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The relationship between dissolved organic carbon in stream water and soil organic carbon pools at different spatial scales

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Abstract:

The relationship between stream water DOC concentrations and soil organic C pools was investigated at a range of spatial scales in subcatchments of the River Dee system in north-east Scotland. Catchment percentage peat cover and soil C pools, calculated using local, national and international soils databases, were related to mean DOC concentrations in streams draining small- (<5 km^2), medium- (12–38 km^2) and large-scale (56–150 km^2) catchments. The results show that, whilst soil C pool is a good predictor of stream water DOC concentration at all three scales, the strongest relationships were found in the small-scale catchments. In addition, in both the small- and large-scale catchments, percentage peat cover was as a good predictor of stream water DOC concentration as catchment soil C pool. The data also showed that, for a given soil C pool, streams draining lowland (<700 m) catchments had higher DOC concentrations than those draining upland (>700 m) catchments, suggesting that disturbance and land use may have a small effect on DOC concentration. Our results therefore suggest that the relationship between stream water DOC concentration and catchment soil C pools exists at a range of spatial scales and this relationship appears to be sufficiently robust to be used to predict the effects of changes in catchment soil C storage on stream water DOC concentration. Copyright © 1999 John Wiley & Sons, Ltd.

KEY WORDS dissolved organic carbon (DOC); soil carbon; spatial scaling

INTRODUCTION

Dissolved organic carbon is a key source of energy in stream ecosystems (Wetzel, 1992) and has an important role in a number of chemical processes within streams, including complexation and mobilization of metals (Perdue *et al.*, 1976; Helmer *et al.*, 1990). Globally, the riverine flux of organic carbon is estimated to be between 1 and 10×10^{11} kg C yr^{-1} (Hope *et al.*, 1994). Whilst this is 1–2 orders of magnitude smaller than the annual exchange between vegetation–atmosphere–oceans (Dixon and Turner, 1991), it is a unidirectional flux which, in some catchments, is similar to the rate at which soils sequester carbon (Hope *et al.*, 1997a). The riverine flux of organic carbon may therefore act as a means of regulating changes in soil carbon pools brought about by climate change.

Of the numerous studies to examine the controls on stream water dissolved organic carbon (DOC) concentrations and fluxes, most have been carried out on small catchments. These have shown that DOC is influenced by catchment physiography, precipitation, vegetation and wetland cover (Eckhardt and Moore, 1990; Dalva and Moore, 1991; Clair *et al.*, 1994; Guyot and Wasson, 1994). Seasonality is associated with summer maxima in stream water DOC concentrations in some, but not all, UK upland catchments (Grieve,

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1984; Tipping *et al.*, 1988). Models of riverine organic carbon concentrations and fluxes based upon variables such as river discharge, precipitation, catchment size and slope, rarely explain more than 50% of the observed variation (Eckhardt and Moore, 1990; Clair *et al.*, 1994; Grieve, 1994). Stream water DOC concentrations are also likely to be determined by a number of factors within the soil environment, including the rate of DOC production in organic soils, adsorption of DOC in mineral soils, and the flow path of water through different soil horizons (McDowell and Wood, 1984; Cronan and Aiken, 1985; McDowell and Likens, 1988; Kennedy *et al.*, 1996). A number of studies have shown that stream water DOC concentration is related to the amount of wetland present (Mulholland and Keunzler, 1979; Mulholland, 1981; Schlesinger and Melack, 1981; Kerekes *et al.*, 1986; Freedman and Clair, 1987; Eckhardt and Moore, 1990). Land-use may also influence stream water DOC concentrations (Likens *et al.*, 1977; Swank, 1986; Grieve, 1990; Soulsby and Reynolds, 1995; Burns, 1996).

In Britain, recent work has indicated that soils are the most useful catchment characteristic in explaining variations in DOC fluxes between streams. In small upland headwater catchments, peatland cover was found to be the single most important predictor of variations in annual DOC exports between streams (Hope *et al.*, 1997b). At larger scales, riverine DOC fluxes also appear to reflect strongly the size of the soil organic carbon pool in the catchment. Within a single river system, the River Dee in NE Scotland, successively larger subcatchments showed a concomitant decrease in DOC flux and soil carbon storage, suggesting that soil organic carbon pool size may influence riverine DOC fluxes across a range of spatial scales (Hope *et al.*, 1996). Differences in soil organic carbon storage were found to explain 91% of the variance in annual stream water DOC fluxes between 17 British rivers with catchments ranging in size from 73 to 1844 km^2 (Hope *et al.*, 1997a).

In a previous study of a similar set of catchments (Hope 1995; Hope *et al.*, 1997b) relationships between a number of catchment variables and riverine carbon fluxes were investigated. Although many catchment variables were co-correlated, slope, peat cover and soil carbon content were important in controlling riverine carbon flux. The aim of this study was to investigate the extent to which these three key variables could be used to predict DOC concentrations in streams draining catchments ranging in size from 0·5 to 150 km^2. The results have implications in terms of our understanding of the processes that control stream water DOC concentrations at a range of spatial scales.

RESEARCH SITES

This study is based in 32 subcatchments of the River Dee in NE Scotland. These were classified according to size and consisted of 12 'small-scale' (<5 km^2), 9 'medium-scale' (12–38 km^2) and 11 'large-scale' (56–50 km^2) catchments (Table I). The catchments were selected to represent the range of soil types found in the River Dee catchment (Table II). These soils can be divided into three broad groups according to altitude: (i) above 600 m peat is dominant in poorly drained areas with alpine and subalpine soils occurring on freely drained slopes; (ii) below 600 m peaty and humus iron podzol soils predominate; and (iii) in the valley bottoms peaty and non-calcareous gleys, brown forest soils and alluvium are present (Glentworth and Muir, 1963; MISR, 1982). Since vegetation is dominantly heather moorland in the upper Dee Valley, with forestry and agriculture becoming more important in the lower Dee Valley (Langan *et al.*, 1997), the catchments were further subdivided into upland and lowland categories, defined as those with a maximum altitude >700 and <700 m, respectively. The climate of the region is cool temperate with an annual mean temperature of 8 °C and an average rainfall varying from 810 mm at the mouth of the Dee to 2100 mm at its source in the Cairngorm Mountains (Warren, 1985).

