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ORIGINAL PAPER

Influence of hydrology and seasonality on DOC exports from three contrasting upland catchments

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Abstract Variation in dissolved organic carbon (DOC) concentrations of surface waters is a consequence of process changes in the surrounding terrestrial environment, both within annual cycles and over the longer term. Long-term records (1987–2006) of DOC concentrations at six catchments (0.44–10.0 km^2) across a climatic transect in Scotland were investigated for intra-annual relationships to evaluate potential long-term seasonal patterns. The intra-annual mode of DOC export contrasted markedly between catchments and appeared dependent on their hydrological characteristics. Catchments in wetter Central Scotland with high rainfall–runoff ratios, short transit times and well-connected responsive soils show a distinct annual periodicity in DOC concentrations throughout the long-term datasets. Increased DOC concentrations occurred between June and November with correspondingly lower DOC concentrations from December to May. This appears unrelated to discharge, and is dependent mainly on higher temperatures driving biological activity, increasing decomposition of available organic matter and solubility of DOC. The drier eastern catchments have lower rainfall–runoff ratios, longer transit times and annual drying–wetting regimes linked to changing connectivity of soils. These are characterised by seasonal DOC concentration–discharge relationships with an autumnal flush of DOC. Temperature influences the availability of organic matter for DOC transport producing a high DOC concentration–discharge relationship in summer/autumn and low DOC concentration–discharge relationship in winter/spring. These two distinct modes of seasonal DOC transport have important implications for understanding changes in DOC concentrations and export brought about by climate change (temperature and precipitation) and modelling of aquatic carbon losses from soil-types under different hydrological regimes.

Keywords DOC export · DOC production · Hydrology · Long-term study · Seasonal

Introduction

Variations in dissolved organic carbon (DOC) concentrations of surface waters signal process changes in the surrounding terrestrial environment although within stream processes can also modify fluvial DOC,

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providing a secondary control on its temporal and spatial variability (Dawson et al. 2001a). Understanding the processes that link soil organic matter decomposition and DOC in leachates, with subsequent DOC concentrations and fluxes in streams is required. This necessitates understanding abiotic and biotic processes that control the quantity and timing of when carbon is available for export from soils to the drainage network (Brooks et al. 1999).

The transport of carbon in upland streams is a key link between soil and ocean carbon pools. These exports can be as high as the long-term carbon sequestration rate of some soils (Schlesinger 1990; Roulet and Moore 2006). Organic carbon is an important source of energy to stream ecosystems and is involved in pH regulation, transport and availability of ions, nutrients, heavy metals and organic pollutants (Hope et al. 1994; Evans et al. 2005). In recent years, the quantity and quality of DOC exported from carbon-rich upland soils has had an economic consequence for the treatment of potable waters (Worrall et al. 2004).

Some long-term time-series studies have shown that DOC concentrations in upland UK surface waters have risen significantly during recent decades (Freeman et al. 2001; Worrall et al. 2004; Evans et al. 2005, 2006), which might reflect increased mobilisation of the stored soil carbon pool (Tipping et al. 2007). This phenomenon is not isolated to the UK but has also been observed in Nordic countries and North America (Monteith et al. 2007; de Wit and Wright 2008). Several contrasting hypotheses as to the reasons for the increasing trend of DOC concentrations in surface waters have been outlined, including rising temperatures, recovery from acidification, decreased sulphur deposition, changes in hydrology (precipitation and discharge), land management changes, eutrophication from nitrogen deposition and CO_2 fertilisation (Evans et al. 2006; Worrall and Burt 2007; Monteith et al. 2007; Eimers et al. 2008; de Wit and Wright 2008). However, these drivers are not mutually exclusive and a combination of factors may influence observed trends in DOC concentrations (Worrall and Burt 2007) with certain mechanisms predominating temporally or in different study environments.

Soils and their associated land-use are the primary influence on the spatial variation in DOC, which can vary markedly between different streams (Clark et al. 2004; Dawson and Smith 2007). Soil type is particularly important in upland areas where DOC is assumed to derive mainly from terrestrial organic matter (Hope et al. 1994; Brooks et al. 1999). This has been supported by work showing a strong correlation between soil carbon pools and stream DOC concentrations, particularly in smaller catchments of $<5\ km^2$ (Aitkenhead et al. 1999; Billett et al. 2006). The transport of DOC losses from the bulk soil has been linked to hydrological processes in response to precipitation events and changing flow paths through different soil horizons containing contrasting amounts of organic matter (Grieve 1990, 1994; Soulsby 1995; Hinton et al. 1998; Dawson et al. 2002).

Temperature, plant residue composition, nutrient and organic matter availability interact with soil physico-chemical attributes to determine the rate of biologically driven organic matter decomposition (Dawson and Smith 2007) and hence production of the potentially mobile organic carbon. Soil temperature and moisture, in particular, are major factors regulating the decomposition rate, which influences observed seasonal patterns of higher soil pore DOC and CO_2 concentrations in the summer compared to the colder winter months (Castelle and Galloway 1990; Hope et al. 2004; Bonnett et al. 2006).

This seasonal effect in soils is parallel, to some extent, with the seasonality of observed surface water DOC concentrations with a tendency in upland catchments of higher concentrations during the summer and autumn months. The seasonal patterns for DOC in surface waters are often explained by enhanced turnover of organic matter, increased solubility of more hydrophilic organic matter and release of DOC with high discharges; the early autumn being considered a time of maximum DOC export (Worrall et al. 2004; Lumsdon et al. 2005; Cooper et al. 2007; Tipping et al. 2007). Discharge regression equations have been used to predict DOC concentrations for approximate ‘summer’ and ‘winter’ periods (Dawson et al. 2002; Clark et al. 2007). However, DOC concentrations from individual catchments may not always be dependent on both discharge and seasonality (Tipping et al. 2007; Clark et al. 2004, 2007). Increased temperatures and changes to the seasonal precipitation patterns (e.g. summer/winter rainfall ratios) as well as a projected increased frequency of storm events have implications for the production and export of DOC (Arnell 1998; Hagedorn et al. 2000; Hulme et al. 2002; Eimers et al., in review).

Integrating hydrological processes (export of DOC) with the seasonal production of DOC in soils in contrasting catchments is important for the modeling of soil carbon losses to surface waters (Grieve 1990; Eimers et al. 2008, in review). Long-term data sets provide an opportunity to assess DOC concentrations over many annual seasonal cycles and enable hydrological characteristics, such as rainfall–runoff ratios, runoff processes and transit times of water passing through a catchment (Soulsby et al. 2000, 2006; McGuire and McDonnell 2006; Tetzlaff et al. 2007a) to aid interpretation of DOC exports. Few long-term DOC studies assess seasonal variability (Eimers et al. 2008), examine patterns specific to individual years or link to the longer-term climatic cycles in terms of the annual hydrological variability over a number of years. Moreover, the interpretation of seasonal data can be limited because of (1) lack of data and (2) lack of data at a broad range of discharges; an issue common to regular but infrequent sampling protocols. However, with the data presented in this study, it was possible to discern patterns of seasonality across time series at three climatologically different regions of Scotland with contrasting hydrological characteristics.

The main aim of this work was to characterise links between seasonal and catchment-specific hydrological patterns and DOC export. Moreover, this will test the hypotheses that seasonal patterns in DOC are (1) temporally consistent over the longer-term (decadal) and (2) show no differences at climatologically different sites across Scotland.

Methods

Study areas

The locations of the three long-term study areas are shown in Fig. 1. The northern site is the Allt a'Mharcaidh catchment, situated on the western edge of the Cairngorm Mountains which forms a tributary of the River Spey (Soulsby et al. 1997). It is part of both the UK Acid Water Monitoring Network (AWMN) and the Environmental Change Network (ECN). The Loch Ard site, operated by FRS Freshwater Laboratory, consists of a number of streams draining forested and non-forested catchments in Central Scotland which subsequently discharge into the River Forth (Harriman and Morrison 1982). The Sourhope catchment is located in the Cheviot Hills in the Borders of SE Scotland. The streams also form part of the ECN and subsequently drain into the River Tweed (Miller et al. 2001). The surface water chemistry for the streams under consideration at each of the three long-term study areas is shown in Table 1.

Loch Ard

The three sites at the Loch Ard study area are tributaries of the Duchray Water and termed Burns 2, 10 and 11 (Harriman and Morrison 1982). Burn 2 (Caorainn Adhaidh Burn) drains an area of 4.27 km^2, ranging from 154 to 974 m at Ben Lomond. Burns 10 (0.92 km^2) and 11 (1.44 km^2) are headwaters of the Castle Burn and have altitudinal ranges of 99–221 and 99–282 m, respectively (Tetzlaff et al. 2007b). Catchments are dominated by acidic peaty and peaty gley soils that cover metamorphic and sedimentary rocks composed of low permeability granitic, schist or quartzite-type rocks, with a change to mica and various undifferentiated schists at the Burn 2 catchment. Burn 2 contains bare rock outcrops and sub alpine soils on higher ground. These merge into peaty podzols and peaty gleys lower down the valley with areas of blanket peat in the centre of the catchment and alluvial soils containing organic deposits (Harriman and Morrison 1982).

Burn 2 drains typical higher altitude moorland. Burns 10 and 11 drain afforested (ca. 95%) catchments, established in the 1950s; The Burn 10 catchment was partially (39%) clear-felled in 1988–1990 and then replanted; the Burn 11 catchment was partially (23%) clear-felled in three phases from 1997 to 2000 and then replanted. Sitka spruce (*Picea sitchensis*) is the dominant tree species at both sites (Tetzlaff et al. 2007b).

