q < 0.75	–	–	–	–	1 (–)	–	–	–	–	–

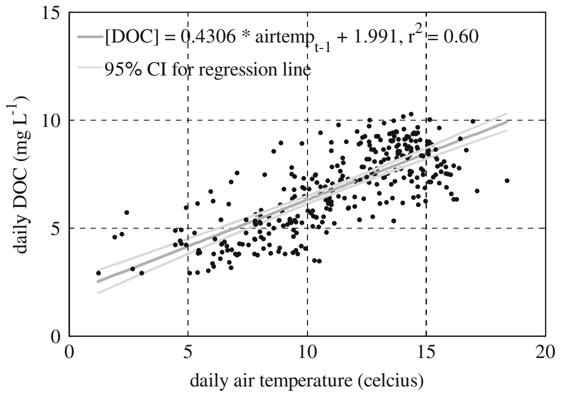

Fig. 6 Relationship between daily DOC concentrations and daily air temperature of the previous day. The bounds shown are the 95% CI on the model

concentrations of DOC and 35% of the annual discharge (Fig. 4a), Table 1). In 2007, December was the month with the highest flux of DOC (about 2 g m^{-2}, Fig. 4b) mainly because it was also the month with the highest discharge (Fig. 4a). By comparison April and May were the months with the lowest flux of DOC (0.4 and 0.5 g m^{-2}, respectively) (Fig. 4b). The DOC concentrations in the stream started to rise in April and May (Fig. 3c) when unseasonal warm temperature for this time of the year was recorded (Fig. 3a). However since the discharge was low in April and May, the DOC flux was also lower than in other months, especially in April. The annual flux of DOC for 2007 was calculated to be 14.1 ± 1.5 g C m^{-2} year^{-1}.

In 2007 about 45% of the DOC flux occurred during storm events corresponding to approximately 10% of the time when the greatest discharge was recorded (data not shown). Similar results were found in a Canadian wetland (Hinton et al. 1997) and a small upland peat catchment in the northern Pennines, UK (Clark et al. 2007) where 41 to 57% of DOC was exported during the top 10% of high flows. Given that most DOC was exported during storm events the likely error of infrequent sampling for the annual DOC flux for Glencar was investigated. Infrequent sampling of once a day, once a week and once a month was simulated and which most likely resulted in omitting some of the DOC concentrations during storm discharges. The annual DOC flux estimates for 2007 were 14.1 (±0.1), 14.1 (±0.6) and 14.1 (±1.8) g C m^{-2} year^{-1} for infrequent sampling of once a day, once a week and once every month, respectively which compare with 14.1 g C m^{-2} year^{-1} measured with 30-min continuous sampling. Therefore infrequent sampling would result in a similar estimation of the DOC flux compared to the half-hourly data. The more frequent samples are taken, the lower the standard deviation of the flux, i.e. the chance to get a flux estimate close to the true value is higher.

As air temperature showed the strongest relationship to DOC concentration (Fig. 6) a simple linear regression model was used to test the potential of using air temperature to estimate the flux of DOC. Compared to the half-hourly data it resulted in an overestimation of about 5% yielding an annual DOC flux of 14.8 g C m^{-2} year^{-1}. The DOC flux was in general overestimated during winter and underestimated during summer (Fig. 4b).

Discussion

Concentration of DOC

Both, the mean (6.5 mg L^{-1}) and the range (2.7–11.5 mg L^{-1}) of DOC concentrations measured in the Glencar Atlantic blanket bog are in the lower range compared to other published data. Clark et al. (2005) measured variations in DOC concentration between 5 and 35 mg L^{-1} for a stream draining an 80% peatland covered area in the North Pennine uplands, UK. Typical annual values of DOC concentration measured in Scottish upland catchments dominated by blanket peatlands ranged between 3.9 and 18.3 mg L^{-1} (Hope et al. 1997; Dawson et al. 2002, 2004). Roulet et al. (2007) reported a mean concentration of DOC of 47.5 ± 12.6 mg L^{-1} at the peatland outflow for the Mer Bleue a peatland in the midcontinental cool-temperate climate zone in Canada.