METHODS

Stream sampling and analysis

Stream water samples were collected on a weekly basis from each of the study catchments for a period of 12 weeks between 4 May and 20 July 1996. Samples were collected in 250 ml prewashed Perspex bottles by

Table I. Physical characteristics of the study catchments

Scale	Catchment name	National Grid Reference	Catchment area (km^2)	Average slope (°)	Elevation range (m)	% forest cover
Small	Newbiggin	NO146850	0·52	42·51	410–834	0
	Stag Burn 2	NO643814	0·78	10·52	380–507	0
	Lamahip Burn	NO555910	1·25	19·23	160–465	0
	Coire Allt à Chlair	NO119897	1·81	30·08	400–859	6
	Stag Burn 1	NO642815	1·92	8·42	380–525	0
	Choire ant-Slugain	NJ300015	2·38	15·57	360–744	0
	Srôn Dubh	NO289955	2·50	19·37	240–650	13
	Allt À Mhaide	NO148134	2·90	20·21	420–834	0
	Fashcilach	NO315871	3·81	11·65	390–721	0
	Allt Glas-choillie	NJ313027	3·94	16·12	330–744	0
	Aultonrea	NO353924	4·71	12·72	280–686	5
	Crathie Burn	NO255965	4·82	11·13	370–700	7
Medium	Pollagach Burn	NO425963	12·63	11·48	180–669	8
	Lary Burn	NO339997	14·43	7·69	330–780	4
	Burn of Cattie	NO582955	14·63	6·55	120–525	34
	Burn of Knock	NO691920	15·75	7·36	90–534	25
	Tullich Burn	NO387972	16·25	9·87	200–871	6
	Baddoch Burn	NO136832	22·25	9·60	430–975	0
	Feardar Burn	NO225937	22·81	7·52	280–900	22
	Girnock Burn	NO322957	29·63	6·08	240–862	3
	Callater Burn	NO156882	38·06	7·99	360–1064	0
Large	Clunie Water	NO153879	55·94	6·24	390–1068	0
	Quoich Water	NO116913	56·25	7·92	350–1177	12
	Lui Water	NO067899	59·93	7·27	379–1309	10
	Ey Burn	NO086891	61·87	5·79	380–1045	2
	Tarland Burn	NO511025	66·81	3·37	120–619	34
	Burn of Canny	NO653971	74·35	2·99	90–480	19
	Water of Dye	NO661909	86·25	3·65	120–778	17
	Water of Tanar	NO503971	89·68	4·44	140–939	34
	Water of Feugh	NO640924	95·81	4·14	90–778	8
	River Muick	NO349929	125·24	6·62	260–1155	9
	Linn of Dee	NO061897	150·25	4·11	420–1309	1

dip sampling. Stream water samples were filtered through precombusted (500 °C for 5 hours) Whatman GF/F 0·7 μm filter papers within 24 hours of collection (Wetzel and Likens, 1991). A vacuum differential not exceeding 0·3 atm was applied to the apparatus during filtration. A LABTOC carbon analyser (Pollution and Process Monitoring Ltd) was used to determine the concentration of DOC in stream water samples: this involves wet chemical oxidation of the sample with a mixture of sodium persulfate and orthophosphoric acid. A comparison in our laboratory of wet oxidation with high temperature oxidation using a TOCSIN II aqueous carbon analyser (Phase Separations), showed that at DOC concentrations <25 mg l^{-1} the LABTOC produced values that were *c.* 10% higher than those determined on the TOCSIN II. This suggests that the determination of refractory DOC by wet chemical oxidation is not a problem at these concentrations. The LABTOC carbon analyser has a reproducibility of ±2% and a detection limit of 0·3 mg l^{-1}; calibration was carried out using potassium hydrogen phthalate as a standard.

Comparison of our data with those collected from three of the same sites sampled in a previous study between 1987 and 1989, show that the 12-week mean stream water DOC concentrations were not significantly different from the annual mean DOC concentrations (Table III). However, comparison of data from another study in 1992–1993 showed that mean DOC concentrations during the 12-week summer period were slightly lower than annual means at 4 of the 6 sites (Hope *et al.*, 1997b). In this latter study, flow over the