Mean annual precipitation varies between 2,000 and 2,500 mm for Burn 2 and is about 2,000 mm at the lower elevation Burns 10 and 11 (Harriman and Morrison 1982; Harriman et al. 2001). Mean monthly air temperatures for the period of record (1991–2003) ranged from 2.8°C in January to 13.7°C in August with an average annual temperature of 8.3°C. The mean daily flow of Burn 2 (1989 and 2002), based on Burn 10 discharge data applying a proportional area approach (Tetzlaff et al. 2007a), ranged between 0.005 and 4.648 $m^3 s^{-1}$. Discharge data at Burns 10 and 11 were obtained from SEPA operated gauging stations. Estimates of mean daily discharge for these Burns

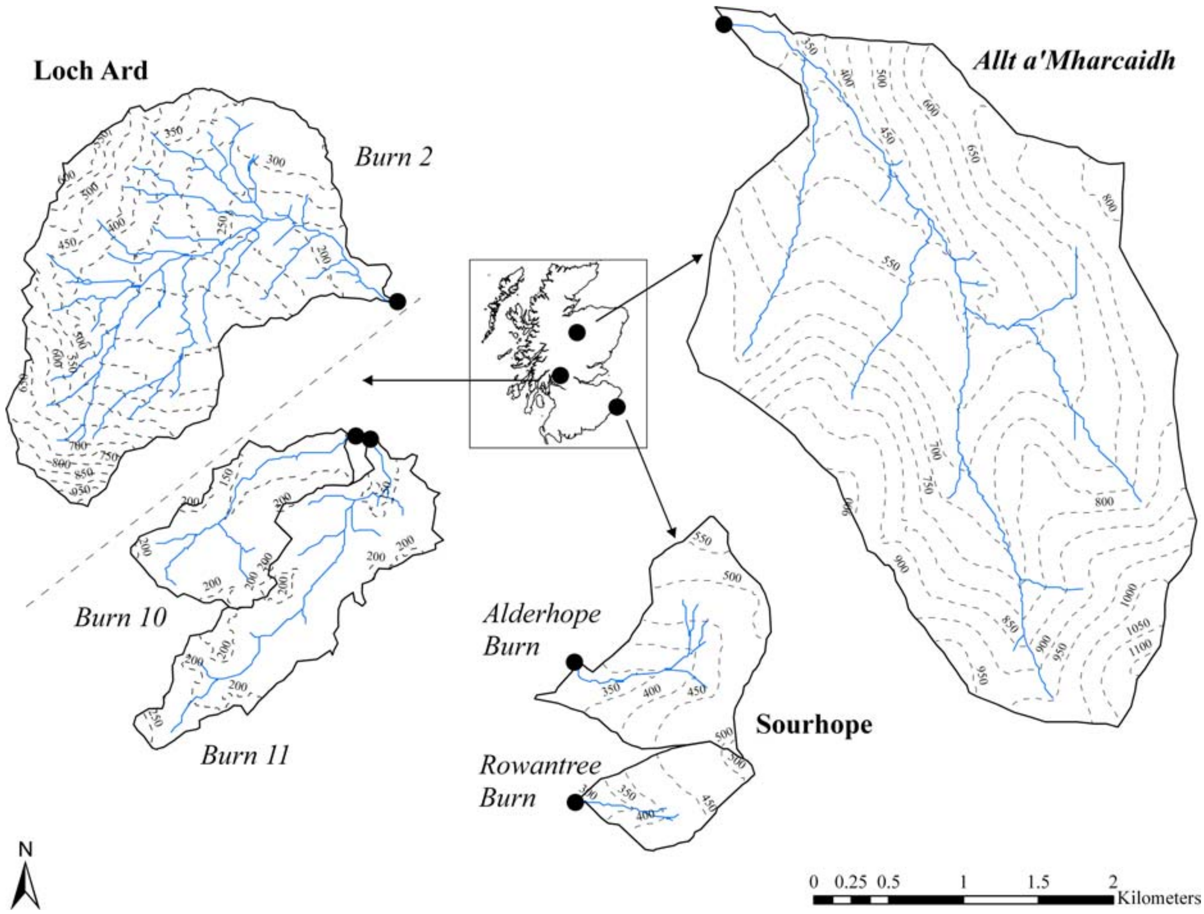

Fig. 1 Location of the three long-term study areas in Scotland, UK, and the catchment boundary, contours and drainage network of each of the six study sites

(1988–2003) ranged between 0.001 and −1.001 $m^3 s^{-1}$ (Burn 10) and 0.001–1.583 $m^3 s^{-1}$ (Burn 11).

Previous work has shown Burns 10 and 11 catchments to be highly responsive, with up to 70% of annual flows being derived from acidic soils with low groundwater inputs (Tetzlaff et al. 2007b). The mean transit time of the Burn 11 catchment, using long-term weekly chloride data has been shown to be correspondingly short and estimated at ca. 5–6 months (Hrachowitz et al., in review). Other literature values have suggested similar mean transit times for both Burns 10 and 11 (Tetzlaff et al. 2007b).

Allt a'Mharcaidh

The Allt a'Mharcaidh drains an area of 10 km^2, with an altitudinal range of 320–1,111 m. The area is underlain by granite, covered by locally derived drift. The gently sloping valley bottom is dominated by peat soils; podzolic soils cover the steeper valley sides and the high plateau is characterised by alpine soils. Mean annual precipitation is ca. 1,100 mm, much of which can fall as snow during October–March although this has been highly variable in recent years. Mean monthly temperatures (at 575 m) range from 1.2°C in February to 10.3°C in July. The climate can be classed as sub-arctic (Harriman et al. 1990, 2001). The mean daily flow (1987–2002) ranged between 0.023 and 5.047 $m^3 s^{-1}$. The annual flow regime usually reflects some influence of snowmelt and has a marked alpine-like character with a distinct period of high flows occurring in late winter/early spring (Soulsby et al. 1997). Despite this, the Allt a'Mharcaidh has been shown to have a surprisingly high groundwater component, accounting for up to 55% of annual runoff. This is thought to be related to the free-draining nature of ca. 70% of the catchment soils. The mean transit time has also been

Table 1 Surface water chemistry, covering the time period under investigation for each of the six study sites

	Years	pH	DOC	Alk	Tot Al	Fe	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	NO_3^-–N	SO_4^{2-}–S
Allt a'Mharcaidh	1987–2002												
Mean		6.31	2.72	47.2	0.03	0.01	3.01	0.24	1.01	0.36	3.43	0.01	0.73
1%		5.41	0.40	3.00	<0.01	<0.01	2.09	0.16	0.55	0.17	2.16	<0.01	0.43
99%		7.01	9.86	93.0	0.14	0.04	4.12	0.43	1.78	0.59	6.09	0.07	1.04
Loch Ard, Burn 2	1989–2002												
Mean		5.15	4.84	4.99	0.06	0.37	3.05	0.22	1.22	0.53	4.89	0.08	0.90
1%		4.55	1.20	−25.2	0.01	<0.01	1.68	0.04	0.56	0.27	1.64	<0.01	0.41
99%		6.65	11.59	84.3	0.13	2.99	8.08	0.63	2.37	1.23	16.70	0.45	1.83
Loch Ard, Burn 10	1988–2003												
Mean		4.63	7.44	−20.4	0.19	0.52	3.95	0.28	1.26	0.75	6.25	0.30	1.52
1%		4.20	2.30	−60.0	0.06	<0.01	2.67	0.04	0.68	0.48	2.37	<0.01	0.74
99%		5.46	17.87	10.0	0.44	1.77	6.71	1.02	2.15	1.26	16.22	1.93	2.62
Loch Ard, Burn 11	1988–2003												
Mean		4.42	11.31	−35.7	0.18	1.15	4.59	0.22	1.17	0.68	7.73	0.10	1.37
1%		4.06	2.85	−84.6	0.09	<0.01	2.75	0.00	0.58	0.36	3.43	<0.01	0.60
99%		5.16	31.32	6.31	0.35	5.43	8.08	1.14	1.91	1.18	19.39	0.41	2.68
Sourhope, Alderhope Burn	1995–2006												
Mean		6.55	2.58	948	0.03	0.01	6.92	0.72	12.82	4.61	7.85	0.14	1.93
1%		6.36	0.80	100	<0.01	<0.01	3.62	0.36	3.69	1.56	4.56	<0.01	1.01
99%		8.42	16.74	1487	0.22	0.09	8.28	1.30	17.66	5.92	11.88	0.57	2.45
Sourhope, Rowantree Burn	1995–2006												
Mean		7.19	2.19	819	0.02	0.01	7.50	0.72	11.17	3.91	8.05	0.22	2.31
1%		6.69	0.80	330	<0.01	<0.01	3.97	0.40	5.13	1.74	4.73	<0.01	1.16
99%		7.87	13.56	1503	0.15	0.04	8.79	1.23	16.09	5.36	10.80	0.46	2.82

All data are in mg l^{-1} except pH and alkalinity (μEq l^{-1})

estimated from ^{18}O input–output relationships as being 12–14 months (Soulsby et al. 2006).

