Biogeochemistry **70:** 71–92, 2004.

Sources and sinks of aquatic carbon in a peatland stream continuum

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Received 17 March 2003; accepted in revised form 14 October 2003

Key words: Carbon fluxes, Carbon dioxide, Methane, Peatlands, River continuum concept, Streamwater

Abstract. Streams draining peatland systems contain a number of different C-species, all of which are linked either directly or indirectly to the cycling of C in the terrestrial environment. Concentrations and fluxes of dissolved, particulate and gaseous forms of carbon were measured along a network of streams draining an acidic peatland catchment (46.3 km^2) in NE Scotland. The main aim was to identify sources and sinks of all the major forms of C in the drainage network and use this to develop a conceptual understanding of the evolution of streamwater chemistry along a peatland stream continuum. The investigation included a small-scale intra-catchment study of three contiguous sites in a 1.3 km^2 headwater catchment (Brocky Burn) and a larger scale integrated study of seven sites. Mean annual fluxes of the main carbon species varied from 115–215 (DOC), 8.15–97.0 (POC), 0.32–6.90 (HCO_3^--C) and 2.62–10.4 (free CO_2-C) kg C ha^{-1} $year^{-1}$; all contributed to the overall carbon flux to varying degrees. Methane-C was only measurable at sites within areas of deep peat (<0.01–0.09 kg C ha^{-1} $year^{-1}$). Downstream spatial changes in the intra-catchment study (Brocky Burn) were characterised by a decrease in DOC, CO_2-C and CH_4-C and an increase in POC fluxes over a distance of 1.1 km from the Upper to the Lower sites. In the context of the integrated catchment study estimated losses and gains of carbon from the water column showed no net change in DOC, a large decrease in POC (−55%) and a slight increase in HCO_3^--C (+7.7%) and CO_2-C (+4.5%). A significant decrease in the CO_2-C flux: HCO_3-C flux ratio with distance downstream from the stream source, illustrates the importance of outgassing of CO_2 from streams draining peatland C reservoirs. These data are interpreted in the context of losses and gains of the various components of the aquatic C flux along the peatland stream continuum.

Introduction

The transport of carbon in upland streams, although small compared to other terrestrial carbon fluxes and reservoirs (Kempe 1979), is a key link between the soil and ocean carbon pools. Whilst carbon is an important source of energy to stream ecosystems (Fisher and Likens 1973; Wetzel 1992), it is also involved in the transport and availability of ions, nutrients, heavy metals and organic pollutants (Tipping et al. 1989; Grieve 1991; Boyer et al. 1996). Carbon compounds also play a central role in the regulation of surface water pH (Stumm and Morgan 1981;

Oliver et al. 1983; Driscoll et al. 1989). In unpolluted, headwater catchments, the main sources of riverine carbon are from soil organic matter, fragmented plant material and microbial processes. Further downstream autochthonous and anthropogenic inputs add to terrestrially derived carbon (Vannote et al. 1980; Sollins et al. 1985; Fiebig et al. 1990).

Organic and inorganic carbon are transported in streamwater as particulate (POC, PIC), dissolved (DOC, HCO_3^-, CO_3^{2-}) and gaseous forms (free CO_2 and CH_4); the relative importance of each depending on a range of catchment characteristics. Organic carbon covers a continuous size spectrum ranging from free monomers, fulvic and humic acids, via macromolecules such as proteins and colloids, to aggregates and large particles (Thurman 1985). Dissolved inorganic carbon (HCO_3^- and CO_3^{2-}) is related to gaseous carbon (free CO_2) via the carbonate equilibria. Although, the relative proportions of these three inorganic forms of carbon are dependent on pH and to a lesser extent temperature, in low pH upland streams the concentration of CO_3^{2-} ions is negligible (Stumm and Morgan 1981). Methane concentrations, which are controlled by flow rate and the degree of anoxia within the catchment, are usually very low in steep, fast flowing sections of upland streams (De Angelis and Scranton 1993; Jones and Mulholland 1998).

In upland acid peat-rich systems, DOC and POC derived from terrestrial sources are an important component of streamwaters (Grieve 1991; Hope et al. 1997a). Dissolved organic carbon concentrations and fluxes in streamwater are known to be strongly related to the size of the soil carbon pool and percentage peat cover (Hope et al. 1997b; Aitkenhead et al. 1999), along with other catchment variables such as discharge, precipitation, slope and catchment size (Eckhardt and Moore 1990; Clair et al. 1994; Grieve 1994). The strongest relationships between catchment variables and streamwater DOC occur in small-scale catchments, which exhibit strong spatial variability, particularly in terms of peat cover (Hope et al. 1997a; Aitkenhead et al. 1999).

Although there is a large amount of published work on carbon concentrations and fluxes from upland streams, many studies concentrate only on one form of carbon or occasionally, a combination of two components (Neal and Hill 1994; Dawson et al. 1995; Hope et al. 1997a, b; Jones and Mulholland 1998). Few however, have estimated the combined particulate, dissolved and gaseous carbon loads in upland streams. In this study, data from a network of sample sites in an upland peatland catchment in NE Scotland, are synthesised at two levels: an intra-catchment study of three contiguous sites in a small ($1.3\,km^2$) headwater catchment, and an integrated catchment study of seven sites within the larger ($46.3\,km^2$) drainage network. Previous research in this study area has illustrated the strong link between spatial variations in soil carbon and streamwater carbon (Rees et al. 1989; Aitkenhead et al. 1999; Dawson et al. 1995, 2001b, 2002; Hope et al 1997a, 2001; Palmer et al. 2001).

The main aims of this study are to:

1. compare changes in concentrations and fluxes of carbon at three contiguous downstream sites in a small headwater catchment,

2. integrate concentration and flux data at a larger scale to identify sources (hotspots) and sinks of carbon within a peatland drainage system, and
3. use the concept of the peatland stream continuum as a framework to discuss the downstream evolution of C-rich drainage water from headwater catchments.

Classically the river continuum concept (RCC) has provided a framework for explaining progressive biological changes in response to dynamic physical gradients within aquatic systems (Vannote et al. 1980). Although it has been refined to encompass climatic, geological and geomorphological changes at a range of spatial and temporal scales (Minshall et al. 1985), the concept is fundamentally linked to stream ecology, rather than stream chemistry. Since the original idea behind the RCC was to provide an 'expanding conceptual framework', we take this opportunity to explore the idea of a peatland stream continuum, based on progressive downstream chemical changes in particulate, dissolved and gaseous forms of carbon.

Methods

Study area

Carbon fluxes were estimated at nine sites in the central part of the Glen Dye catchment, NE Scotland (Figure 1). The main river within the area, the Water of Dye (46.3 km^2), is a major tributary of one of Scotland's largest rivers, the Dee (2100 km^2). The main catchment characteristics of the study sites, including four headwater tributaries of the Water of Dye (Brocky Burn, Water of Charr, Small Burn and Burn of Waterhead) and three contiguous sites on the river itself (Upper, Middle, Lower), are summarised in Table 1.