Table II. Percentage distribution of soil types in the study catchments

Scale	Catchment name	Peaty podzol	Peat	Brown forest soil	Humus iron podzol	Upland soils*	Other†
Small	Newbiggin	38·0	—	31·4	—	30·6	—
	Stag Burn 2	7·0	93·0	—	—	—	—
	Lamahip Burn	17·3	—	—	54·6	14·8	13·3^{b}
	Coire Allt a Chlair	18·0	—	7·1	17·3	57·6	—
	Stag Burn 1	—	100·0	—	—	—	—
	Choire ant-Slugain	34·1	8·3	—	17·0	14·4	26·2^{a}
	Srôn Dubh	31·6	11·1	16·3	3·4	9·4	28·2^{a}
	Allt À Mhaide	4·1	2·4	—	—	93·5	
	Fasheilach	61·0	39·0	—	—	—	—
	Allt Glas-choillie	15·0	50·9	—	14·2	4·6	15·3^{b}
	Aultonrea	28·9	—	15·6	11·1	13·7	30·7^{a}
	Crathie Burn	50·4	38·1	—	—	11·5	—
Medium	Pollagach Burn	39·6	11·4	22·7	19·7	6·6	—
	Lary Burn	6·1	25·8	1·8	31·4	8·1	26·8^{a,b}
	Burn of Cattie	14·2	1·6	5·0	59·6	13·1	6·5^{b,c}
	Burn of Knock	26·3	14·6	—	33·3	5·0	20·8^{b,c}
	Tullich Burn	4·7	12·2	16·9	31·6	11·9	22·7^{a,b}
	Baddoch Burn	1·6	35·7	3·6	9·0	50·1	—
Large	Feardar Burn	11·7	1·1	15·8	25·9	42·2	3·3^{a}
	Girnock Burn	32·6	8·9	16·0	11·1	10·3	21·1^{a}
	Callater Burn	15·4	3·4	—	12·2	58·9	10·10^{b,c}
	Clunie Water	12·1	23·8	3·4	8·7	49·8	2·2^{a,c}
	Quoich Water	21·9	—	—	3·3	74·8	—
	Lui Water	13·3	0·5	—	6·0	76·3	3·9^{a,c}
	Ey Burn	11·5	13·4	0·5	11·7	61·2	1·7^{b}
	Tarland Burn	5·8	0·5	33·6	46·9	—	13·2^{b,c}
	Burn of Canny	6·1	3·4	6·9	66·9	—	17·7^{a,b,c}
	Water of Dye	25·0	48·1	0·1	15·5	35·0	7·8^{a,b,c}
	Water of Tanar	30·4	13·6	2·9	13·1	25·2	14·8^{a,b,c}
	Water of Feugh	19·4	29·3	2·9	31·0	9·6	7·8^{a,b,c}
	River Muick	25·9	21·7	9·3	6·0	27·7	9·4^{a,c}
	Linn of Dee	24·5	12·4	—	0·9	60·4	1·8^{b,c}

* Upland soils include alpine soil, subalpine soil and rankers.
† Other soils, (a) peaty gley, (b) non-calcareous gley and (c) alluvial soils.

summer months was low, in marked contrast to the remainder of the year, which was characterized by numerous high flow events. Since DOC concentrations increase markedly with increasing flow in all these streams (Hope, 1995), our results include a greater number of samples collected at higher flows. In a study of similar catchments on the River Dee, the inclusion of samples taken during all flow conditions with those taken at low flows was found to increase the amount of unexplained variance and decrease the significance of the correlation slightly, but did not significantly alter the main findings (Hope *et al.*, 1997b). It was assumed, based on these results, that a 12-week study of the relationship between mean stream water DOC concentration and a number of independent variables would reflect the findings of a one-year study, especially if the summer sampling period included some samples collected during storm flow conditions. Since all 32 sites were sampled on the same day each week under similar flow conditions, it was therefore assumed that the mean stream water DOC concentrations presented in this study reflect consistent differences between sites, and are likely to be broadly similar to patterns in annual mean DOC concentrations across these sites.

Table III. Comparison of 12-week and annual mean stream water DOC concentrations. Mean values for the present study are also shown

Catchment name	Catchment size (km^2)	Billett[1] Billett and Cresser[2]		Hope[3] Hope *et al.*[4]	This study
		1987 1988	1988 1989	1992 1993	
Allt À Mhaide	2·90	1·75 (1·3)	2·15 (2·3)	1·90 (0·9)*	2·31
Girnock Burn	29·63	–		3·98 (3·2)	3·41
Tullich Burn	16·25	2·60 (2·6)	2·82 (3·2)	2·88 (2·2)	2·52
Baddoch Burn	22·25	2·09 (1·6)	2·60 (2·7)	2·24 (1·2)*	3·95
Water of Tanar	89·68			2·62 (1·9)*	3·23
Quoich Water	56·25	–		1·04 (0·5)*	0·76

Values in parentheses indicate 12-week mean DOC concentrations from the beginning of May until the end of July

* Significant difference between the 12-week and annual mean stream water DOC concentration (unpaired *t*-test, $p < 0.05$).

[1] Billett (unpublished results).

[2] Billett and Cresser (1992).

[3] Hope (unpublished results).

[4] Hope *et al.* (1997b).

Soil distribution

Each catchment was delineated on 1 : 50 000 topographic maps and the distribution of soils superimposed from the appropriate soil maps (MISR, 1982). The aerial extent (km^2) and percentage cover for each soil type was then determined for individual catchments. Prior to analysis, the data for percentage peat cover (Table II) were normalized using the following arcsine transformation (Fowler and Cohen, 1990)

$$\sin^{-1}\sqrt{\%\text{peat cover}} \tag{1}$$

Soil carbon content

Three separate estimates of the carbon content of individual soil types were made using data from different sources. These were: (i) local reference material including data from unpublished studies carried out at Aberdeen University; (ii) a national database compiled for the UK Department of the Environment (Howard *et al.*, 1995; Milne and Brown, 1997); and (iii) published information on the organic carbon content of world soil types derived from the World Inventory of Soil Emission Potentials Database (Batjes, 1996). These three sources of soil carbon data will be henceforth referred to as the AU, DoE and WISE databases, respectively.

In the AU database, soil depths and percentage organic carbon content for each of the mapped soil types in the catchments (Table II) were derived from studies by Sanger (1993), Rattray (personal communication) and Glentworth and Muir (1963). Additional information on dry bulk density for specific soil types was obtained from Avery (1990). The soil carbon content of each horizon in the various soil types was then estimated from the mean depth, mean dry bulk density and mean percentage carbon content using the following equation:

$$\text{Soil carbon content (kt C km}^{-2}) = (D \times \gamma_d \times C) \times 10 \tag{2}$$

where D = average depth of the soil horizon (cm), γ_d = average dry bulk density of soil ($g\ cm^{-3}$) and C = average % carbon content.