Sourhope

Both Alderhope and Rowantree Burns flow into the Sourhope Burn and drain areas of 1.20 and 0.44 km^2 moorland, respectively, The Rowantree Burn ranges from 295 to 508 m with discharge monitored upstream from the confluence with the Sourhope Burn. The Alderhope Burn catchment (300–601 m) outflow is not gauged and is based on the Rowantree Burn discharge data (Tetzlaff et al. 2007a). The dominant geology is stony glacial drift derived mainly from intermediate andesitic lavas of the Lower Old Red Sandstone age and undifferentiated volcanic rock likely to contain pyroclastics (Younger, pers. comm.). Acid brown forest soils are found on lower slopes, while acid peaty podzols and peaty gleys occur on upper slopes with small areas of hill peat on the summit (Bain et al. 1997; Miller et al. 2001).

Mean annual precipitation is just under 1,000 mm. Mean monthly temperatures (1995–2006) ranged from 2.0°C in December to 14.8°C in August with an average annual temperature of 7.5°C. The mean daily flow ranged between 0.001 and 0.336 m^3 s^{-1} at the gauged Rowantree Burn. The system has been found to have a remarkably high groundwater component, accounting for ca. 75% of annual runoff and a correspondingly high mean transit time, estimated at >3.5 years (Hrachowitz et al., in review).

Data collection

Dissolved organic carbon

Surface water DOC concentration data were obtained from long-term datasets. Loch Ard streams were sampled predominantly weekly from January 1989–December 2002 (Burn 2) to January 1988–December 2003 (Burns 10 and 11); the Allt a'Mharcaidh was sampled at a maximum twice weekly frequency from January 1987–December 2002. At the two Sourhope sites, samples were collected weekly from January 1995 to December 2006. DOC can be defined as comprising any organic compound passing through a 0.45-μm filter (Evans et al. 2005). All samples taken from the six study sites were filtered accordingly and stored at below 4°C, prior to analysis for DOC concentration. Although the samples were analysed by different organisations, all have taken part in the UKAWMN analytical quality control programme providing a quantitative assessment of laboratory performance (Gardner 2008). For DOC, a tolerable error of 10% for concentrations >2.5 mg l^{-1} has been permitted between institutions. At lower concentrations, a fixed tolerable error of 0.25 mg l^{-1} was applied (Dixon and Gardner 1998; Gardner 2008). This performance assessment and criteria continued through for the period under investigation.

Other parameters

Other physical and chemical parameters at the six study sites covering the time period of the long-term data were used to aid interpretation (Table 1). Discharge data was obtained from continuously gauged stations at Burns 10 and 11 for Loch Ard; the Allt a'Mharcaidh and the Rowantree Burn at Sourhope. Mean monthly air temperature (Fig. 2) and rainfall data (Fig. 3) were obtained to give an indication of climatic variation and aid in DOC seasonal analyses.

Data analyses

Dissolved organic carbon

Time-series data for DOC concentrations was plotted with a linear regression trend line (±95% confidence intervals) for these larger annual datasets of $n \geq 25$/year (Monteith et al. 2001) to assess potential increases in DOC concentrations at each study site over the time period under investigation.

Periodicity of the mean monthly DOC concentrations from each of the long-term datasets was estimated. This was determined by deconstructing the time series using a Discrete Fourier Transform into

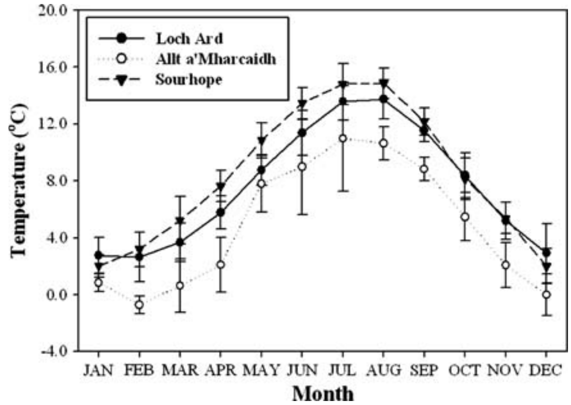

Fig. 2 Mean monthly temperatures from the three long-term study areas: Loch Ard (1991–2003), Allt a'Mharcaidh (1999–2002) and Sourhope (1995–2006)

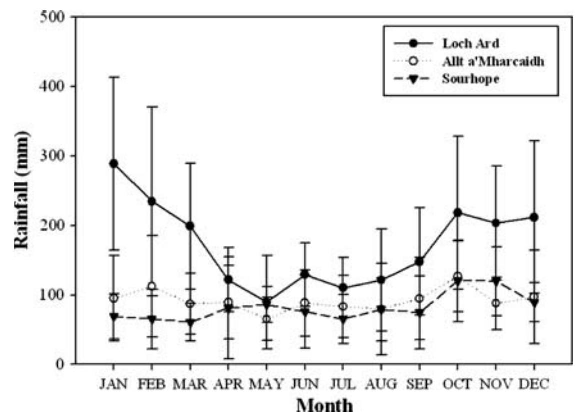

Fig. 3 Mean monthly rainfall at the three long-term study areas: Loch Ard (1989–2003), Allt a'Mharcaidh (1987–2002) and Sourhope (1995–2006)

$n/2$ wavelengths, where n is the number of samples. For each site, the three wavelengths with the highest Fourier coefficients (i.e. amplitudes) were used to illustrate the dominating DOC periodicities on the composite signal. The variance of the composite signal explained by the respective wavelength was estimated from the square of the Fourier coefficients.

The DOC data at each of the six sites were seasonally separated by one of two methods to produce 'high' DOC (summer/autumn) and 'low' DOC (winter/spring) concentration periods for each calendar year. For the Allt a'Mharcaidh and Sourhope study areas, the two seasonal categories were delineated using seasonal DOC concentration–discharge relationships (Dawson et al. 2002, Ågren et al. 2008). For the three Loch Ard study sites, a second mode of separation was utilised based on the mean monthly air temperature and DOC concentration data as this had shown no relationship with discharge.

Initially, the delineation was somewhat arbitrary at the Loch Ard sites as most data points could be easily assigned to either a high (summer/autumn) or low (winter/spring) DOC concentration category. However, in order to calculate objectively whether samples taken on the cusp of switchovers should be placed in either high or low DOC concentration categories, the mean monthly air temperature was utilised, where required, and a cut off of 6.5°C used to separate categories.

With the DOC concentration–discharge method, e.g. at the Allt a'Mharcaidh, autumnal storms (late October/November) were used to distinguish the switchover from high to low DOC concentration–discharge relationships. Earlier storms in September/October occasionally produced data that did not relate well to the predicted high DOC relationship, but these flow events occurred too early in autumn for subsequent concentrations to be considered as part of the 'low DOC' sample grouping. Moreover, occasionally during high DOC concentration time periods (July/August), high concentrations were observed, irrespective of discharge. The switchover from low to high DOC concentration categories in spring was more arbitrary and data points in this period tended to be equally applicable to either high or low DOC concentration categories.

Box plots were obtained detailing seasonal variation in DOC concentrations at the six sites by plotting the summer/autumn and winter/spring DOC categories for each individual year of the long-term time-series data. For each individual year at each site, a two sample *t*-test (Mann–Whitney for non-normalised data) was undertaken to determine significant differences between DOC concentrations in the summer/autumn category compared to the winter/spring category. A paired *t*-test (one sample signed rank test on the paired differences for non-normalised data) between each of the seasonal median DOC concentrations was also performed for the time period under investigation at each of the sites. In order to investigate long-term changes in the seasonal amplitude of DOC concentrations, the inter-quartile DOC concentration range of each seasonal category was determined from the box plot data and linear regression analysis was used to determine significant trends of DOC concentration amplitudes in either summer/autumn or winter/spring categories.

Hydrological data

Comparative hydrographs of the three study areas, for a typical annual cycle (1999), are shown in Fig. 4. Flow duration curves were determined at the three long-term study areas (Loch Ard, Burn 11, Allt a'Mharcaidh and Sourhope, Rowantree Burn) using mean daily specific discharge data. Annual curves were produced initially for the time periods under investigation, from which a single median flow duration curve was determined for each study area. These curves allow interpretation of specific discharge characteristics between the study areas throughout the period of the study: Q_5 is the discharge value that is exceeded for only 5% of the time

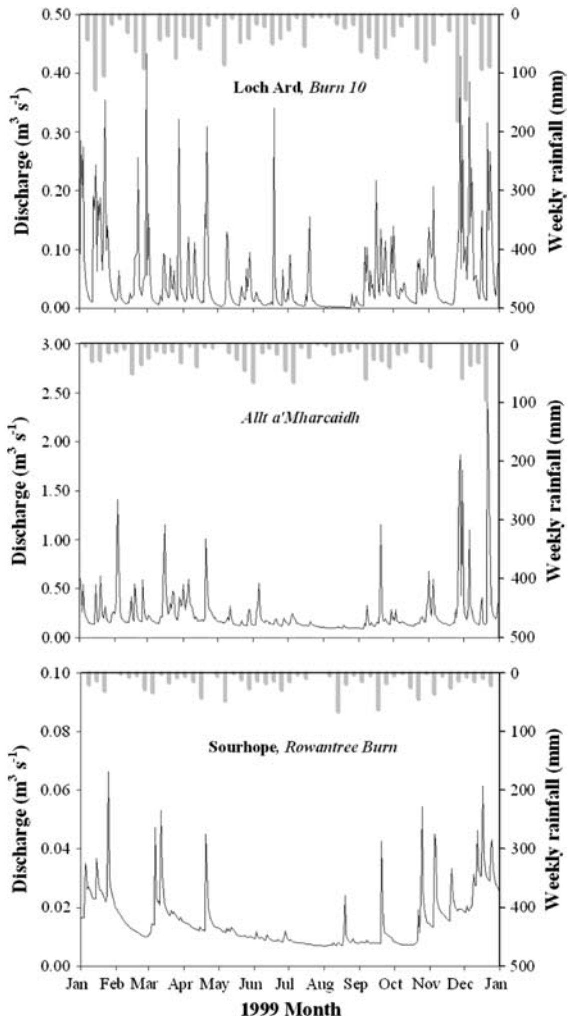

Fig. 4 Typical annual hydrographs (1999) from three study sites: Burn 10, Loch Ard; the Allt a'Mharcaidh and the Rowantree Burn, Sourhope

(high flow) whereas Q_{95} is the discharge value that is exceeded for 95% of the time (low flow).