The Glencar bog results did show only small changes in DOC concentration over the full storm hydrograph with only three out of 130 events over the whole year reaching the highest change in DOC concentration of about 3 mg L^{-1} (Table 2). This is in line with most studies on DOC concentration and flow conducted in peatlands or wetlands showing only weak correlations with discharge (Hinton et al. 1997; Schiff et al. 1998; Clark et al. 2007). The observed small changes in DOC concentration during storm events and the typical small concentrations of DOC in the stream in Glencar could be caused by: (1) a dilution by rainfall given the high annual amount of rain (over 2,200 mm in 2007); or (2) the DOC production in Glencar may be smaller than in other peatland systems; or (3) the sulphate concentrations in the soil water may be higher compared to other peatlands. (1) The dilution of DOC by rainfall is confirmed by hydrological studies that highlighted the importance of near surface flow paths for peatlands (Schiff et al. 1997; Palmer et al. 2001; Holden 2003). The upper peat layer is the region where DOC accumulates during times with low runoff and temperatures high enough for biological activity (Adamson et al. 2001; Worrall et al. 2002). Stream water during storm events is then likely to come from peat soil water being rich in DOC and surface runoff having a chemical signature close to rainfall (Worrall et al. 2002; Holden 2005; Clark et al. 2007). (2) Compared to the Mer Bleue peatland the rather low DOC concentrations in Glencar are probably due to less production of DOC in the soil as the summer is colder (temperature of the warmest month about 20.9°C compared to 14.5°C in Glencar) and the water table is closer to the surface throughout the year (Mer Bleue between about −20 and −70 cm, Glencar between about 0 and −20 cm). The second hypothesis is further supported by measurements of DOC concentration in the soil water taken at 10 cm depth on two occasions during the summer time at three different locations in the blanket bog part of the catchment. They showed that DOC concentrations were similar to DOC concentrations in the stream water. This finding might explain the lack of a relationship between a change in DOC concentration and time between events and the in general low concentration of DOC in the stream. The time between storm events in other peatlands have been observed to be critical for the amount of carbon released in any event as it is the time during which oxidation processes generate a reservoir of available carbon (Worrall et al. 2002). If DOC production in Glencar is lower than in other peatland systems a significant DOC pool might not be generated. Furthermore the summer of 2007 in Glencar was unusually wet (Fig. 3b); Table 1), which might have additionally contributed to the rather low DOC concentrations in the soil water as the available carbon pool was continuously depleted. Nevertheless the low DOC concentrations in the soil water need to be confirmed with more frequent measurements. (3) The third hypothesis is supported by the location of Glencar close to the Atlantic coast resulting in high concentrations of sulphate from sea-salt sources in the precipitation (Aherne and Farrell 2002). In combination with the high annual amount of rainfall this might result in increased sulphate concentrations in the soil that drive changes in soil water chemistry resulting in an increase in H^+ and an increase in conductivity/ionic strength. These two factors were found to reduce the solubility of DOC in the soil (Clark et al. 2005).

Rainfall is the driver for both discharge and DOC release. The correlation between DOC concentration and stream flow was weak which explains why no significant relationship between DOC concentration and rainfall could be established.

The measurements in Glencar indicated a strong seasonal pattern of DOC concentration, as previously observed in other peatland catchments (Naden and McDonald 1989; Scott et al. 1998; Clark et al. 2005; Billett et al. 2006). Temperature appears to be a good predictor of DOC concentration in the stream water (Fig. 6), and it does so much better than changes in stream flow. Increasing temperature was shown to enhance biological activity and accelerate DOC production more than DOC consumption (Freeman et al. 2001; Moore and Dalva 2001). Fenner et al. (2005) observed the presence of a thermal optimum for carbon processing in a given season where higher production during the summer might not only depend on increasing temperature but also on a shift in the microbial community.

Comparisons of DOC concentration for a further 2 years are planned. The goal is to verify the seasonally dependent relationship between DOC concentration and variations in stream flow and to investigate how sensitive the relationship of DOC concentration and air temperature is to inter-annual climatic changes.