Values for each horizon were summed to produce an estimate of the organic carbon content of each soil type (Table IV), each estimate being then multiplied by the area covered by that soil type in the catchment. Values for individual soil types were then summed to give an estimate of the total soil organic carbon pool in

Table IV. A comparison of carbon contents of soils based on the Scottish classification system (MISR, 1984) and the FAO/UNESCO system (FAO/UNESCO, 1974). These values were used to estimate the catchment carbon content from the AU and WISE databases, respectively

Scottish soil classification system				FAO/UNESCO soil classification system			
Soil type	Depth (cm)	*n*	Carbon content (kt C km^2)	Soil type	Depth (cm)	*n*	Carbon content (kt C km^2)
Sub-alpine	13·5	3	5·7	Leptic podzol	30	10	12·8
Alpine	23·6	3	9·2	Leptic podzol	30	10	12·8
Brown forest	55·4	5	14·1	Dystric cambisol	100	59	12·5
Humus iron podzol	22·9	6	8·1	Placic podzol	100	3	22·4
Alluvium	97·5	2	18·7	Eutric fluvisol	200	7	16·7
Non-calcareous gley	66·7	5	9·3	Eutric gleysol	100	54	9·7
Ranker	26·3	4	21·7	Ranker	30	6	15·9
Peaty podzol	40·0	3	27·0	Humic podzol	200	4	43·0
Peaty gley	57·0	5	53·7	Humic gleysol	200	2	86·6
Peat	200	5	139·7	Dystric histosol	200	1	123·0

each catchment. This figure was divided by the catchment area and expressed as a mean soil carbon content, in kt C km^2, for each study catchment.

Estimates of soil carbon content contained in the national DoE database were based on the dominant soil type in 1 km × 1 km national grid squares (Howard *et al.*, 1995; Milne and Brown 1997). The boundaries of each study catchment were first delineated using national grid reference co-ordinates at a resolution of 1 km^2; these co-ordinates were then used to extract a value for soil carbon content for every km^2 of each catchment from the DoE database. The frequency distribution of soil carbon data from the grid squares was normal for most of the study catchments, so the mean value was used to represent the soil organic carbon content, again expressed in kt C km^2.

As the WISE database is based on the FAO/UNESCO system of soil classification (FAO/UNESCO, 1974; FAO-ISRIC, 1990), soil types in the study catchments were also classified according to the FAO/UNESCO system (Table IV). Values for the organic carbon content of each soil type (Batjes, 1996) were then used with information on the areas they covered in the study catchments to estimate total soil carbon content in the catchment, as described for the estimates based on the AU database.

Slope

The average slope for each catchment was determined using an equation adapted from Eckhardt and Moore (1990)

$$\text{Slope (degrees)} = \tan^{-1}[(\Delta\text{altitude}/\surd\text{area}/\pi)/1000] \qquad (3)$$

where Δaltitude is the mean difference in elevation between the sample point and a number of points around the watershed boundary.

Analysis and modelling of stream water DOC concentration

Mean stream water DOC concentrations over the 12-week sampling period were calculated for each sampling site in the present study. The relationships between mean stream water DOC concentration, catchment slope, peat cover and soil carbon content were initially examined using linear regression of the data from 27 of the 32 catchments. The catchments used in this 'all-scales' subset were selected to (i) be independent, i.e. a catchment did not fall downstream of another sample site, and (ii) give an equal number of catchments ($n = 9$) in each size range. Linear regression analyses were subsequently carried out on the data for the small-, medium- and large-scale catchments.

RESULTS

All catchment scales

There were strongly significant positive linear relationships between mean stream water DOC concentration and peat cover ($r^2 = 0{\cdot}83$, $p < 0{\cdot}0001$), AU soil carbon content ($r^2 = 0{\cdot}84$, $p < 0{\cdot}0001$) and WISE soil carbon content ($r^2 = 0{\cdot}83$, $p < 0{\cdot}0001$) for the 27-catchment independent subset containing catchments of all sizes. However, there was no relationship between mean stream water DOC concentration and DoE soil carbon content or catchment slope. In general lowland catchments tended to plot either on or above the regression line, whilst upland catchments mostly fell below the line (Figure 1).

Small-scale catchments

Mean stream water DOC concentration ranged from 1·2 (±0·2) to 10·6 (±1·7) mg l^{-1} (values in parentheses indicate standard error of the mean) and showed a significant positive linear relationship with peat cover ($r^2 = 0{\cdot}86$, $p < 0{\cdot}0001$) and catchment carbon content based on both the AU database ($r^2 = 0{\cdot}88$, $p < 0{\cdot}0001$) and the WISE database ($r^2 = 0{\cdot}85$, $p < 0{\cdot}0001$). In each case, mean stream water DOC concentrations from upland catchments tended to fall below the regression lines (Figure 2). As with the 'all-scales' catchment data, there was no significant relationship between DOC concentration and catchment carbon content estimated using the DoE database. There was, however, a weak inverse relationship between mean stream water DOC concentration and catchment slope ($r^2 = -0{\cdot}40$, $p < 0{\cdot}05$).

Medium-scale catchments

Mean stream water DOC concentration ranged from 1·8 (±0·2) to 4·0 (1·9) mg l^{-1}. Peat cover showed no significant relationship with mean stream water DOC concentration, whilst the relationship with AU and WISE soil carbon content was less significant ($r^2 = 0{\cdot}46$, $p < 0{\cdot}05$ and $r^2 = 0{\cdot}50$, $p < 0{\cdot}05$, respectively) (Figure 3). There was no significant relationship between mean stream water DOC concentration and DoE soil carbon content or catchment slope. There was also no clear distinction between upland and lowland catchments at this scale, although there were only three lowland catchments in this group.