Annual rainfall–runoff ratios were calculated for four of the study sites (Loch Ard, Burns 10 and 11, Allt a'Mharcaidh and the Rowantree Burn at Sourhope). Burn 2 (Loch Ard) and the Alderhope Burn (Sourhope) ratios are not shown, as discharge and precipitation were calculated on an area basis with Burn 10 (Loch Ard) and the Rowantree Burn (Sourhope), respectively, producing identical values. The average annual wetness of a catchment can be indicated by collating rainfall–runoff ratios. However, as precipitation was only measured at one or two points, these values are considered indicative and should not be taken as an absolute water balance. In 2001, the foot and mouth outbreak resulted in a substantial proportion of missing precipitation data at Sourhope, thus the rainfall–runoff ratio was not calculated for this year. One-way ANOVA was performed on the annual data to determine significant differences between sites.

Results

The three study areas have contrasting stream water chemistry (Table 1). Loch Ard was the most acidic of the study areas with mean pH values at the three sites between 4.42 and 5.15, reflected in low mean concentrations of (frequently negative) alkalinity, Ca and Mg. The Allt a'Mharcaidh contained typical granitic montane chemistry with a mean pH of 6.13 and lowest mean base cationic and chloride concentrations. The Sourhope sites had stream water chemistry that reflected their more basic catchment geology. Sulphate concentrations in the surface waters were dependent on depositional characteristics and buffering potential of soils; the Rowantree Burn had the highest concentrations, which maybe a consequence of its closer proximity to the marine environment (as indicated by the highest mean chloride concentrations of all the sites). Mean DOC concentrations across the study sites ranged from 2.19 mg l^{-1} at the Rowantree Burn (Sourhope) to 11.31 mg l^{-1} at Burn 11 (Loch Ard) but absolute values ranged from a minimum of 0.20 mg l^{-1} to a maximum of 36.80 mg l^{-1}.

Hydrological data

Median flow-duration curves from the three study areas are shown in Fig. 5. The Loch Ard flow duration curve is markedly different from the other two study areas, which have very similar properties. The Q_5 at Loch Ard exceeds the Q_{95} by more than two orders of magnitude, while this difference is less pronounced at the Allt a'Mharcaidh and Sourhope sites, suggesting a less variable and slower runoff response, consistent with their higher groundwater contribution identified by earlier studies.

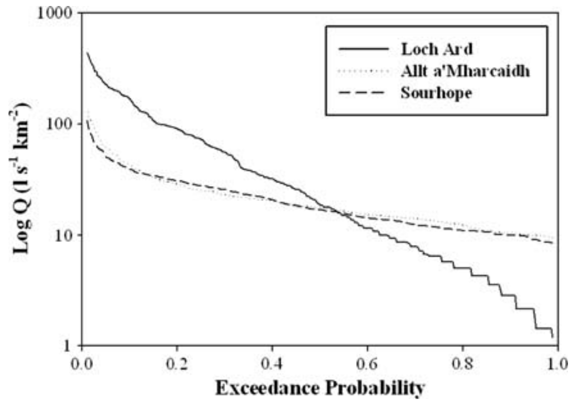

Fig. 5 Median flow duration curves of specific daily discharge against exceedance probability for the three long-term study areas at Loch Ard, Allt a'Mharcaidh and Sourhope

The rainfall–runoff ratios for individual years from four of the study sites are shown in Table 3. There was substantial variation between years within individual sites with Loch Ard ranging between 0.64 at Burn 11 and 0.98 at Burn 10; Allt a'Mharcaidh 0.56 and 0.85 and Sourhope 0.20–0.55. However, overall, both Loch Ard sites had significantly higher ($P < 0.05$) mean ratios (0.82 $\pm$ 0.10 Burn 10 and 0.82 $\pm$ 0.08 Burn 11) than the Allt a'Mharcaidh (0.69 $\pm$ 0.08) or Rowantree Burn (0.44 $\pm$ 0.11).

Long-term trends in DOC concentration

The long-term trends in DOC concentrations at each study site are expressed as time-series data (Fig. 6) and cover particular time periods within the years 1987–2006. The available data for each site within this time period was enough to produce a minimum of 12 years of at least fortnightly DOC concentrations.

Annual mean increases in DOC concentrations (mg l^{-1} year^{-1}) at the Loch Ard sites increased by between 0.22 and 0.79 mg l^{-1} year^{-1} (Table 2). All three sites showed a marked seasonal pattern of high summer and low winter DOC concentrations. The increasing amplitude in latter years of the time series

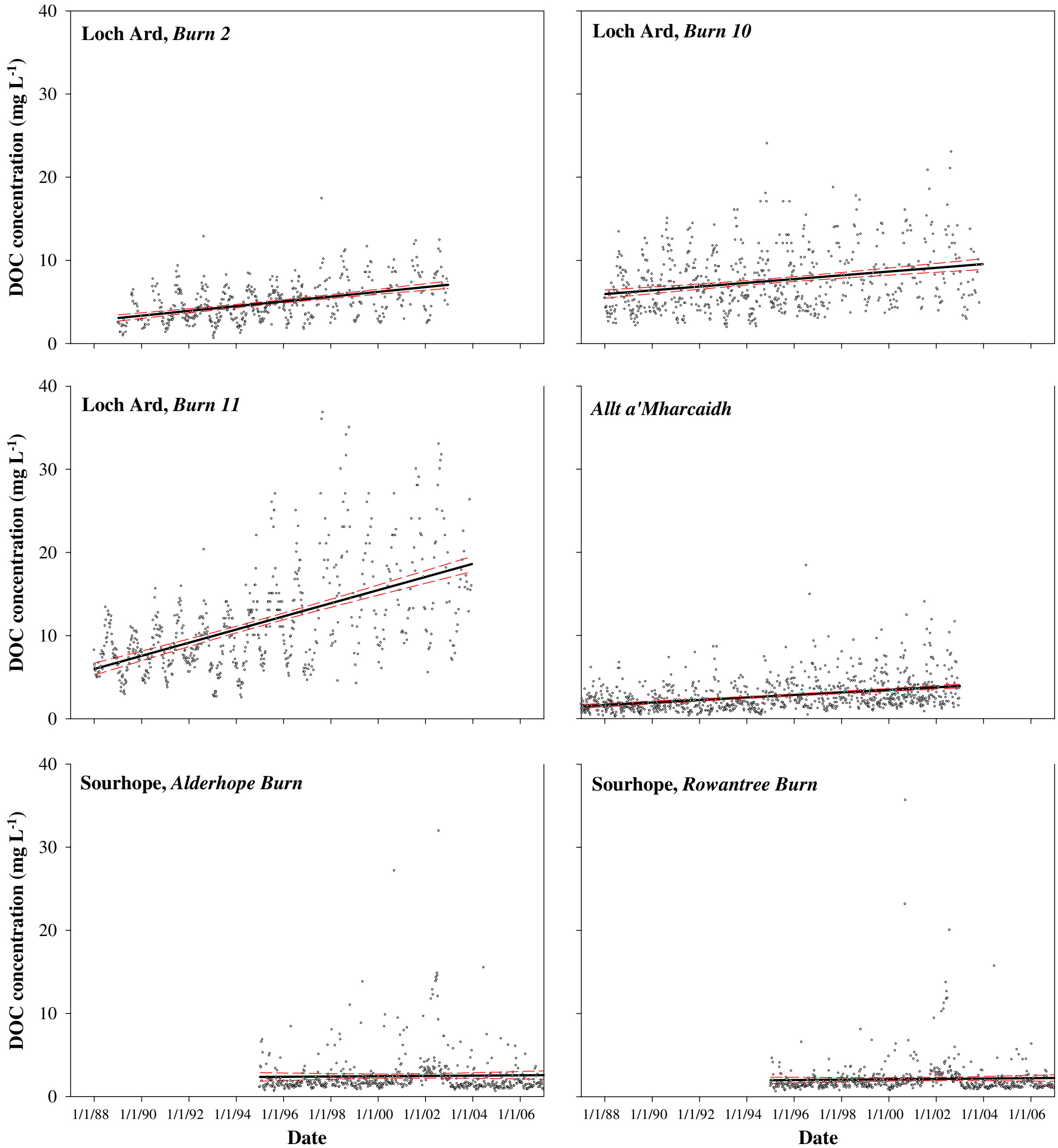

Fig. 6 Time series of surface water DOC concentrations (mg l^{-1}) from the six long-term study sites over various sampling time periods ranging from 1987 to 2006

was particularly evident in Burn 11, where the range of concentration was >30 mg l^{-1} within a single year. At the Allt a'Mharcaidh, annual changes in mean DOC concentration were shown to increase by 0.15 mg l^{-1} $year^{-1}$ on average. The DOC concentrations produced limited seasonality although highest values tended to occur in late summer/autumn of each year. Moreover, the most recent years also exhibited greater annual amplitude of DOC concentrations. At the Sourhope study sites, any indication of significantly increasing DOC concentrations was not apparent (95% confidence intervals between −0.04 and 0.09 mg l^{-1} $year^{-1}$) over the time period under investigation. There was also a lack of marked seasonal