The Glen Dye catchment, which is managed for grouse by periodic burning, consists largely of heather (*Calluna vulgaris*, *Erica tetralix and E. cinerea*) moorland dominated by *Sphagnum* sp., and *Eriophorum* sp. with rushes and grasses present in the riparian zone and flush sites. The majority of the Glen Dye catchment (74%) is underlain by the Kincardineshire granite with small amounts of granitic gneisses, schists and tills. The source of the Water of Charr is associated with slightly more base-rich semipelitic schist. Hill peats (histosols) cover 61.7% of the Water of Dye catchment and humic podzols occupy a further 27.9%; small amounts of ferric podzols, humic gleysols, fluvisols and rankers are also present (Reid et al. 1981; Cresser et al. 1986). The streams draining the Glen Dye catchment are typical of many acidic upland areas in the UK with a stony bed and limited algae growth during spring and summer. More detailed descriptions of the Water of Dye and Brocky Burn, the more intensively studied headwater catchment, can be found in Dawson et al. (2001a, b) and Hope et al. (2001).

Discharge was monitored continually every 5 min at two flumes located at the Middle site on the Water of Dye (56°56.6′N:2°37.2′W) and the lowermost site of

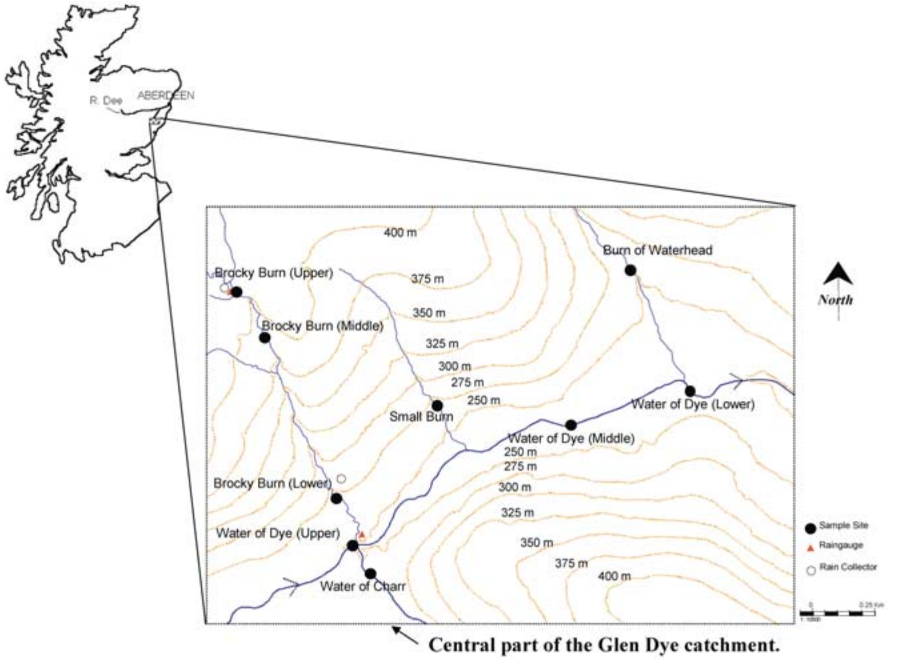

Figure 1. The central part of the Glen Dye catchment showing the location of sites used for intra- and integrated catchment studies.

Brocky Burn (56°56.5′N:2°38′W). Mean annual discharge values were 1.228 $m^3\,s^{-1}$ on the Water of Dye and 0.036 $m^3\,s^{-1}$ on Brocky Burn (Table 1). Mean annual precipitation (September 1996 to September 1998) was 1131 mm and average annual evapotranspiration loss (precipitation–discharge) was estimated to be 25.6%.

Sampling and analysis

To determine streamwater carbon concentrations (DOC, POC, HCO_3-C, free CO_2 and CH_4) and fluxes, intensive water sampling and analysis was undertaken over a 2 year period (1 September 1996 – 31 August 1998) using methods described in Dawson et al. (2002). Water samples were filtered to 0.7 µm (Whatman GF/F) and the filtrate used to determine DOC by ultra-violet oxidation and infrared gas analysis. The material remaining on the filter paper was used to determine particulate organic matter and subsequently POC by loss-on-ignition. Bicarbonate-C was calculated from alkalinity measurements derived from Gran-titrations (Neal et al. 1998). Both free CO_2 and CH_4 were determined directly using headspace analysis (Kling et al. 1991, 1992; Hope et al. 1995). This involves headspace equilibration

Table 1. Characteristics of the nine sub-catchments used in the intra-catchment (1–3) and integrated catchment (3–9) studies

Catchment	Area (km^2)	Altitude (m)	Stream				[b]Catchment slope (m km^{-1})	%Soil coverage		
			Temp. (°C)	Q – mean (range) (m^3 s^{-1})	Length (m)	[a]Gradient (%)		% Peat[c]	% Humic podzol	% Other[d]
1. Brocky Burn (Upper)	0.68	405–549	6.5	0.019 (0.001–0.489)	1.6	9.0	117	66.6	4.2	29.2[g,h]
2. Brocky Burn (Middle)	0.83	390–549	6.7	0.023 (0.001–0.595)	1.9	8.3	115	65.9	9.2	24.8[g,h]
3. Brocky Burn (Lower)	1.3	270–549	7.5	0.036 (0.002–0.930)	2.7	10.3	154	59.0	22.0	19.0[g,h]
4. Water of Charr	14.2	255–544	8.1	0.503 (0.060–21.94)	6.3	4.6	136	81.1	9.3	9.6[f,g,h]
5. Small Burn	0.41	275–469	8.0	0.010 (0.001–0.116)	0.8	24.5	175	52.5	47.5	–
6. Burn of Waterhead	3.4	255–529	8.6	0.090 (0.005–4.422)	2.7	10.1	158	34.8	62.3	3.0[e,g]
7. Water of Dye (Upper)	24.6	250–778	8.0	0.711 (0.081–17.55)	8.0	6.6	157	56.7	32.7	10.6[e,f,g,h]
8. Water of Dye (Middle)	41.4	245–778	8.0	1.228 (0.135–36.99)	9.1	5.9	145	65.2	24.1	10.9[e,f,g,h]
9. Water of Dye (Lower)	46.3	230–778	8.3	1.414 (0.155–42.57)	9.6	5.7	145	61.7	27.9	11.0[e,f,g,h]

[a] Stream gradient = altitude range (km)/stream length (km) × 100.

[b] Mean catchment slope was calculated between 6 and 30 random spot heights and the stream.

[c] Hill peat is defined as organic soils >0.5 m depth with >60% organic matter (Macaulay Institute for Soil Research 1982).