Flux of DOC

The annual export of DOC was calculated to be 14.1 ± 1.5 g C m^{-2} for 2007. Gorham (1995) estimated the DOC export from a 'typical' northern peatland to be approximately equal to the long-term carbon sink term (20–30 g C m^{-2} $year^{-1}$) of these ecosystems. A lower value of 10.8 g C m^{-2} $year^{-1}$ was estimated by Worrall et al. (2003) for a catchment with 100% peatland land cover using data from a Scottish study and regressing peat cover and DOC flux. In the North Pennine upland region Worrall et al. (2003) reported annual DOC fluxes ranging between 9.4 and 15 g C m^{-2} $year^{-1}$ for the Trout Beck catchment with 90% covered by blanket peat and some areas being either naturally eroded or damaged by artificial drainage channels. For a small upland peat catchment almost entirely covered with peat in the same upland region, estimated annual DOC fluxes varied between about 16.5 and 26.0 g C m^{-2} $year^{-1}$ within a 10 year period (Clark et al. 2007). Roulet et al. (2007) estimated in a 6 year study the average loss of DOC from the Mer Bleue a peatland in the midcontinental cool-temperature climate zone in Canada as 16.4 ± 3.4 g m^{-2} $year^{-1}$. Compared to Mer Bleue complex the Glencar bog receives much higher annual precipitation and is not influenced by snowmelt. Despite these differences the DOC flux in Glencar is similar to the Mer Bleue bog and to some British upland peatland catchments. Nevertheless the origin of the high flux values is different for Glencar and the other catchments as the DOC concentrations are much lower in Glencar but combined with a huge runoff of the order of 2,000 mm per annum.

The annual DOC flux calculated from 30-min measurements was similar to simulations of infrequent sampling of once a day, once a week and once a month. In contrast, Clark et al. (2007) found that by excluding storm events fluxes were overestimated in the order of 10–16% when comparing DOC flux estimates calculated from weekly data and from 4-hourly data over a 45-day monitoring period (during autumn). The difference can be at least partly explained by the different integration periods as the high-frequency monitoring done by Clark et al. (2007) took place during the only season where the DOC concentration at their study site was not flow invariant. The adequacy of infrequent sampling results suggests that it is unlikely that the flux of DOC in Glencar was significantly influenced by the observed changes in DOC concentrations during storm events. The changes in flow were the bigger contributor to DOC flux than DOC concentration. Our results from the Glencar bog in 2007 would justify coarse resolution monitoring, (e.g. weekly) for annual peatland DOC flux estimates. However this might not hold for different peatland catchments or years where the summer is dry.

Acknowledgments This study was funded by the ERTDI Programme 2000–2006, financed by the Irish Government under the National Development Plan and administered on behalf of the Department of Environment and Local Government by the Environmental Protection Agency (CELTICFLUX 2001-CC-C2-M1). AK was funded by Environmental Protection Agency PhD fellowship (Grant code 2006_PhD_AQ-4). We thank Caitriona Douglas of NPWS and Coillte Teoranta for permission to use the study site. We wish to acknowledge the assistance of Dr. Xie Quishi of the Aquatic Services Unit of University College Cork in the water quality analyses. Useful discussions with Anne Brune, James Eaton, Kenneth Byrne and Paul Leahy are appreciated. Thanks for the helpful comments from three anonymous reviewers on the manuscript.

References

Adamson JK, Scott WA, Rowland AP et al (2001) Ionic concentration in a blanket peat bog in northern England and correlations with deposition and climate variables. Eur J Soil Sci 52:69–79. doi:10.1046/j.1365-2389.2001.t01-1-00350.x

Aherne J, Farrell EP (2002) Deposition of sulphur, nitrogen and acidity in precipitation over Ireland: chemistry, spatial distribution and long-term trends. Atmos Environ 36: 1379–1389. doi:10.1016/S1352-2310(01)00507-6

Billett MF, Deacon CM, Palmer SM et al (2006) Connecting organic carbon in stream water and soil in a peatland catchment. J Geophys Res 111:G02010. doi:10.1029/2005JG000065

Boyer EW, Hornberger GM, Bencala KE et al (1997) Response characteristics of DOC flushing in an alpine catchment. Hydrol Process 11:1635–1647. doi:10.1002/(SICI)1099-1085(19971015)11:12<1635::AID-HYP494>3.0.CO;2-H