Table 2 Annual mean increase of DOC concentrations (mg l^{-1} $year^{-1}$) in surface waters at the six long-term study sites

	Time series (year)	DOC (mg l^{-1} $year^{-1}$)	95% Range (mg l^{-1} $year^{-1}$)	*P*-value
Allt a'Mharcaidh	16	0.15	0.12–0.18	<0.001
Loch Ard, Burn 2	14	0.28	0.23–0.34	<0.001
Loch Ard, Burn 10	16	0.22	0.15–0.29	<0.001
Loch Ard, Burn 11	16	0.79	0.69–0.89	<0.001
Sourhope, Alderhope Burn	12	0.02	−0.07[a] to 0.10	0.627
Sourhope, Rowantree Burn	12	0.02	−0.04[a] to 0.09	0.404

Trend determined from linear regression plots (±95% confidence intervals) of each time-series data

[a] Negative value indicates decrease in DOC over time period under investigation

variability, although occasional high DOC concentrations were measured throughout the year above the general baseline concentrations (median value 1.7 mg l^{-1}); some of these isolated concentrations were substantially higher at >20 mg l^{-1}.

The three study areas illustrate contrasting periodicity functions of mean monthly DOC concentrations for the length of periods under investigation (Fig. 7). A significant annual periodicity was observed at Loch Ard (Burn 2), explaining 65.4% of the data variance. This was the highest of the three Loch Ard sites (annual periodicity variance at Burn 10 = 46.6% and Burn 11 = 46.8%). However, an annual periodicity was less noticeable with the Allt a'Mharcaidh data (17.1% explained) and no annual periodicity was detected at the Sourhope data, with the primary frequency determined as a 10 year period but explaining only 8.0% of the variance.

Seasonal DOC concentrations

For individual calendar years, the DOC concentration data were split into two distinct seasonal data categories using one of the two methods outlined in Sect. 'Data analyses'. This segregation of data was consistent over the long-term data for individual sites and is detailed in Table 4. The seasonal separation of datasets produced high (mainly May/June to October/November) and low (remaining months, i.e. November/December to April/May) DOC concentration periods.

A graphical representation of DOC concentration plotted against discharge at each of the six sites is shown following data delineation into its seasonal categories for one annual cycle (Fig. 8). At the Loch Ard study sites, there was a clear seasonal separation of DOC concentrations irrespective of discharge. This temperature derived seasonal separation was most marked at Burn 2 as some semblance of high DOC concentration–discharge relationships at low flows was apparent at Burn 10 in some years. With the DOC concentration–discharge method, e.g. at the Allt a'Mharcaidh and Sourhope, some years produced clearer relationships than others as data surrounding the concentration–discharge regression line were less variable (Walling 1977).

Figure 9 shows seasonal variation in DOC concentration within each of the six study sites, portrayed over the long-term time series. Loch Ard study sites, (again Burn 2 being the most distinct), showed significant differences for all years ($P < 0.05$) between DOC concentrations at high DOC concentration periods (summer/autumn) compared with the corresponding low DOC concentration period (winter/spring) of that year. However, the DOC concentrations between the two seasonal categories at the Allt a'Mharcaidh and Sourhope were only occasionally significantly higher ($P < 0.05$) within individual years. Across the long-term data as a whole, there was no significant difference between paired median DOC concentrations of the seasonal categories. This also reflects the lack of any annual periodicity within these data sets.

Furthermore, the box plots also indicate the variation in DOC concentrations for each applied seasonal delineations. Over the long-term, the amplitude (inter-quartile range) of seasonal DOC concentrations increased significantly at the Allt a'Mharcaidh ($P < 0.001$, summer/autumn; $P = 0.023$, winter/spring) and Burn 2 ($P < 0.001$, winter/spring). The inter-annual variability was particularly marked in Burn 11 ($P < 0.001$ for both seasonal categories) where the variation from 1997 to 2002 increased substantially compared to previous years, particularly for

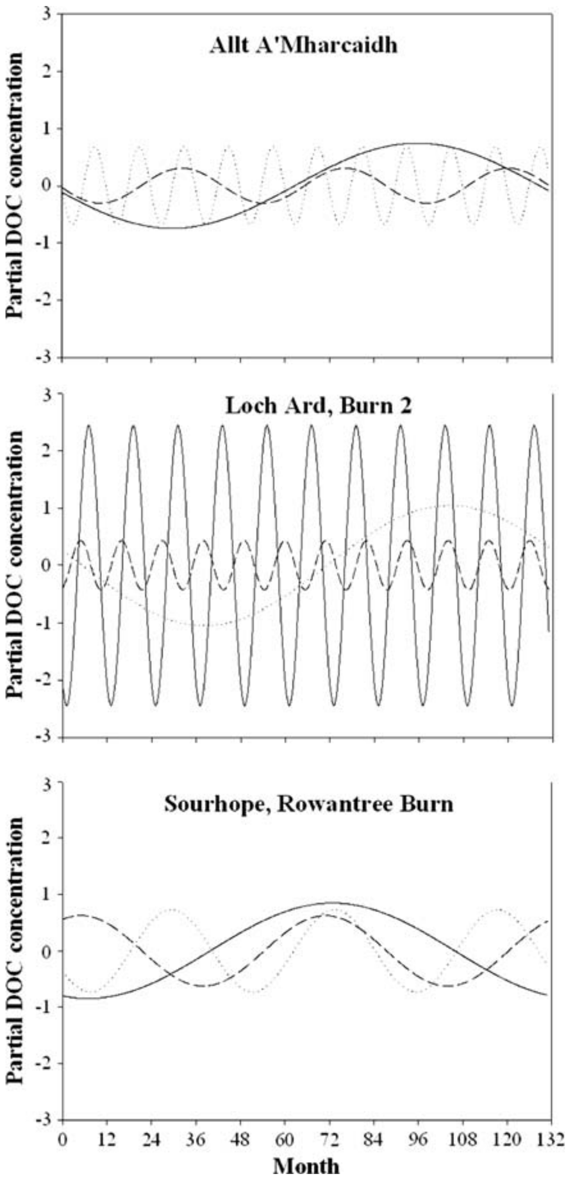

Fig. 7 Periodicity functions of the de-trended DOC time series for the three study areas (unforested sites) at Loch Ard, Allt a'Mharcaidh and Sourhope. The primary (*dotted line*), secondary (*dashed line*) and tertiary (*straight line*) frequencies are shown with variance explaining 79.3% of the data at Loch Ard; 41.0% at the Allt a'Mharcaidh and 18.3% at Sourhope

the summer/autumn category. The Sourhope study sites indicated limited variation within seasonal delineations with no significant increase in long-term DOC concentration amplitudes but did contain more incidences of outliers where DOC concentrations increased substantially above the norm.

Discussion

The three study areas cover a marked climatic gradient across mainland Scotland. All study sites contain varying depths and spatial covering of organic soils but are underlain by different geologies and receive varying precipitation volumes resulting in the contrasting stream water chemistry observed over the time periods.

As the six upland catchments contain different soil characteristics, the total organic matter pool in each catchment will vary resulting in proportionally different amounts of DOC export to the surface waters (Aitkenhead et al. 1999; Billet et al. 2006). The wide range of observed DOC concentrations is typical of upland streams in the UK, which show similar ranges between ca. 1.00 and 45.0 mg C l^{-1} (Scott et al. 1998; Dawson et al. 2002, 2004; Clark et al. 2007). The Loch Ard study area contains the highest proportion of organic soils, producing the highest DOC concentrations at its three study sites. The lower DOC concentrations in the colder Allt a'Mharcaidh maybe partly temperature dependent (Fig. 2) but both the Allt a'Mharcaidh and Sourhope study areas also have differences in their organic matter pool as they are dominated by soils which contain substantially lower organic matter than the soils prevalent at Loch Ard (Milne and Brown 1997).

Hydrological data

In order to understand the catchment processes underpinning the two types of mechanisms controlling terrestrially derived surface water DOC concentrations detailed in this study, hydrological characteristics of each catchment were assessed to distinguish factors that control export of DOC by hydrologically mediated processes. Quantifying hydrological characteristics for a catchment, such as mean transit times, is essential for understanding the controlling factors that determine transport of water and solutes, including DOC (Kirchner et al. 2000; Dunn et al. 2006).