[d] Other soils: [e]Ferric podzol [f]Humic gleysol [g]Ranker [h]Fluvisol.

of the sample with air followed by analysis of CO_2 and CH_4 using a gas chromatograph with an attached methanizer and FID. Stream temperature and pH were also measured at each site. The streams were sampled once a week, weather and access permitting, in the 1st year and once every 2 weeks during the 2nd year.

Continuous discharge (Q) was measured at the flumes situated on the Water of Dye and Brocky Burn. On the other three tributaries stream height was recorded at the time of sampling using gauge boards; these were calibrated for a wide range of discharges by dilution (Small Burn, $n = 11$) and flow gauging (Water of Charr, $n = 10$ and Burn of Waterhead, $n = 11$) using a 'Braystoke' BFM002 miniature current flow meter (Valeport Ltd.). Using the values determined by gauging, discharge on the tributaries were related to discharge at the Water of Dye (Middle) or Brocky Burn (Lower) flumes, providing a rating equation to determine continuous discharge on the other tributaries. The discharge values for the Upper and Middle Brocky Burn sites were calculated on an area-weighting basis (Dawson et al. 2001a). Discharges at the two remaining sites on the main stem were calculated by the addition/subtraction of discharge from adjoining sample sites (Equations (1) and (2)):

$$\begin{aligned} Q_{\text{Water of Dye(Upper)}} = {} & Q_{\text{Water of Dye(Middle)}} \\ & - (Q_{\text{Brocky Burn}} + Q_{\text{Water of Charr}} + Q_{\text{Small Burn}}) \end{aligned} \tag{1}$$

$$Q_{\text{Water of Dye(Lower)}} = Q_{\text{Water of Dye(Middle)}} + Q_{\text{Waterhead}} \tag{2}$$

Numerical analysis

Mean annual fluxes (kg C ha^{-1} year^{-1}) at each study site were calculated for all C-species (dissolved, particulate and gaseous) using 'Method 5' (Walling and Webb 1985). This method was the most appropriate as it can be used for all C-species at all sites. Concentration-discharge relationships were not used because of the lack of correlation between Q and the gaseous components at some sites (Hope et al. 2001; Dawson et al. 2002). 'Method 5' utilises both instantaneous concentration and discharge at the time of sampling and the mean discharge determined from continual discharge measurements. For each C-species, flux errors were calculated using 95% confidence intervals as described by Hope et al. (1997a). Error terms varied between 11 and 250% with most ca. 50% and are of the same order of magnitude as those calculated for DOC and POC using 'Method 5' for a range of sites in NE Scotland (Hope et al. 1997a). The percentage contribution that each C-species made to the overall riverine carbon flux from each site was also calculated. Fluxes of each C species, measured as total loads (kg C year^{-1}), were used to determine the contribution that each of the four tributaries and the Water of Dye (Upper) site made to the flux at the lowest downstream site in the drainage system (Water of Dye, Lower). Using this approach, it was possible to estimate gains and losses of individual C-species between the Upper and Lower sites on the Water of Dye, a distance of 1.6 km.

Results

Intra-catchment study

Changes in pH and carbon concentrations

Differences between soil coverage (Table 1) and the mean and range in concentration of all C-species and pH (Table 2) are evident for the Upper, Middle and Lower sites on Brocky Burn; temporal changes are shown in Figure 2. As catchment size increases the % coverage of peats, rankers and fluvisols decreases, whereas the podzols become spatially more important. A downstream increase in mean pH was associated with a decrease in both mean DOC and POC concentration. However, mean HCO_3^--C concentration was lowest at the Upper site, increased at the Middle site, but subsequently decreased at the Lower site. The largest decline in carbon concentrations between sites was in the gaseous components reflecting the progressive outgassing of CO_2 and CH_4 from the stream surface to the atmosphere. At the Upper site, the mean free CO_2-C concentration and *ep*CO_2 (supersaturation level presented as the ratio of pCO_2 in sample to the pCO_2 in the atmosphere at time of sampling) values were $1.92\,mg\,l^{-1}$ and 7.8, respectively, while *ep*CO_2 varied from 2.4 to 18.8. Mean CO_2-C concentration at the Middle site was lower than the Upper site, but still four times greater than the atmospheric concentration. At the Lower site mean CO_2-C concentration and *ep*CO_2 had decreased to $0.32\,mg\,l^{-1}$ and 1.3 respectively. Methane concentration showed a similar decrease downstream, although the concentrations were significantly lower than CO_2.

Dissolved organic carbon concentrations followed a seasonal pattern, rising during the summer and peaking during the autumn. Concentrations then decreased during the winter and early spring. Concentrations of POC increased substantially during periods of high discharge, but during baseflow were mostly between 0.2 and $0.8\,mg\,l^{-1}$ with little seasonal variation. Concentrations of HCO_3^--C were low throughout the 2 years with highest concentrations occurring at low flow. At the Brocky Burn (Upper) site, strong relationships existed between CO_2-C concentrations and discharge, pH, HCO_3^--C and CH_4-C (Dawson 2000, 2002; Hope et al. 2001). However, at the Lower site, CO_2-C concentration showed little relationship with other C-species, except with water temperature. Carbon dioxide concentrations tended to be highest in the warmer summer months and lowest during the colder, winter months.

Annual fluxes

The combined flux of all C-species decreased downstream in the Brocky Burn catchment on a per unit catchment area basis (Figure 3). The dominant component of the flux, DOC, was highest at the Upper site ($194\,kg\,C\,ha^{-1}\,year^{-1}$) and decreased downstream to $167\,kg\,C\,ha^{-1}\,year^{-1}$ at the Lower site. In contrast, average annual POC fluxes increased downstream from $14.8\,kg\,C\,ha^{-1}\,year^{-1}$ at the Upper site to $16.9\,kg\,C\,ha^{-1}\,year^{-1}$ at the Lower site. Fluxes of HCO_3^--C were lowest at the Upper site and highest at the Middle site. Free CO_2-C and CH_4-C fluxes showed

Table 2. Mean concentration and range in pH and C species of the 9 sites used in the intra-catchment (1–3) and integrated catchment (3–9) studies