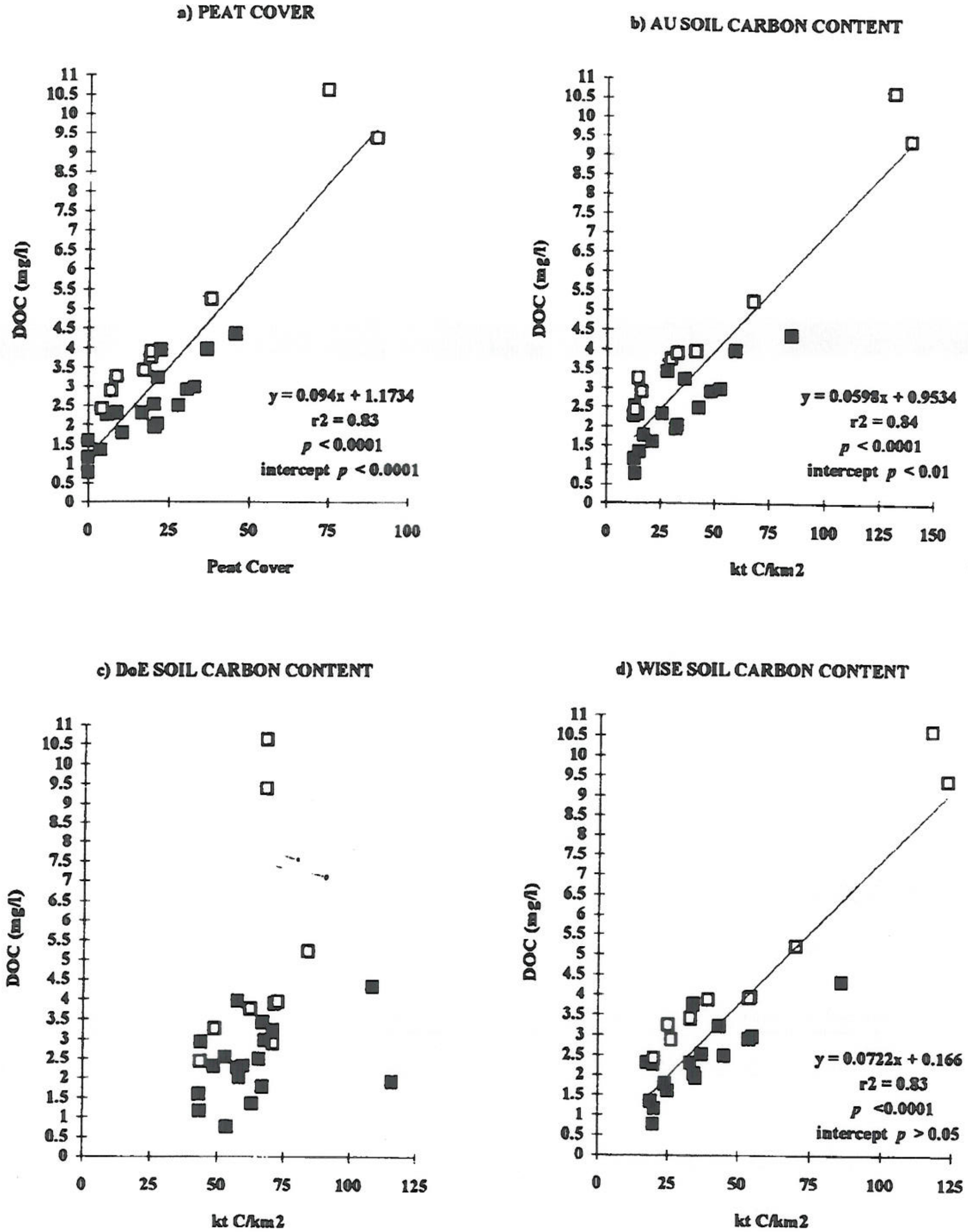
Large-scale catchments

Mean stream water DOC concentration ranged from 0·8 (±0·1) to 5·3 (±1·2) mg l^{-1} and showed a positive linear relationship with peat cover ($r^2 = 0{\cdot}55$, $p < 0{\cdot}01$), AU soil carbon content ($r^2 = 0{\cdot}58$, $p < 0{\cdot}01$) and WISE soil carbon content ($r^2 = 0{\cdot}66$, $p < 0{\cdot}01$), and an inverse linear relationship between mean stream water DOC concentration and catchment slope ($r^2 = -0{\cdot}45$, $p < 0{\cdot}05$). There was no significant relationship between mean stream water DOC concentration and DoE soil carbon content. Although only two of the large-scale catchments were classified in the lowland category, both plotted above the regression line (Figure 4).

DISCUSSION

Relationship between catchment soils and stream water DOC concentration

The positive linear relationship found between peat cover and stream water DOC concentrations in this study is similar to that found for annual DOC exports in a previous study of headwater streams in the River Dee system (Hope *et al*., 1997b). It also agrees with the correlation found between wetland cover and stream water DOC concentration in temperate and boreal catchments (e.g. Eckhardt and Moore, 1990). The proportion of the variation in DOC concentration explained by peat cover across all catchments scales ($r^2 = 0{\cdot}83$) was higher than reported in previous studies, this being largely due to the high degree of variance


a) PEAT COVER

b) AU SOIL CARBON CONTENT

c) DoE SOIL CARBON CONTENT

d) WISE SOIL CARBON CONTENT

Figure 1. The relationship between mean stream water DOC concentration and (a) peat cover, (b) AU soil carbon content, (c) DoE soil carbon content and (d) WISE soil carbon content at all catchment scales. Filled squares indicate upland (maximum altitude > 700 m) and unfilled squares lowland (maximum altitude < 700 m) catchments

explained for small (< 5 km^2) catchments ($r^2 = 0.86$), compared with the medium- and large-scale catchments ($r^2 = 0.14$ and 0.55, respectively). The greater proportion of unexplained variation in catchments larger than 5 km^2 is likely to reflect the decrease in the relative importance of peat soils, along with the presence of additional variables, such as land use, which become more important as the catchment size increases.