Hydrological pathways may control initial amounts of carbon reaching the stream but, particularly as stream order increases, organic inputs from up-stream and in-stream processes (e.g. biofilm retention and heterotrophic DOC respiration) can further modify these terrestrial inputs (Vannote et al. 1980; McDowell 1985). Although it has been shown

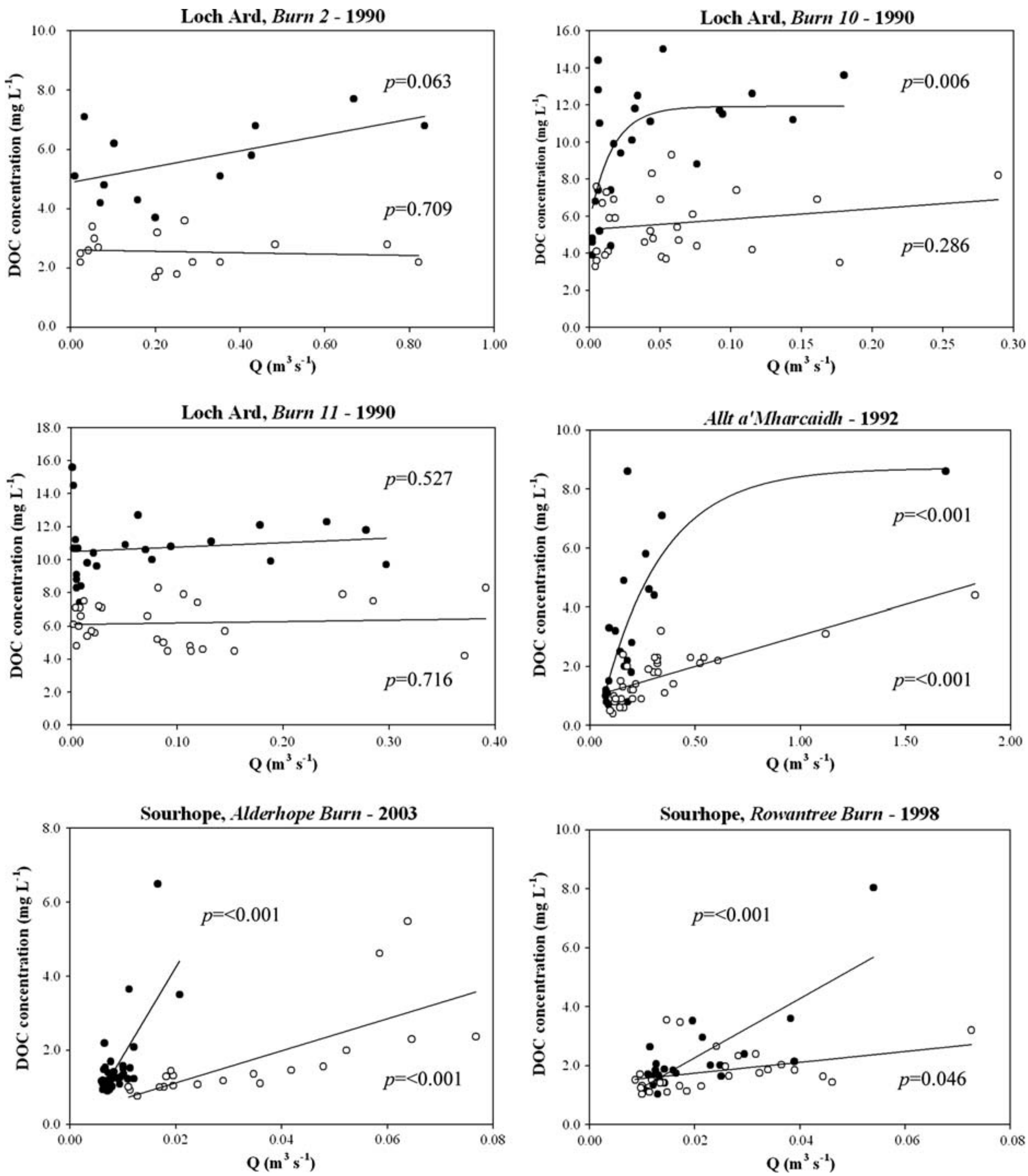

Fig. 8 Graphical examples of the annual delineated seasonal categories of high and low DOC concentrations from each of the six long-term study sites plotted against discharge at time of sampling. The data at each site has been split according to the dates in Table 4 as summer/autumn (*dark filled circle*) and winter/spring (*open circle*)

that in-stream processes reduced the final DOC flux at a typical Scottish upland catchment outlet by 11.6–17.6% (Dawson et al. 2001a), this was during periods (spring/summer) of optimum in-stream activity (Dawson et al. 2001b). Annually, there was no significant net in-stream loss of DOC as in-stream

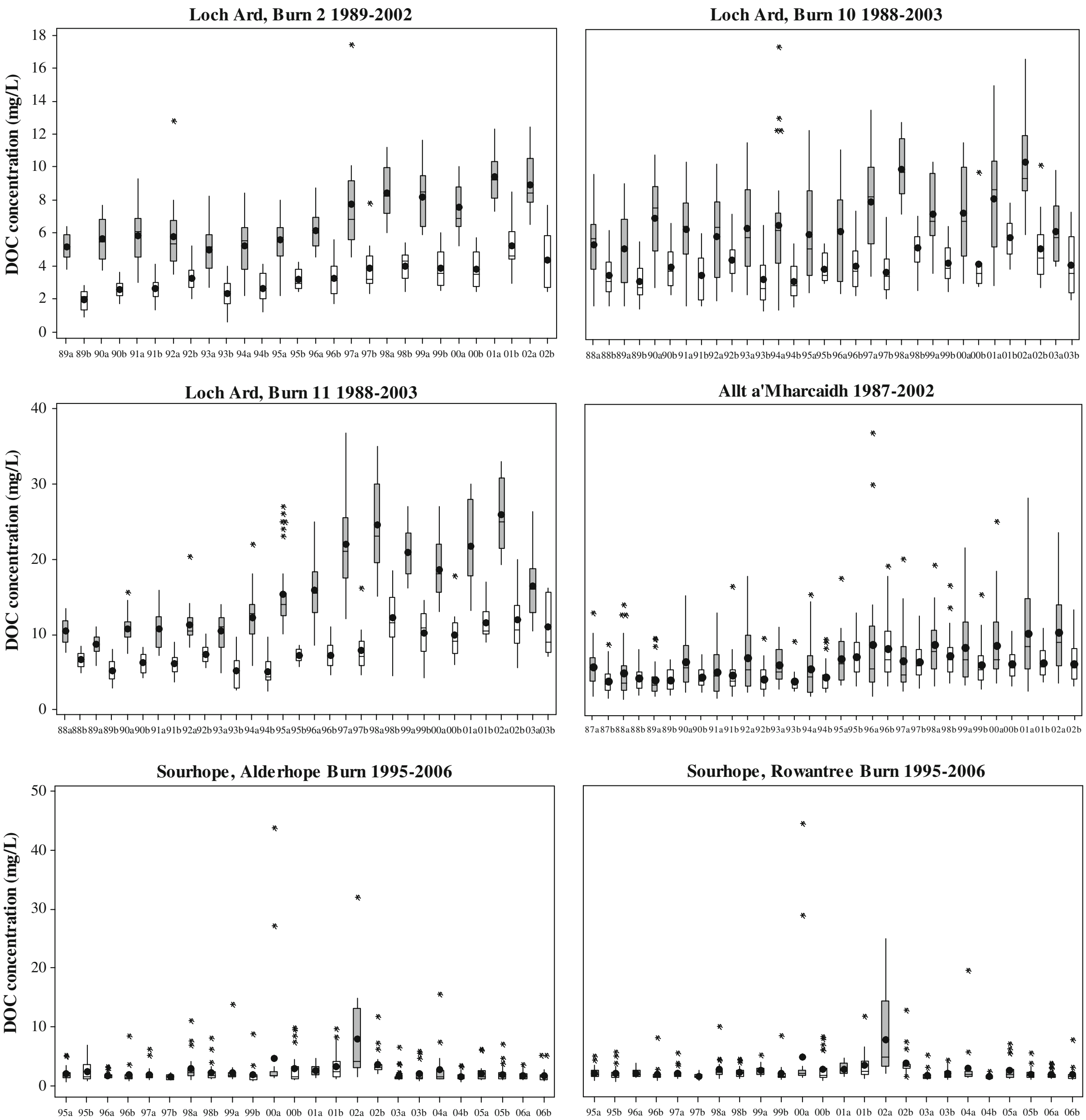

Fig. 9 Boxplot presentation of long-term surface water DOC concentration data from the six long-term study sites over various sampling times ranging from 1987 to 2006. The data is separated into a summer/autumn time period, denoted by '*a*' after each year and a *grey box* on the plot and a winter/spring period, denoted by a '*b*' after each year and a *clear box* on the plot. Mean (*dark filled circle*) and median DOC concentration values (*straight line*) are also shown within individual seasonal *boxes*

processes continually cycled and recycled the different forms of aquatic carbon (Dawson et al. 2004; Dawson and Smith 2007).