Catchment	Mean (range)						
	pH	DOC	POC	HCO_3^--C	CO_2-C	*ep*CO_2	CH_4-C
1. Brocky Burn (Upper)	4.82 (3.98–6.22)	18.3 (7.83–43.6)	0.87 (0.22–3.07)	0.57 (<0.01–2.04)	1.92 (0.77–3.35)	7.8 (2.4–18.8)	0.025 (0.003–0.091)
2. Brocky Burn (Middle)	4.98 (4.06–6.80)	16.6 (6.65–43.5)	0.82 (0.14–3.21)	0.88 (<0.01–2.83)	0.99 (0.49–1.37)	4.0 (2.0–6.8)	0.004 (<0.001–0.013)
3. Brocky Burn (Lower)	5.11 (4.11–7.11)	14.5 (5.78–41.0)	0.49 (0.06–4.54)	0.69 (<0.01–2.19)	0.32 (0.22–0.54)	1.3 (0.9–2.4)	nd
4. Water of Charr	5.72 (4.32–7.80)	10.9 (3.34–39.0)	0.87 (0.02–22.9)	2.37 (<0.01–5.47)	0.30 (0.15–0.50)	1.2 (0.7–2.7)	nd
5. Small Burn	4.89 (4.06–7.07)	10.6 (4.53–25.3)	0.52 (0.04–4.26)	0.13 (<0.01–0.46)	0.43 (0.27–0.68)	1.8 (1.0–3.1)	nd
6. Burn of Waterhead	5.29 (4.12–7.07)	7.22 (2.13–29.1)	0.37 (0.00–4.06)	0.57 (<0.01–1.50)	0.39 (0.21–0.68)	1.6 (1.1–4.2)	nd
7. Water of Dye (Upper)	5.72 (4.34–7.77)	7.39 (1.84–33.7)	0.41 (0.00–6.86)	1.73 (<0.01–3.76)	0.32 (0.13–0.53)	1.3 (0.6–2.0)	nd
8. Water of Dye (Middle)	5.73 (4.31–7.69)	8.65 (2.43–35.4)	0.47 (0.00–4.97)	1.91 (0.02–4.48)	0.32 (0.15–0.55)	1.3 (0.7–1.9)	nd
9. Water of Dye (Lower)	5.66 (4.21–7.80)	8.46 (2.28–33.5)	0.44 (0.00–4.79)	1.78 (<0.01–4.13)	0.31 (0.06–0.51)	1.3 (0.3–3.0)	nd

All C-forms are in $\mathrm{mg\,l^{-1}}$ except for *ep*CO_2, which is a ratio.

nd = not detected.

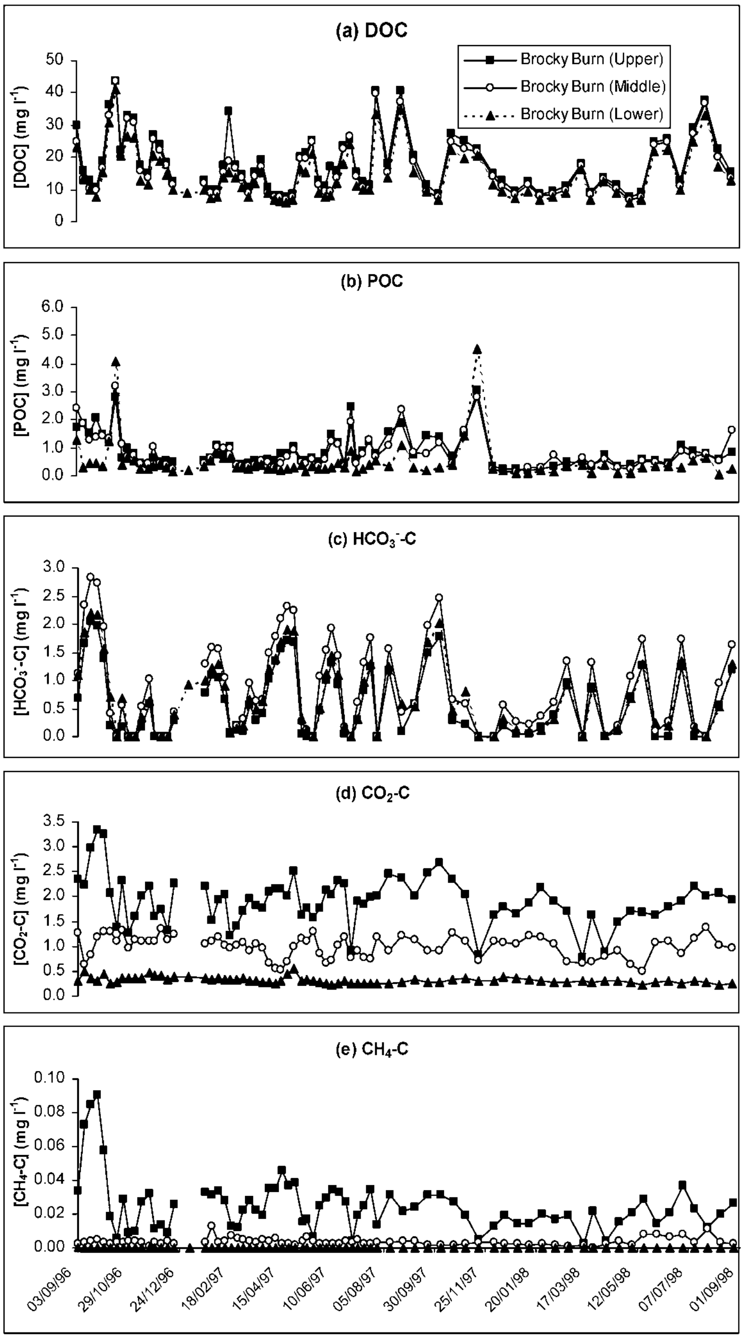

Figure 2. Temporal changes in (a) DOC, (b) POC, (c) HCO_3^--C, (d) CO_2-C and (e) CH_4-C between 1 September 1996 and 31 August 1998 at the three sites on Brocky Burn.

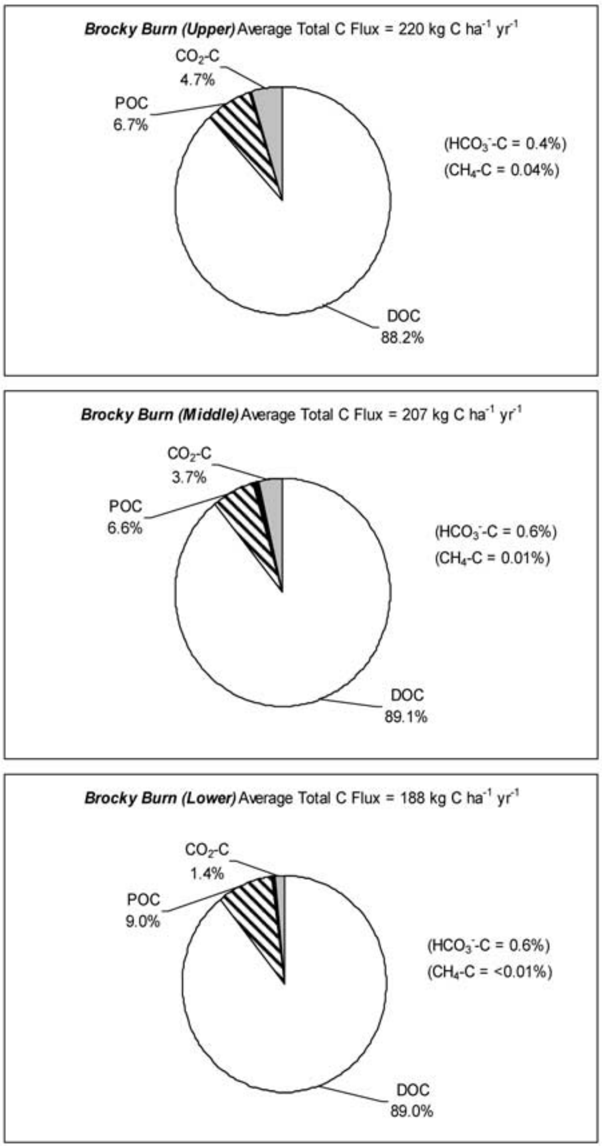

Figure 3. Downstream changes in the relative contribution (%) of each C-species to the overall annual C flux in Brocky Burn.