Buffam I, Galloway JN, Blum LK et al (2001) A stormflow/baseflow comparison of dissolved organic matter concentrations and bioavailability in an Appalachian stream. Biogeochemistry 53:269–306. doi:10.1023/A:1010643432253

Clark JM, Chapman PJ, Adamson J et al (2005) Influence of drought-induced acidification on the mobility of dissolved organic carbon in peat soils. Glob Change Biol 11:791–809. doi:10.1111/j.1365-2486.2005.00937.x

Clark JM, Lane SN, Chapman PJ et al (2007) Export of dissolved organic carbon from an upland peatland during storm events: implications for flux estimates. J Hydrol (Amst) 347:438–447. doi:10.1016/j.jhydrol.2007.09.030

Dawson JJC, Billett MF, Neal C et al (2002) A comparison of particulate, dissolved and gaseous carbon in two contrasting upland streams in the UK. J Hydrol (Amst) 257: 226–246. doi:10.1016/S0022-1694(01)00545-5

Dawson JJC, Billett MF, Hope D et al (2004) Sources and sinks of aquatic carbon in a peatland stream continuum. Biogeochemistry 70:71–92. doi:10.1023/B:BIOG.0000049337.66150.f1

Eaton JM, McGoff NM, Byrne KA et al (2007) The impact of agricultural land cover change on soil organic carbon stocks in Ireland. COST 639:75–80

Evans CD, Monteith DT, Cooper RJ (2005) Long-term increases in surface water dissolved organic carbon: observations, possible causes and environmental impacts. Environ Pollut 137:55–71. doi:10.1016/j.envpol.2004.12.031

Fenner N, Freeman C, Reynolds B (2005) Observations of a seasonally shifting thermal optimum in peatland carbon-cycling processes; implications for the global carbon cycle and soil enzyme methodologies. Soil Biol Biochem 37: 1814–1821. doi:10.1016/j.soilbio.2005.02.032

Fraser CJD, Roulet NT, Moore TR (2001) Hydrology and dissolved organic carbon biogeochemistry in an ombrotrophic bog. Hydrol Process 15:3151–3166. doi:10.1002/hyp.322

Freeman C, Evans CD, Monteith DT et al (2001) Export of organic carbon from peat soils. Nature 412:785–786. doi: 10.1038/35090628

Gorham E (1991) Northern peatlands: role in the carbon cycle and probable responses to climate warming. Ecol Appl 1: 182–195. doi:10.2307/1941811

Gorham E (1995) The biogeochemistry of northern peatlands and its possible responses to global warming. Oxford University Press, New York

Hammond RF (1981) The peatlands of Ireland. An Foras Talúntais, Dublin

Heppell CM, Worrall F, Burt TP et al (2002) A classification of drainage and macropore flow in an agricultural catchment. Hydrol Process 16:27–46. doi:10.1002/hyp.282

Hinton MJ, Schiff SL, English MC (1997) The significance of storms for the concentration and export of dissolved organic carbon from two Precambrian Shield catchments. Biogeochemistry 36:67–88. doi:10.1023/A:1005779711821

Holden J (2003) Runoff production in blanket peat covered catchments. Water Resour Res 39:1191. doi:10.1029/2002WR001956

Holden J (2005) Peatland hydrology and carbon release: why small-scale process matters. Philos T R Soc A 363:2891–2913. doi:10.1098/rsta.2005.1671

Hope D, Billett MF, Cresser MS (1994) A review of the export of carbon in river water—fluxes and processes. Environ Pollut 84:301–324. doi:10.1016/0269-7491(94)90142-2

Hope D, Billet MF, Cresser MS (1997) Exports of organic carbon in two river systems in NE Scotland. J Hydrol (Amst) 193: 61–82. doi:10.1016/S0022-1694(96)03150-2

Hornberger GM, Bencala KE, McKnight DM (1994) Hydrological controls on dissolved organic-carbon during snowmelt in the Snake River near Montezuma, Colorado. Biogeochemistry 25:147–165. doi:10.1007/BF00024390