The annual hydrograph (Fig. 4) and steep flow duration curve (Fig. 5) identified the comparatively 'flashy' properties of the Loch Ard catchments and the responsive nature of its soils with their quick routing of precipitation to the drainage network. Mean transit times are low (of between 5 and 9 months) consistent with low groundwater contributions (Tetzlaff et al. 2007b; Hrachowitz et al., in review). The Loch Ard catchments were the wettest catchments with highest rainfall–runoff ratios (Table 3) due to the larger areas of highly responsive peat, peaty gleys

Table 3 Annual rainfall–runoff ratios at four of the long-term study sites covering the time periods of investigation at each site

Year	Allt a'Mharcaidh	Loch Ard, Burn 10	Loch Ard, Burn 11	Sourhope, Rowantree Burn
1987	0.85	–	–	–
1988	0.83	nd	nd	–
1989	0.60	0.76	0.75	–
1990	0.69	0.72	0.76	–
1991	0.75	0.85	0.81	–
1992	0.70	0.90	0.86	–
1993	0.72	0.98	0.91	–
1994	0.68	0.92	0.91	–
1995	0.65	0.95	0.93	0.41
1996	0.72	0.93	0.89	0.43
1997	0.73	0.81	0.86	nd
1998	0.56	0.80	0.84	0.55
1999	0.59	0.72	0.81	0.39
2000	0.68	0.66	0.80	0.55
2001	0.67	0.77	0.64	nd
2002	0.60	0.81	0.79	0.52
2003	–	0.76	0.74	0.20
2004	–	–	–	0.36
2005	–	–	–	0.54
2006	–	–	–	0.41
Mean	0.69 ± 0.08^{b}	0.82 ± 0.10^{a}	0.82 ± 0.08^{a}	0.44 ± 0.11^{c}

The mean values ± SD are also shown for each site

Due to uncertainty in stage discharge relationship, Sourhope data was estimated by annual precipitation-mean annual evapotranspiration (530 mm—http://www.nerc-wallingford.ac.uk)

nd not sufficient data

Superscript letters denote significance at $P < 0.05$

and/or shallow alpine soils and bedrock coverage and highest amounts of precipitation (2,000–2,500 mm). These catchments will tend to maintain a low moisture deficit throughout the year indicating high connectivity between its soils and the drainage network for much of the time.

In contrast, at the Allt a'Mharcaidh and Sourhope, the hydrographs and flow duration curves suggested a more subdued stream response due to freely draining less responsive soils and increased recharge to deeper soil horizons and fractured bedrock. These differences are associated with longer transit time estimates and higher groundwater contributions to the runoff in these two catchments compared to those at Loch Ard. The Allt a'Mharcaidh catchment maintained slightly lower catchment wetness and rainfall–runoff ratios (0.69 ± 0.08) indicative of lower percentages of responsive soils and consequently a longer mean transit time of ca. 12–14 months (Soulsby et al. 2006). Although, peat is present in the lower catchment, overall soils will tend to undergo regular wetting–drying cycles as less responsive peaty podzols on steep valley sides enable free drainage and loss of connectivity between soils and the drainage network at times of lower precipitation, prevalent during the summer in this catchment. The lowest mean annual rainfall–runoff ratio (0.44 ± 0.11) was observed at the Rowantree Burn at Sourhope and this site was estimated to have the longest mean transit time of >3.5 years (Hrachowitz et al., in review), indicative of a generally drier catchment with highest groundwater contributions (Soulsby et al. 2006). The soils at Sourhope are typically freely draining with a slow hydrological response. This results in a non-linear response of discharge due to sparse and sporadic connectivity of the soils with the drainage network (Fig. 4).

Long-term trends in DOC concentration

The long-term increases in DOC concentration observed at Loch Ard and the Allt a'Mharcaidh study sites (0.15–0.79 mg C l^{-1} $year^{-1}$) are consistent with the data published elsewhere in these areas and across the UK (Harriman et al. 2001; Monteith et al. 2001; Worrall et al. 2004). However, the Sourhope study streams showed no increase in DOC concentrations between 1995 and 2006. It has been suggested that catchments showing no significant annual increase in DOC concentrations are buffered against environmental changes, which elsewhere seem to have been integral to increasing DOC concentrations in surface waters (Worrall et al. 2004). The Sourhope study sites are characterised by high alkalinities and base cation concentrations due to their soil and geological characteristics; increasing their ability to buffer against factors, such as atmospheric sulphate deposition, that have affected more acid sensitive areas of the UK uplands.

There is increasing evidence that the decrease in atmospheric sulphate deposition and recovery from acidification maybe the main drivers for increased solubilisation of organic matter leading to the observed long-term increases in DOC concentrations (Evans et al. 2006; Monteith et al. 2007; de Wit and Wright 2008). This phenomenon has not been evident in early time-series datasets until recently when sulphate and sea salt deposition began to decline sharply between 1990 and 2004 (Monteith et al. 2007). This recent rate of increase in DOC concentrations was evident in both Loch Ard and the Allt a'Mharcaidh time-series data (Table 2; Fig. 6), with increasing concentration trends and annual DOC concentration amplitudes observed in the latter years of the time series.

However, annual DOC concentrations over the time period of the Loch Ard study at Burn 11 increased significantly more than those at both Burns 2 and 10 (Table 2). In particular from 1997 onwards, the overall increase in annual mean and annual amplitudes of DOC concentrations were more evident at Burn 11. Assuming that atmospheric sulphate deposition declined at a similar rate in the Loch Ard catchments, (although the status of soils could vary), it is notable that the Burn 11 catchment was partially clear-felled in three phases from 1997 to 2000, whereas Burn 10 was partially clear-felled 10 years earlier (Tetzlaff et al. 2007b). Forestry, depending on the particular stage in its cycle, influences DOC concentrations in surface waters, with a tendency to increase following felling (Neal et al. 1998; Stott and Mount 2004; Dawson and Smith 2007). Thus, by the mid to late 1990s, it can be hypothesised that increased disturbance in Burn 11, due to felling, may have concomitantly accentuated the sulphate affect on DOC concentrations, during a period when sulphate deposition was concurrently declining more rapidly (Monteith et al. 2007). Moreover, 10 years earlier, sulphate suppression of DOC export may have been more effective, as relatively lower DOC concentration increases and no significant change in amplitude range were observed in the early part of the time series during the 1988–1990 felling years at Burn 10. Harriman et al. (2003) found that DOC trends in surface waters draining forests and moorlands were similar, and concluded that forest impacts on DOC export were relatively minor, as at Loch Ard between Burn 2 (moorland) and Burn 10 (forested). This might be the case except during certain periods when soil physico–chemical conditions are appropriate to accentuate disturbance of soil processes such as occurred at the Burn 11 catchment.

Thus, a combination of factors could influence observed DOC concentrations, suggesting some interaction of hypotheses for increasing DOC long-term trends. Potentially, there may be incidences when reduced sulphate deposition coinciding with other factors such as disturbance (erosion or management effects), higher summer temperatures or higher discharges may cause stochastic incidences of higher and more varied DOC concentrations, producing increased DOC concentration amplitudes, compared with the long-term record to date.

Seasonal DOC concentrations

Significant positive correlations between DOC and discharge have been found in many upland catchments (Tipping et al. 1988; Grieve 1994; Hope et al. 1997) but not always over an entire annual cycle (Dawson et al. 2002; Clark et al. 2007; Ågren et al. 2008). Relationships between DOC concentrations and discharge (Fig. 8) at both Allt a'Mharcaidh and Sourhope showed an annual pattern with both 'high' and 'low' periods of DOC concentration–discharge relationships. These relationships varied between seasons in a similar way every year at each site (e.g. Table 4 and Ågren et al. 2008). Following major high flows in the autumn, the catchments enter a dormant period associated with a reduction in biological processing of soil carbon. This lowers the mobile DOC pool available to be exported from the catchment (Brooks et al. 1999) and hence lowers DOC concentrations in the stream for a given discharge. This dormancy tends to begin (Table 4), on average, by early

November at both Sourhope sites but at the Allt a'Mharcaidh, it can be as late as the end of December as deeper snow packs may insulate soils, preventing freezing and maintaining higher organic matter decomposition rates (Groffman et al. 2001; Monson et al. 2006). The DOC concentration–discharge method (Fig. 8) in some years produced clearer relationships than others, possibly as a consequence of random sampling and other biogeochemical and hydrological variation at time of sampling (e.g. storm flow hysteresis as a sample taken on the descending limb following peak discharge or after large storms with potential overland flow or exhaustion of material producing a diluted DOC concentration for a given discharge).

At the Loch Ard study area, seasonal delineation occurs again similarly each year throughout the time series (Table 4) but the splitting into significantly high and low DOC concentrations was independent of discharge. At these sites, DOC concentrations that enter surface waters are primarily controlled by temperature changes with available carbon being exported continuously from the well-connected soils. The main seasonal effect of temperature is the control on plant rhizodeposition and soil biological activity on DOC production (Castelle and Galloway 1990; Brooks et al. 1999; Bonnett et al. 2006). As with the other two study areas, by winter, the summer/autumn 'store' of DOC has reduced and been exported (Scott et al. 1998).

The biological activity appears to rise at all three of the long-term study areas in late spring (May/June) with increasing DOC concentrations appearing in the surface waters, consistent with the temperature increases at this time of year. However, during this period of the annual cycle, some data points are clustered in the middle of the DOC concentration range and the date of switchover between high DOC concentrations starting and low DOC concentrations ending is open to interpretation, as there is a steady increase in DOC concentrations from early May through to June. Lower DOC concentrations during the relatively warm April period may be due to delayed increases in soil temperature, as well as internal carbon cycling. These trigger an increase in soil carbon processing but the DOC is not necessarily available for removal (Dawson et al. 2002). Moreover, in-stream community respiration will tend to be higher during the spring and summer months (Dawson et al. 2001a), leading to potentially lower surface water DOC concentrations at these times of year than the initial concentration exported from terrestrial sources. This may delay the seasonal delineation switchover during spring but has less of an impact by the early summer as higher DOC concentrations exported from terrestrial sources maintained the seasonally higher DOC concentrations in the surface waters.