the greatest downstream changes as rapid outgassing of gaseous carbon occurred. The average annual dissolved free CO$_2$-C flux at the Upper site (10.4 kg C ha^{-1} year^{-1}) decreased to 7.62 kg C ha^{-1} year^{-1} at the Middle site and to 2.62 kg C ha^{-1} year^{-1} at the Lower site. Methane fluxes were small (<0.01–

0.09 kg C ha^{-1} $year^{-1}$) compared with the other C-species determined, but like CO_2-C decreased downstream.

Over the 2 year study, 88–89% of total carbon was exported as DOC at all three sites in Brocky Burn. Particulate organic carbon export was most important at the Lower site where discharge was highest, while the relative importance of free CO_2 transported *within* the stream decreased rapidly downstream from 4.7% at the Upper site to 1.4% at the Lower site. The combined flux of HCO_3^--C and CH_4-C was less than 1% of the total carbon flux at all three sites on Brocky Burn.

Integrated catchment study

Changes in pH and carbon concentrations

The pH, DOC, POC, HCO_3^--C and CO_2-C concentration data for the seven sites used in the larger scale integrated catchment study are shown in Table 2; methane was undetectable at all the sites. Mean streamwater pH in the four tributaries varied from 4.89 (Small Burn) to 5.72 (Water of Charr), while the three sites on the main river (Water of Dye) showed relatively little variation (5.66–5.73). Although mean DOC concentrations ranged from 7.22 mg l^{-1} at Burn of Waterhead to 14.5 mg l^{-1} at Brocky Burn, at times of high flow concentrations of DOC exceeded 30 mg l^{-1}. The three main stem sites had similar mean DOC concentrations (7.39–8.65 mg l^{-1}). As with the intragrated catchment study, DOC varied seasonally, with concentrations rising during the summer, peaking in autumn, then decreasing during the winter and early spring. Although mean POC concentrations were all <1 mg l^{-1}, the maximum POC concentrations during storm flow ranged from 4.06 to 22.9 mg l^{-1}, especially during the first major storm in autumn, the highest concentrations being consistently recorded on the Water of Charr. The lowest mean HCO_3^--C concentration (0.13 mg l^{-1}) was in the most acidic stream (Small Burn). All three sites on the Water of Dye exhibited higher mean HCO_3^--C concentrations (1.73–1.91 mg l^{-1}) relative to most of the tributary sites, although the highest mean HCO_3^--C concentration (2.37 mg l^{-1}) occurred on the Water of Charr tributary. Concentrations of HCO_3^--C tended to be at their lowest for a short period of time during the winter and were often below the detection limit during periods of high discharge. Free CO_2-C concentrations were very similar at all sites with mean concentrations varying between 0.30 and 0.43 mg l^{-1}. Although mean CO_2-C concentrations were always in excess of atmospheric concentrations (i.e., *ep*CO_2 values >1.0), values <1.0 were measured occasionally at all sites, with the exception of Small Burn and the Burn of Waterhead. Consistently higher CO_2-C concentrations occurred in Small Burn compared to other sites involved in the integrated catchment study.

Annual fluxes

Average annual DOC fluxes from the tributaries ranged from 122 to 215 kg C ha^{-1} $year^{-1}$; the highest being from the Water of Charr, the lowest from Small Burn. Dissolved organic carbon fluxes at the three sites on the main stem of the Water of Dye increased steadily downstream (115–140 kg C ha^{-1} year^{-1}). Particulate organic carbon fluxes were comparable (8.15–18.9 kg C ha^{-1} year^{-1}) at all sites except the Water of Charr, which was associated with a much higher POC export (97.0 kg C ha^{-1} year^{-1}). Bicarbonate-C fluxes were low in all three south-facing tributaries (0.3–1.8 kg C ha^{-1} year^{-1}) compared to the Upper, Middle and Lower sites on the Water of Dye (6.1–6.4 kg C ha^{-1} year^{-1}) and the Water of Charr, which had the highest measured flux (6.9 kg C ha^{-1} year^{-1}). Free CO_2-C fluxes were similar at all sites and ranged from 2.6 kg C ha^{-1} year^{-1} at Brocky Burn (Lower) to 3.5 kg C ha^{-1} year^{-1} on the Water of Dye (Upper).

The contributions of the various C-species to the total carbon fluxes were relatively similar in the three south facing tributaries with DOC comprising 89.1–91.5% of the flux, POC 6.1–9.0% and DIC 2.0–3.2% (Figure 4). The main difference between these streams occurred in the relative proportions of free CO_2 and HCO_3^-, which collectively comprise the DIC flux. In Small Burn, the ratio of the free CO_2-C flux:HCO_3^--C flux was 9.2:1, whereas in Brocky Burn (Lower) and the Burn of Waterhead it was 2.4:1 and 1.8:1, respectively. Although, DIC made up a similar component of the overall carbon flux compared to the other tributaries, the proportion that comprised HCO_3^--C was higher than that of free CO_2-C in the Water of Charr. Meanwhile POC comprised a significantly higher component (30.1%) of the total carbon flux in the Water of Charr, compared to the other three tributaries.

By summing the individual carbon loads of the four tributaries and the Upper site of the Water of Dye, the relative contributions of these five inputs to the overall load at the lowest downstream site on the river system (Water of Dye, Lower) can be assessed (Figure 5). In terms of the total loads of carbon leaving the catchment expressed in kg C year^{-1}, the Water of Dye (Upper) and the Water of Charr made the most important contribution to the overall flux of all the determinants measured at the lowest downstream site. If the DOC loads from all five upstream sites are summed, the value (6.6×10^5 kg C year^{-1}) was similar to that of the Water of Dye (Lower) site (6.5×10^5 kg C year^{-1}). In contrast, the summed POC loads (1.7×10^5 kg C year^{-1}) were substantially higher than the POC load at the downstream site (0.75×10^5 kg C year^{-1}), suggesting a significant component of the POC load is retained or processed within the stream system. However, the collective HCO_3^--C and free CO_2-C loads from the five upstream sites were slightly lower than the final loads at the Water of Dye (Lower) site by 7.7 and 4.5%, respectively. As the stream system evolves it therefore appears to gain HCO_3^--C and free CO_2-C, lose POC and show little or no gain/loss in DOC.