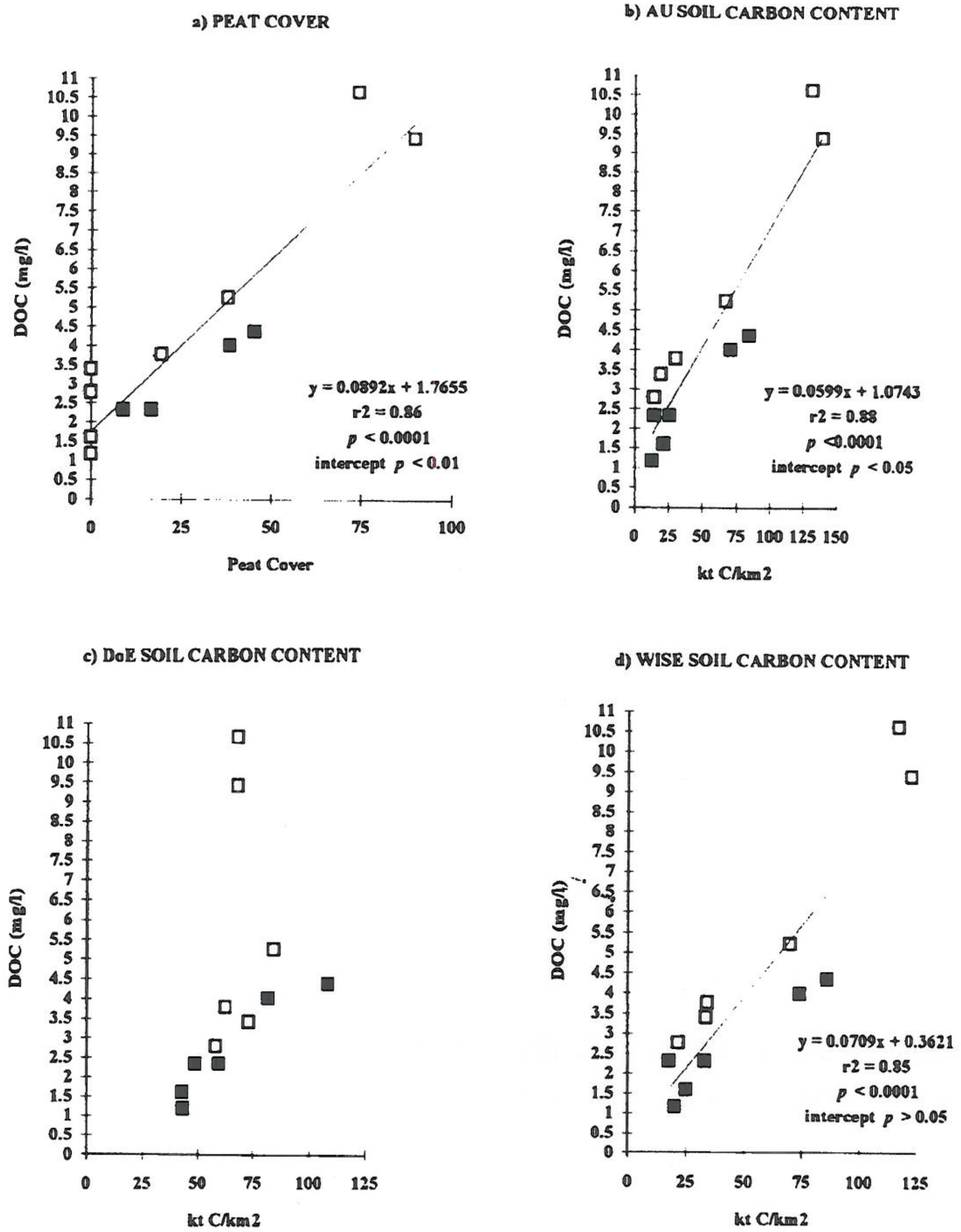


Figure 2. The relationship between mean stream water DOC concentration and (a) peat cover, (b) AU soil carbon content, (c) DoE soil carbon content and (d) WISE soil carbon content in small-scale catchments. Filled squares indicate upland (maximum altitude > 700 m) and unfilled squares lowland (maximum altitude < 700 m) catchments

The inclusion of cover data for other soil types in multiple regression analysis failed to improve the amount of variance explained by the relationship with peat cover alone, indicating that the large pool of organic carbon constituted by peat soils is the dominant factor determining the concentrations of stream water DOC draining from catchments in upland Britain. Nevertheless, while peatlands account for the largest single organic carbon pool in British catchments (Howard *et al.*, 1995; Milne and Brown, 1997), many