Other parameters are also known to affect soil organic matter decomposition and production of DOC. Lumsdon et al. (2005) have described a model of DOC loss from organic-rich soils based upon solubility limitation. Soil organic matter is more hydrophilic in summer, possibly due to increased cleaving activity of heterotrophic microorganisms, increasing solubility of organic matter to DOC and hence availability for transport from the soil system. The organic matter tends to be more hydrophobic characteristically in winter, reducing its solubility and preventing higher losses of carbon as DOC (Scott et al. 1998; Lumsdon et al. 2005; Sharp et al. 2006). In an attempt to model the DOC cycle at another Scottish catchment, it was shown that the linkage of hydrophobicity/hydrophilicity and charge characteristics to the annual temperature cycle (as a surrogate for biological activity in the catchment) was strong (Lumsdon et al. 2005). Thus, this temperature related solubility also corresponds with the observed seasonal delineation in terms of the timing of DOC production at the three areas in this study.

There appears to be at least two types of mechanism controlling the terrestrially derived surface water DOC concentrations across upland Scotland. Both mechanisms have similar high and low DOC production periods based on temperature-dependent (seasonal) decomposition of organic matter but have two distinct modes of action in terms of export mechanisms. This difference in export of the available DOC is ultimately due to the hydrological characteristics of the sites, which are also dependent on seasonal climatic variations. These different mechanisms are evident when the DOC concentrations are split seasonally (Fig. 9).

In wetter catchments, Burns 2, 10 and 11 at Loch Ard, a consistent temperature-dependent significant seasonal separation in mean DOC concentration across each time series is observed, which produces annual cycle of DOC concentrations i.e. DOC

Table 4 Seasonal delineation of high DOC concentrations in surface waters at the six long-term study sites

Year	Allt a'Mharcaidh	Loch Ard, Burn 2	Loch Ard, Burn 10	Loch Ard, Burn 11	Sourhope, Alderhope Burn	Sourhope, Rowantree Burn
1987	1st Jun–16th Nov	–	–	–	–	–
1988	13th Jun–27th Dec	–	1st Jun–2nd Nov	1st Jun–2nd Nov	–	–
1989	25th May–13th Nov	6th Jun–15th Nov	31st May–28th Nov	31st May–28th Nov	–	–
1990	4th Jun–3rd Dec	13th Jun–21st Nov	13th Jun–21st Nov	13th Jun–21st Nov	–	–
1991	3rd Jun–31st Oct	22nd May–6th Nov	15th May–13th Nov	15th May–13th Nov	–	–
1992	22nd Jun–29th Oct	27th May–28th Oct	13th May–4th Nov	27th May–4th Nov	–	–
1993	10th Jun–20th Dec	28th Apr–17th Nov	28th Apr–17th Nov	28th Apr–17th Nov	–	–
1994	27th Jun–5th Dec	4th May–30th Nov	11th May–14th Dec	11th May–21st Dec	–	–
1995	15th May–20th Nov	19th Apr–19th Dec	12th Apr–19th Dec	12th Apr–19th Dec	24th May–8th Nov	24th May–8th Nov
1996	29th Apr–28th Oct	22nd May–30th Oct	29th May–7th Nov	15th May–7th Nov	26th Jun–27th Nov	19th Jun–27th Nov
1997	5th May–17th Nov	14th May–12th Nov	25th Jun–9th Dec	25th Jun–9th Dec	7th May–26th Nov	7th May–26th Nov
1998	1st Jun–5th Nov	13th May–28th Oct	24th Jun–28th Oct	13th May–28th Oct	27th May–28th Oct	13th May–28th Oct
1999	24th May–29th Nov	12th May–27th Oct	12th May–27th Oct	12th May–27th Oct	12th May–20th Oct	12th May–17th Nov
2000	22nd May–13th Nov	7th Jun–22nd Nov	10th May–6th Dec	10th May–6th Dec	10th May–1st Nov	10th May–1st Nov
2001	4th Jun–27th Nov	6th Jun–24th Oct	9th May–21st Nov	9th May–21st Nov	23rd May–28th Nov	23rd May–28th Nov
2002	21st May–19th Nov	23rd May–23rd Oct	5th Jun–23rd Oct	23rd May–5th Nov	1st May–17th Oct	1st May–17th Oct
2003	–	–	21st May–22nd Oct	23rd Apr–19th Dec	30th Apr–26th Nov	30th Apr–26th Nov
2004	–	–	–	–	19th May–27th Oct	19th May–27th Oct
2005	–	–	–	–	1st Jun–26th Oct	1st Jun–26th Oct
2006	–	–	–	–	17th May–25th Oct	17th May–25th Oct

Remainder of the year, DOC concentrations are categorised as low DOC concentrations

concentrations are production controlled. Burn 2 showed the most distinct separation, which collated with the highest annual periodicity of DOC concentrations (Fig. 7) throughout the time series. Although Burns 10 and 11 had relatively similar responses, the mean concentrations were consistently significantly higher in the summer/autumn category compared with winter/spring, enabling annual periodicity of DOC concentrations to explain >45% of the variance.

At the Allt a'Mharcaidh and Sourhope sites, the combined discharge and temperature controls in DOC export, lead to low and high DOC concentrations throughout the year, producing in the main similar average seasonal DOC concentrations and loss of any seasonal delineation and annual periodicity of DOC concentrations throughout the time series. However, highest DOC concentrations occurred during the period of summer/autumn, particularly at the Allt a'Mharcaidh (Grieve 1990; Scott et al. 1998; Dawson et al. 2002; Tipping et al. 2007), evidenced by DOC concentration outliers at times of higher discharge, i.e. DOC concentrations at these sites are export limited.

Linkage of DOC production and export

Concentration–discharge relationships are not as apparent at the three Loch Ard study sites and temperature-regulated soil organic matter decomposition appears to be the main controlling parameter in determining the surface water DOC concentrations, although in-stream abiotic and microbial processes will act as a secondary controls on the terrestrially exported DOC (Dawson et al. 2001a). There is no distinct autumnal flush at Loch Ard; just a continual production and relatively rapid export. This is explained by the higher precipitation evident throughout the summer/autumn months (Fig. 3) compared to the other two study areas, preventing soil moisture deficits and permits continuous removal of DOC in runoff, i.e. connectivity of the surface waters with the soil system is maintained throughout most of the year. These results do not imply that the long-term increasing trend in DOC export is explicable by temperature increase but suggest that seasonal temperature fluctuations may be a key factor regulating the variation in intra-annual DOC concentrations and an important component of long-term models for determining DOC exports (Bonnett et al. 2006).

At the Allt a'Mharcaidh and Sourhope study areas, more DOC is exported with increasing discharge, as previously drier areas of the soil become connected to the drainage network delivering further carbon to the stream. Thus, DOC concentrations often increase with increasing discharge as new sources in upper organic horizons become increasingly important as the water table rises (Grieve 1990). Although the rate of production of DOC in the soil is greatest during the warmer summer months, the maximum export of DOC occurs in the early and late autumn. Soil moisture deficits occur in summer at these catchments, and rainfall initially recharges the deficit, resulting in lower discharge but with relatively high DOC concentrations compared to similar discharges in winter (Scott et al. 1998). The parameters that determine the release of high DOC in autumn high flow events are influenced by event magnitude, the length of time since the soil profile was last flushed, and rewetting of the upper organic horizons (Cooper et al. 2007). These factors affecting DOC export are intrinsically linked with moisture-dependent biological activity (Castelle and Galloway 1990; Cooper et al. 2007). Therefore, the DOC remains stored in the soil system (or further mineralised to CO_2) until it is flushed from the soil. The timing of this depends on precipitation patterns from year to year. At Sourhope, the driest study area, these high DOC events occur intermittently due to the non-linear nature of the discharge response and sporadic connectivity of its upper soil horizons with the drainage network.

At both the Allt a'Mharcaidh and Sourhope study areas, the late autumn higher flows represent the switchover time after which subsequent production of DOC is limited. However, September/early October high flows, did not cause a switchover to low DOC concentrations. The temperature in early autumn was either still sufficient for soil biological activity to produce further high DOC concentrations for export; soils were still recovering from their summer moisture deficits or the high flow was not of sufficient intensity to completely 'flush' the mobile DOC from the soils.

High DOC concentration periods at the height of summer (July/August), indicated that DOC concentration–temperature relationships also occurred irrespective of discharge at these sites, increasing variation of the high DOC concentration–discharge relationship. These seasonal and hydrological variations are important for determining accurate concentration–discharge relationships to calculate carbon losses from soils to surface waters (Walling 1977; Dawson et al. 2002).

Conclusions

Both climate and land-use changes are key to understanding future terrestrial carbon pools and fluxes (Dawson and Smith 2007). Climate (i.e. temperature and precipitation), interaction with soil processes, production of DOC and export are all important in understanding hydrologically mediated carbon exports from soils for estimating loss of soil carbon and modelling of carbon concentrations and fluxes in surface waters. This paper shows the importance of how climatic variables can interact in a contrasting manner at different upland sites within Scotland.

There is a strong link between seasonal and catchment specific hydrological patterns controlling DOC export. The data indicate that different seasonal patterns of DOC concentration occur at climatologically varied sites across Scotland. Moreover, these seasonal changes in DOC are temporally consistent over the longer-term at individual sites. Although DOC processes controlling production may be similar, the timing and extent of DOC export contrasts sharply, depending on how precipitation patterns and quantities and catchment soil types control responsiveness and hydrological connectivity in different sites across Scotland.

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