Discussion

Intra-catchment study

The Brocky Burn headwater catchment is a significant point source of C within the drainage network. On a per unit catchment area basis there was a 15% decrease in the total C flux from the Upper to the Lower site. This change in DOC is broadly

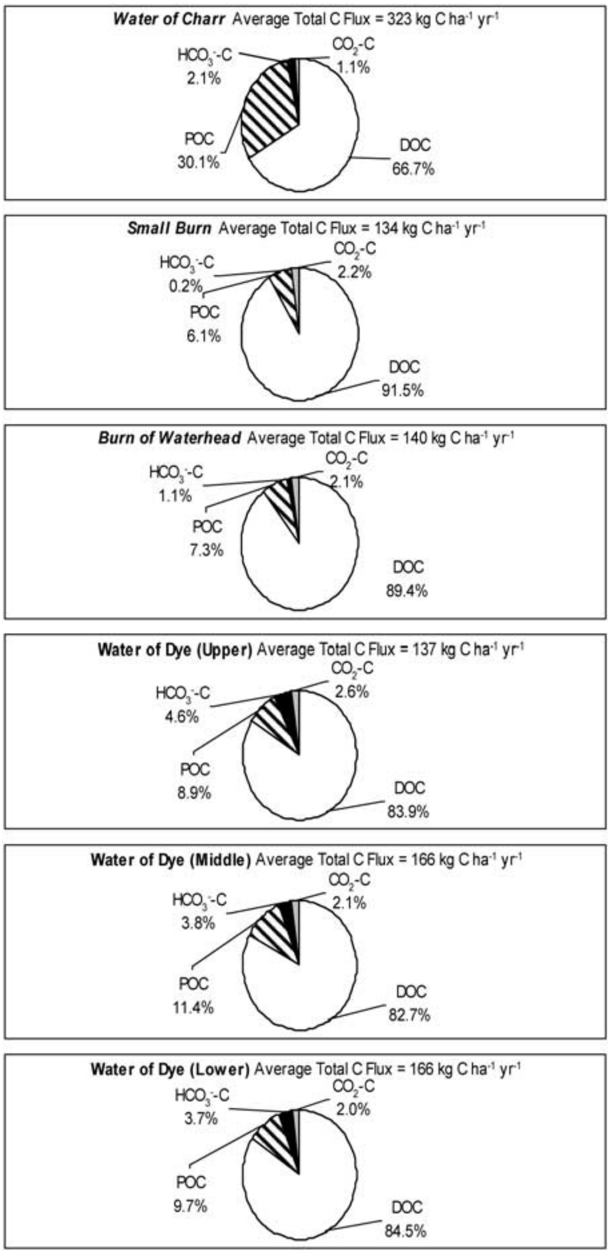

Figure 4. The relative contribution of each C-species (%) to the overall annual C flux at sites from the integrated catchment study.

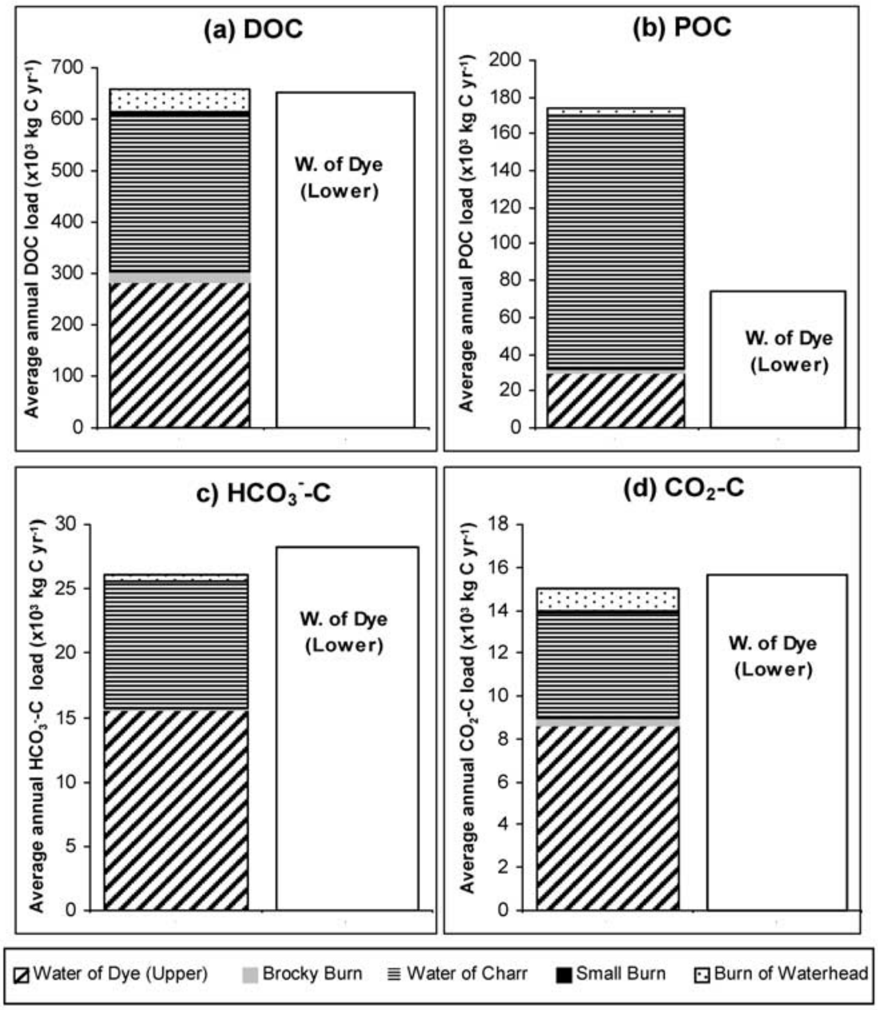

Figure 5. The relative contribution of each of the five upstream sites to the C load at the lowest downstream site for (a) DOC, (b) POC, (c) HCO_3^--C and (d) CO_2-C.

associated with intra-catchment changes in soil type (Rees et al. 1989), in particular the increase in distance from the central peat-dominated area (Hope et al. 2001; Dawson et al. 2002). However, the increase in the relative importance of POC and decrease in dissolved free CO_2-C transport from the Upper to Lower site, also reflects the importance of increased discharge and turbulence as gradient increases downstream (Table 1). This allows more particulate material to be re-suspended and transported and free CO_2 degassed from the water column. Fluxes of HCO_3^--C are insignificant in Brocky Burn reflecting both a lack of groundwater sources within the catchment area and the low pH environment.