Inamdar SP, O'Leary N, Mitchell MJ et al (2006) The impact of storm events on solute exports from a glaciated forested watershed in western New York, USA. Hydrol Process 20:3423–3439. doi:10.1002/hyp.6141

Littlewood IG (1992) Estimating contaminant loads in rivers: a review. Institute of Hydrology, Wallingford

McDowell WH, Likens GE (1988) Origin, composition, and flux of dissolved organic carbon in the Hubbard brook valley. Ecol Monogr 58:177–195. doi:10.2307/2937024

Meybeck M (1993) Riverine transport of atmospheric carbon: sources, global typology and budget. Water Air Soil Pollut 70:443–463. doi:10.1007/BF01105015

Moore TR, Dalva M (2001) Some controls on the release of dissolved organic carbon by plant tissues and soils. Soil Sci 166:38–47. doi:10.1097/00010694-200101000-00007

Naden PS, McDonald AT (1989) Statistical modelling of water colour in the uplands: the upper Nidd catchment 1979–1987. Environ Pollut 60:141–163. doi:10.1016/0269-7491(89)90224-8

Palmer SM, Hope D, Billett MF et al (2001) Sources of organic and inorganic carbon in a headwater stream: evidence from carbon isotope studies. Biogeochemistry 52:321–338. doi: 10.1023/A:1006447706565

Roulet NT, Lafleur PM, Richard PJH et al (2007) Contemporary carbon balance and late Holocene carbon accumulation in a northern peatland. Glob Change Biol 13:397–411. doi: 10.1111/j.1365-2486.2006.01292.x

Schiff SL, Aravena R, Trumbore SE et al. (1997) Export of DOC from forested catchments on the Precambrian Shield of Central Ontario: clues from C-13 and C-14. Biogeochemistry 36:43–65

Schiff S, Aravena R, Mewhinney E et al (1998) Precambrian shield wetlands: hydrologic control of the sources and export of dissolved organic matter. Clim Change 40:167–188. doi:10.1023/A:1005496331593

Scott MJ, Jones MN, Woof C et al (1998) Concentrations and fluxes of dissolved organic carbon in drainage water from an upland peat system. Environ Int 24:537–546

Skjelkvåle BL, Stoddard JL, Jeffries DS et al (2005) Regional scale evidence for improvements in surface water chemistry 1990–2001. Environ Pollut 137:165–176. doi:10.1016/j.envpol.2004.12.023

Sottocornola M, Kiely G (2005) An Atlantic blanket bog is a modest CO_2 sink. Geophys Res Lett 32:L23804. doi:10.1029/2005GL024731

Sottocornola M, Laine A, Kiely G et al. (2009) Vegetation and environmental variation in an Atlantic blanket bog in South-western Ireland. Plant Ecol 203(1):69–81. doi:10.1007/s11258-008-9510-2

Tomlinson RW (2005) Soil carbon stocks and changes in the Republic of Ireland. J Environ Manage 76:77–93. doi:10.1016/j.jenvman.2005.02.001

Turunen J, Tomppo E, Tolonen K et al (2002) Estimating carbon accumulation rates of undrained mires in Finland—application to boreal and subarctic regions. Holocene 12:69–80. doi:10.1191/0959683602hl522rp

Walling DE, Webb BW (1985) Estimating the discharge of contaminants to coastal waters by rivers: some cautionary comments. Mar Pollut Bull 16:488–492. doi:10.1016/0025-326X(85)90382-0

Worrall F, Parker A, Rae JE et al (1997) A study of adsorption kinetics of isoproturon on soil and subsoil: the role of dissolved organic carbon. Chemosphere 34:87–97. doi:10.1016/S0045-6535(96)00369-4

Worrall F, Burt TP, Jaeban RY et al (2002) Release of dissolved organic carbon from upland peat. Hydrol Process 16:3487–3504. doi:10.1002/hyp.1111

Worrall F, Reed M, Warburton J et al (2003) Carbon budget for a British upland peat catchment. Sci Total Environ 312:133–146. doi:10.1016/S0048-9697(03)00226-2

Worrall F, Harriman R, Evans C et al (2004) Trends in dissolved organic carbon in UK rivers and lakes. Biogeochemistry 70:369–402. doi:10.1007/s10533-004-8131-7