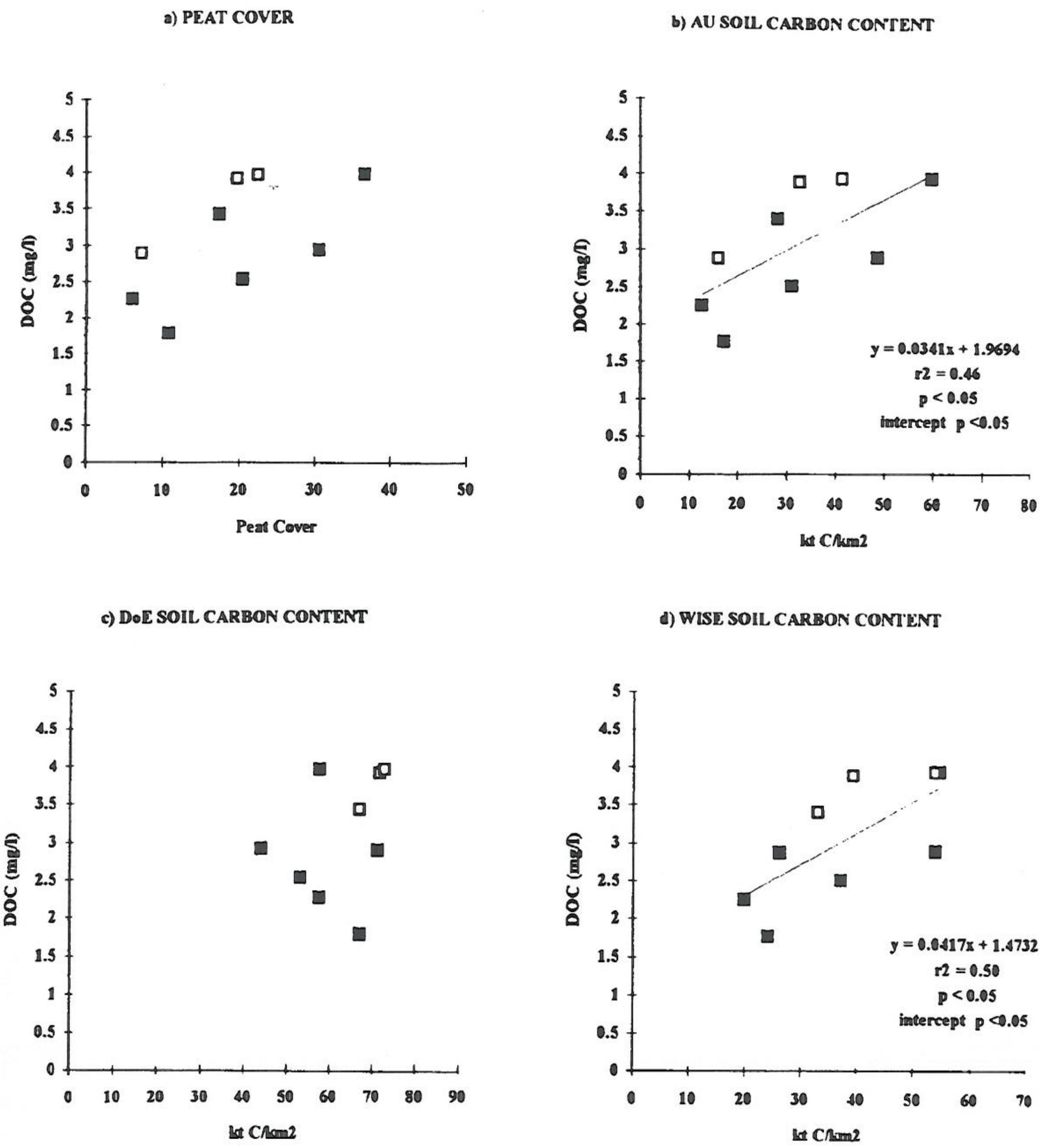


Figure 3. The relationship between mean stream water DOC concentration and (a) peat cover, (b) AU soil carbon content, (c) DoE soil carbon content and (d) WISE soil carbon content in medium-scale catchments. Filled squares indicate upland (maximum altitude > 700 m) and unfilled squares lowland (maximum altitude < 700 m) catchments

other soil types also contain significant amounts of organic matter (Table IV). Therefore, the estimates of the soil organic carbon pool made using the AU, DoE and WISE databases might be expected to be more strongly correlated with stream water DOC concentrations than with peatland cover alone, particularly in the medium- and large-scale catchments, where other soil types are much more extensive. This was indeed true for the AU and WISE soil organic pool estimates, which improved the amount of variance explained by between 3 and 50%, the most significant improvement occurring in the medium-scale catchments (Figure 3).

The DoE soil organic carbon pool estimates failed to show a significant correlation with mean stream water DOC at any scale. Given that the DoE data estimates were made using only a single value for each