Methane concentrations were relatively insignificant in terms of total aquatic C transport, except at the upper two sites at Brocky Burn. This part of the catchment, which is characterised by flat topography and slow stream flow through a large area of peat, is likely to be more anaerobic (Jones and Mulholland 1998). As gradient increased further downstream, freely draining humic podzols predominate, anoxia is minimised and CH_4 production is much lower. In addition, CH_4 produced upstream has already degassed at the point where streamwater from the Brocky Burn tributary reached the main stem (Hope et al. 2001). Mean *ep*CH_4 at the Upper site was $254 + 236$ compared to the range (10–1216) observed by Jones and Mulholland (1998) at the Great Smoky Mountains National Park, Eastern Tennessee. In contrast to the Brocky Burn catchment, these authors found that CH_4 concentrations increased downstream as anoxic conditions associated with fine-grained stream sediments increased.

Integrated catchment study

Collectively the seven sites included in the integrated catchment study show that streamwater pH increases with increasing stream size. Although the Water of Charr is geochemically more base-rich than the other three tributaries, it makes relatively little difference to the streamwater pH of the Water of Dye. In the three smaller acidic catchments dominated by peat and humic podzols, hydrophobic and hydrophilic acids are likely to account for 90% of the DOC in streamwater (Easthouse et al. 1992), thus maintaining the acidic properties of the streams.

Inputs from the three peat-dominated catchments elevate DOC concentrations in the main stem, particularly in the case of the Water of Charr (>80% peat). Concentrations then decrease as less DOC-rich water from the Burn of Waterhead (34.8% peat) enters the main stem. We therefore conclude that DOC concentrations in the Water of Dye are primarily controlled by simple hydrological mixing of different packages of water as shown by the mass balance (Figure 5(a)). Although the average annual DOC fluxes were higher than export rates for most temperate river systems, which in the UK typically range from 10 to 100 $\mathrm{kg\,C\,ha^{-1}\,year^{-1}}$ (Hope et al. 1994, 1997a, b), they were within the range of DOC losses reported for peat-dominated upland catchments, of up to 500 $\mathrm{kg\,C\,ha^{-1}\,year^{-1}}$ (Hope et al. 1994; Billett et al. in review).

Mean POC concentrations were lower in the main stem than the tributaries with the exception of the Burn of Waterhead, which had the lowest peat coverage. However, at higher flows, the main stem sites were generally associated with the highest amounts of POC, possibly due to enhanced physical erosion by fluid entrainment and re-suspension of benthic material (Lawler et al. 1997). During storms streamwater draining the Water of Charr tributary had the highest POC concentrations due to its large catchment size, which produces enough stream energy to transport available POC generated from the extensive areas of peat in the catchment, some of which are exposed and actively eroding. Average annual POC fluxes comprise 10–30% of the total organic C flux (Figure 4) and are comparable to fluxes found in other small catchments in the UK (Reynolds 1986; Hope et al. 1997a). The flux of POC as a percentage of the organic C flux varies substantially and POC generally becomes more important with increasing stream order and size (Thurman 1985).

Low HCO_3^--C concentrations within all the streams reflects both a lack of inorganic C from groundwater sources and low pH, although the higher mean HCO_3^--C concentrations in the Water of Charr, compared to other catchments, reflects the presence of less acidic underlying parent material. Fluxes of HCO_3^--C were low (0.3–6.9 kg C ha^{-1} $year^{-1}$) compared to many upland stream systems (Hope et al. 1994). Slope may also have an indirect affect on HCO_3^--C fluxes because less steep catchments will retain soil water longer increasing contact with the mineral horizons and raising pH. A decrease in stream gradient also reduces DIC loss downstream (in the form of CO_2 outgassing) through reduced turbulence (Herman and Lorah 1987; Rebsdorf et al. 1991) and lower water surface:water volume ratios. Thus more DIC is retained within the aquatic system, which combined with an increase in pH downstream, shifts the carbonate equilibria towards increased HCO_3^-.

Mean free CO_2 concentrations were low at the tributary outlets and on the main stem sites ($epCO_2$ 1.2–1.8), compared to many temperate upland streams, where $epCO_2$ values of 1–28 have been recorded (Rebsdorf et al. 1991; Neal and Hill 1994; Dawson et al. 1995; Jones and Mulholland 1998). On rare occasions $epCO_2$ values <1.0 were recorded at most of our sites. This infers that at certain times CO_2 was being removed from the water column as photosynthetic uptake exceeded CO_2 inputs. In the less acidic and productive main stem and in the Water of Charr, $epCO_2$ minimum values were substantially lower than 1.0, suggesting increased photosynthetic activity in the larger streams compared to the other tributaries. However, over a 24 h period the study streams produced a primary production/respiration (P/R) ratio <1.0, maintaining their heterotrophic character (Dawson et al. 2001b). The sampling sites in the integrated catchment study were generally in the vicinity of well-aerated soils (humic podzols), where much of the soil respired CO_2 is dispersed directly to the atmosphere and fails to reach the stream. However, upstream peatland source areas such as those in Brocky Burn, generate large amounts of terrestrially derived CO_2 in streamwater. This is a consistent pattern in upland headwater catchments in the UK associated with peatland source areas (Dawson et al. 1995, 2002; Hope et al. 2001) and may be caused by differences in the lateral and vertical hydraulic conductivity of peats, resulting in greater lateral water movement to streams (Chason and Siegel 1986).

Compared to the other tributaries Small Burn had the highest free CO_2 concentrations at its outlet. This stream is relatively short with high acidity, suggesting that outgassing of soil-respired CO_2 was still occurring at the point the tributary joined the Water of Dye. Hence the majority of DIC within Small Burn was present as CO_2, rather than HCO_3^-. However, while the proportion of DIC in the form of free CO_2 versus HCO_3^- varies to some extent with pH and streamwater temperature (Stumm and Morgan 1981), there was also a clear spatial pattern at the sites. The CO_2-C flux:HCO_3-C flux ratio significantly decreased with distance downstream, such that at >5 km from the stream source, the ratio drops below one and the system becomes dominated by HCO_3^- (Figure 6).

Average annual dissolved free CO_2 fluxes at the confluence of the tributaries with the main stem (2.6–3.5 kg C ha^{-1} $year^{-1}$) were slightly lower than a value of 4.4 kg C ha^{-1} $year^{-1}$ reported for another stream in the Glen Dye area (Dawson et al. 1995). Flux estimates for dissolved free CO_2 in streams close to non-aerated peatland sources at sites such as Brocky Burn (Upper and Middle) and the Upper Hafren in Mid-Wales (Dawson et al. 2002) are significantly higher. Riverine CO_2 fluxes of 2.3-11.9 kg C ha^{-1} $year^{-1}$ were estimated for several major European rivers (Hope et al. 1994), although these were made using indirect measurements. It is also important to note that the flux values for the study streams generated using daytime measurements are probably under-estimates, because stream CO_2 concentration increases during darkness due to the absence of photosynthesis (Dawson et al. 2001b). This work suggests that the mean annual CO_2-C flux may be significantly (40%) higher (up to 3.67 and 14.6 kg C ha^{-1} $year^{-1}$) at the Brocky Burn (Lower and Upper) sites, respectively.

Losses and gains of carbon along the peatland stream continuum

The Water of Dye drainage system shows significant changes in the transport of C from the upstream to downstream reaches, which are reflected in both flux and concentration values, the latter largely controlled by simple hydrological mixing. The stream continuum in this peat-dominated system appears to be both spatially and temporally dynamic in terms of the mechanisms by which losses and gains of individual C-species occur. Downstream spatial changes in the intra-catchment study showed a decrease in DOC, CO_2-C and CH_4-C and an increase in POC fluxes (calculated on an area basis) over a distance of 1.1 km. In the context of the integrated catchment study estimated net losses and gains of C from the water column over time showed no substantial change in DOC, a large decrease in POC and slight increases in HCO_3^--C and CO_2-C. All the catchments contained relatively large areas of peat supplying high DOC and CO_2-C concentrations to the stream from decomposition of the available OM. The majority of DOC load at the lowest downstream site on the Water of Dye was derived from the two largest upstream catchments by hydrological mixing; the Water of Dye (Upper) and Water of Charr contributing 90% of flow even though two smaller tributaries (Small Burn and Brocky Burn) regularly produced higher DOC concentrations. In some systems losses of OM through in-stream respiration and outgassing of respired CO_2 are known to result in significant losses of C from the river channel (Hope et al. 2001); in the central part of the Water of Dye catchment, physical processes such as degassing appear to be more important than biological processes in terms of CO_2 flux changes.

In contrast to other studies (Vannote et al. 1980; McDowell 1985; Minshall et al. 1985; Fiebig and Lock 1991), our results suggest that there was no measurable annual net loss of DOC from the stream system. This does not mean that in-stream

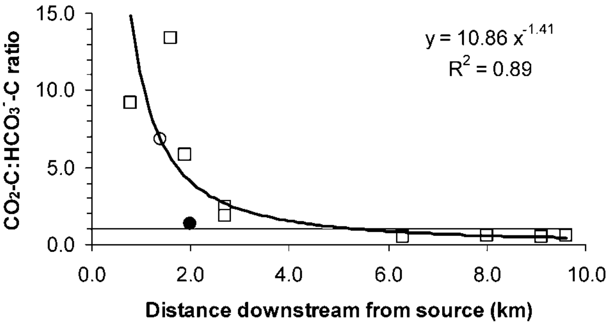

Figure 6. Changes in the CO_2-C flux: HCO_3-C flux ratio with distance downstream from the stream source. □ = Glen Dye study sites; ○ = Plynlimon, Mid-Wales (Dawson et al. 2002); ● = Auchencorth Moss, Central Scotland (Billett et al. in review).

processing of DOC is not occurring, but that a dynamic equilibrium exists in this part of the continuum. This is confirmed in a separate study on Brocky Burn, when DOC losses of between 11.6 and 17.6% of the daily flux were estimated on three separate occasions during optimal summer conditions (Dawson et al. 2001a). The study also suggested that unmeasured inputs of DOC from diffuse sources (e.g., bank seepage, streambed inputs) might increase estimates of within-stream DOC loss. Particulate organic carbon loads were 55% lower at the Water of Dye (Lower) site compared with the collective loads from the upstream sites, suggesting that in-stream processing reduces POC loads downstream (Vannote et al. 1980). Moreover, breakdown of POC can add DOC to the water column (Meyer and Tate 1983), potentially contributing to the apparent lack of net removal of DOC from the stream. Particulates may also be deposited within the stream channel as gradient decreases downstream, only being resuspended during high flow events (Cushing et al. 1993).

Dissolved inorganic carbon loads appeared to increase slightly between the upstream and the furthest downstream sites as inputs of DIC within the stream channel occurred. Heterotrophic in-stream processing of DOC and POC may have contributed free CO_2 to this increase in DIC, while an increase in pH in the main stem will shift the carbonate equilibria towards HCO_3^- (Stumm and Morgan 1981). These streams are typically heterotrophic in character as community respiration (0.99–4.00 g CO_2 m^{-2} day^{-1}) adds CO_2 to the stream at a faster rate than gross primary production (0.21–1.51 g CO_2 m^{-2} day^{-1}) removes it (Dawson et al. 2001b). The gains in DIC in the lower parts of this system were in marked contrast to upstream DIC losses from degassing of free CO_2 in the low pH headwaters. Such outgassing of CO_2 and CH_4 in upland streams tends to be unaccounted for in most stream flux measurements, yet measurements in Brocky Burn show that CO_2 evasion losses from the stream surface to the atmosphere (141 kg C ha^{-1} $year^{-1}$), are of the same order of magnitude as the total amount of C transported downstream within the water column (Hope et al. 2001).

This study highlights the importance of C-rich headwater catchments in the peatland stream continuum, as small but important ‘hotspots’ for significant gaseous C loss. In contrast, CO_2 and CH_4 in the lower reaches of headwater tributaries and the main stem are close to equilibrium with the atmosphere. We suggest that the outlets of headwater tributaries and upper reaches of second order streams are a critical area in the peatland stream continuum. At this point (around 2 km downstream from the stream source in our study) there is a transition from aquatic C loss predominantly in the form of DIC (via CO_2 outgassing) to retention or gain in DIC, as pH increases and the outgassing rates slow or cease as the stream reaches equilibrium with the atmosphere (Figure 6). The proportion of DIC transported as CO_2 rather than HCO_3^- in two other UK peatland streams fall on the same trend line found for the Glen Dye streams, suggesting that this may be a consistent pattern in peatland systems.

Conclusions

We conclude that with respect to C transport the peatland stream continuum is primarily dominated by abiotic, physical processes such as degassing, deposition and re-suspension of particulates and hydrological mixing, and is therefore fundamentally different than the classic downstream continuum described by Vannote et al. (1980). Although in-stream biotic retention and breakdown of C-species are important processes, the most important component of the aquatic C flux in this system is DOC which, after initial large inputs from peats adjacent to the stream channel in the headwater catchments, shows little or no net loss down the river system. The gaseous C and POC fluxes are more dynamic and show a distinct spatial pattern, which in the case of POC is similar to that found in the RCC as originally published (Vannote et al. 1980). The behaviour of free CO_2 is dominated by significant degassing ‘hotspots’ in the headwater regions containing the C-rich soil reservoirs. We suggest that this conceptual framework needs to be expanded to include peatland dominated stream systems where the continuum is a less biotically reactive conduit, in which many of the downstream patterns in aquatic C transport are dominated by physical processes. Our findings also highlight the transition from headwater sources to second order streams as a critical point in the peatland stream continuum, where a switch occurs from DIC loss (via CO_2 degassing) to retention and/or gain.

Acknowledgments

The authors thank Fasque Estates for allowing access to the site and their support for the research. J.J.C. Dawson wishes to thank the Natural Environment Research Council for providing financial support.

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