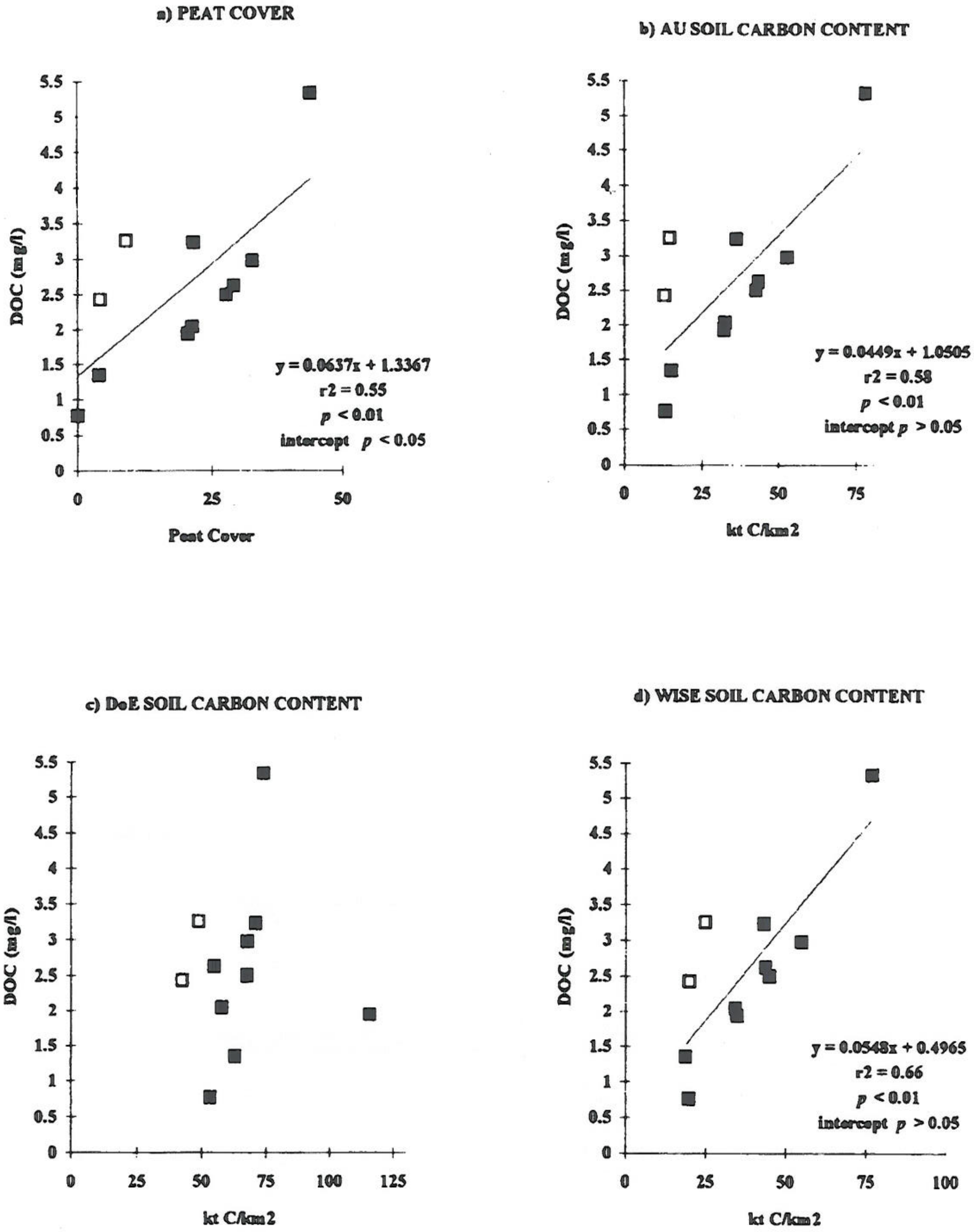


Figure 4. The relationship between mean stream water DOC concentration and (a) peat cover, (b) AU soil carbon content, (c) DoE soil carbon content and (d) WISE soil carbon content in large-scale catchments. Filled squares indicate upland (maximum altitude > 700 m) and unfilled squares lowland (maximum altitude < 700 m) catchments

1 km × 1 km grid square based on dominant soil type, grid squares with 51 and 100% peat cover would be assigned the same soil organic carbon content. The lack of significance when using the DoE soil carbon pool estimates is in contrast to the results of a previous study in larger catchments. In this case the DoE database was used to estimate mean soil organic carbon content in 17 British river catchments of between 73 and 1844 km^2; soil organic carbon content explained 91% of the variation in annual DOC exports between these

rivers (Hope *et al.*, 1997a). It is therefore concluded that both DOC concentrations and DOC exports can be readily predicted from estimates of the soil organic carbon pool across a range of spatial scales, provided that the soil information on which the soil organic carbon pool estimates are based is available at a spatial resolution appropriate to the scale of the study catchments. Furthermore, in catchments of only a few square kilometres in size, peat cover alone may be sufficient to model stream water DOC successfully. This is because peat soils tend to be concentrated in the upper reaches of many temperate upland river systems and effectively control DOC concentration.

Where significant linear relationships were found between peat cover or soil carbon content and stream water DOC concentration, regression gradients were steepest for the small-scale catchment subset of data, i.e. changes in peat cover and/or soil carbon content produced a proportionally larger increase in stream water DOC concentration in the smallest catchments. However, no systematic decrease was apparent in the slope of the regression line with increasing catchment size.

Other catchment characteristics influencing DOC concentration

Another feature of the linear regression of peat cover, and the various estimates of soil carbon content with DOC concentration, was that the regression line intercepted the DOC concentration axis at values between 0·4 and 1·8 mg l^{-1}; in most cases these were significantly different from zero. Although in terms of peat cover this can be explained by contributions of DOC from other soils within the catchments, this cannot be the case for the soil C content. This range of values is similar to that reported for the mean annual DOC concentration in precipitation, which generally lies between 0·95 to 1·40 mg l^{-1} (Likens *et al.*, 1977; Moore and Jackson, 1989). The concentrations of DOC in precipitation may therefore provide a low level background input of DOC into streams, which is not dependent upon catchment soil characteristics.

The tendency for lowland catchments to fall on or above the regression line and most upland catchments to fall below (Figures 1–4), suggests that, for a given soil carbon pool, upland catchments with a maximum altitude greater than 700 m have lower mean stream water DOC concentrations than lowland sites. This may be related to differences in land use in such catchments, since lowland catchments are utilized more for agriculture and commercial forestry than upland catchments. Similar findings have been reported by several other authors (e.g. Moeller *et al.*, 1979; Mulholland and Keunzler; 1979; Eckhardt and Moore, 1990), who suggest that land use change is an important factor in increasing stream water DOC concentration, especially where this involves the drainage of land for agriculture and afforestation. Hence, while soil carbon pools may be smaller in lowland catchments, disturbance caused by agriculture and forestry operations may enhance the concentration of DOC in stream water.

CONCLUSIONS

While several studies have shown a positive correlation between the extent of wetland and DOC concentration/export in small catchments, other soil processes, particularly adsorption in podzols, are known to regulate the flux of carbon from surface organic horizons to streams (McDowell and Likens, 1988). This paper examines the hypothesis that DOC concentrations in streams are controlled by the size of the organic carbon pool in the catchment, which in temperate upland British catchments is dominated by the soil pool (Howard *et al.*, 1995; Milne and Brown, 1997). While processes such as adsorption in mineral soils do regulate transport of organic carbon within the catchment, the single most important determinant of the amount of DOC transported out of catchments in streams is the size of the soil carbon pool. The link between soil C pool and DOC concentration is strongest at the small catchment scale (< 5 km^2) and weaker, but still statistically significant, at the medium (12–38 km^2) and large catchment scale (56–150 km^2).

The importance of this finding is that it suggests that estimates of soil carbon content can be successfully used to predict mean stream water DOC concentrations over a range of catchment scales, providing that soil data are available at a sufficiently detailed scale. Hence, in the future it may be fairly straightforward to extrapolate and extend results found in small catchments, where in the past most studies on DOC have been made, to larger catchment scales. The approach should be transportable to other river systems, as long as they contain subcatchments with a range of soil types with different carbon contents.

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