Biogeochemistry (2010) 101:281–294
DOI 10.1007/s10533-010-9474-x

Changes in water colour between 1986 and 2006 in the headwaters of the River Nidd, Yorkshire, UK

Pippa J. Chapman · Adrian T. McDonald · Rosa Tyson · Sheila M. Palmer · Gordon Mitchell · Brian Irvine

Received: 23 October 2009 / Accepted: 14 May 2010 / Published online: 30 May 2010

Abstract This study compares the spatial and temporal variability of water colour for fifteen sub-catchments of the River Nidd, northeast England, in 1986 and 2006/2007. Between 1986 and 2006/2007, mean annual water colour increased in all the sub-catchments. However, there was considerable variation in the increase, which ranged from 22 to 155%. Statistical analysis revealed that the sub-catchments could be split into two 'types' based on water chemistry and therefore dominant source of runoff; type 1 where flow was dominated by runoff from peat and type 2 where a greater contribution of flow appears to originate from mineral soil horizons, as indicated by the higher silicon, base cation concentrations and pH values. Largest proportional increases in water colour were observed in the sub-catchments that had the smaller mean annual water colour values in 1986 which were, in general, the type 2 sub-catchments. The higher rate of water colour increase in the type 2 catchments, in comparison to the type 1 catchments, may be related to changes in adsorption of dissolved organic carbon (DOC) within the mineral horizons of the organo-mineral soils on the lower catchment slopes possibly as a result of changes in acid sulphur deposition.

Keywords Water colour · Dissolved organic carbon (DOC) · Peat · Organo-mineral soils · Catchment characteristics

P. J. Chapman (✉) · A. T. McDonald · R. Tyson · S. M. Palmer · G. Mitchell · B. Irvine
water@leeds, School of Geography, University of Leeds, Leeds LS2 9JT, UK
e-mail: p.j.chapman@leeds.ac.uk

Present Address:
R. Tyson
Environment Agency, Red Kite House, Howbery Park, Wallingford OX10 8BD, UK

Introduction

In Britain, upland and marginal upland landscapes represent 37% of the total land area of 230,800 km^2 and are located predominantly in the north and west (Barr et al. 1993). Due to their topography, high rainfall (ranging from 3,000 mm in the west to 1,000 mm in the east), remote location and low intensity land use, they are well suited to the gathering and storage of raw waters for potable supply. Waters draining these areas tend to be acidic, coloured and low in nutrients and other solutes. However, over the last 20–30 years, the colour of surface waters derived from the British uplands has been increasing (Naden and McDonald 1989; Watts et al. 2001; Worrall et al. 2003) associated with the increase in dissolved organic carbon (DOC) concentrations (Worrall et al. 2004; Evans et al. 2006). This increase in water colour (e.g. Forsberg 1992; Hongve et al. 2004) and DOC (e.g. Skjelkvåle et al. 2005; Vuorenmaa et al. 2006; Monteith et al. 2007; Lepistö et al. 2008) has also been observed across other regions of northern Europe and NE America.

Water colour is a major problem for the water industry, particularly where the uplands represent the single most important source of potable water in the region. Deterioration in water colour results in breaches of European Union drinking water standards and an increase in water treatment costs. It also has health implications as the chlorination of highly coloured water can result in the production of carcinogenic disinfection-by-products such as trihalomethanes (THMs) (Rook 1977; Nikolaou et al. 2004). In addition to these effects on drinking water quality and treatment, the potential environmental implications of the increasing trends in water colour and DOC are wide ranging, from local effects on water transparency, acidity (Driscoll et al. 1989) and metal toxicity (Tipping et al. 2003) through to effects on aquatic organisms, such as macro-invertebrate assemblages (Heino et al. 2003) and possible destabilisation of the terrestrial carbon stores (Freeman et al. 2001), with peatlands acting as a net exporters of carbon rather than a sink, and consequent climatic feedbacks.

Water from upland areas is coloured due to the presence of naturally occurring high molecular weight organic carbon compounds, such as humic and fulvic acids, that are derived from the decomposition of soil organic matter. Theses humic and fulvic acids make up 50–75% of DOC in water and hence a strong relationship is usually observed between water colour and DOC (e.g. Tipping et al. 1988; Grieve 1990a; Worrall et al. 2003; Hongve et al. 2004). Given that in most streams and rivers the majority of organic carbon is allochthonous, the spatial variation in water colour and DOC concentration is usually explained in terms of the amount of organic rich soils, such as peat or wetland, within a catchment (e.g. McDonald et al. 1991; Clair et al. 1994; Mitchell and McDonald 1995; Hope et al 1997; Aitkenhead et al. 1999; Chapman et al. 2001). Although other factors, including proximity of wetland/peatland to the stream (e.g. Bishop et al. 1994), runoff generation (Naden and McDonald 1989; Grieve 1990b; Dawson et al. 2008), season (e.g. Naden and McDonald 1989; Grieve 1990b; Mitchell and McDonald 1992; Dawson et al. 2008) and land management (e.g. Mitchell and McDonald 1995; Wallage et al. 2007; Yallop and Clutterbuck 2009) have also been shown to be important in controlling spatial variability in DOC concentrations and water colour.

Given that DOC, and thus water colour, are controlled by a number of interacting factors, a wide range of potential driving mechanisms for the observed increase in DOC and colour have been proposed, many of which are linked to climate change. These include increased biological production of DOC by warming and drying (e.g. Mitchell and McDonald 1992; Freeman et al. 2001), changes in the distribution and volume of rainfall on the hydrological regime, including increasing flow volumes and changes in flow pathways (e.g. Tranvik and Jansson 2002; Hongve et al. 2004; Erlandsson et al. 2008; Lepistö et al. 2008) and, increased biological activity due to elevated atmospheric carbon dioxide (CO_2) (Freeman et al. 2004). In contrast, others have suggested that changes in atmospheric deposition of sulphur and/or seasalt (Evans et al. 2006; Monteith et al. 2007) or nitrogen (Findlay 2005) may be the key driver. It is likely that more than one single mechanism is responsible for the increasing trends in DOC and colour (e.g. Erlandsson et al. 2008; Lepistö et al. 2008). However, resolving the relative importance of each potential driver in ecosystems where processes interact at different spatial and temporal scales remains a challenge (Roulet and Moore 2006; Clark et al. 2010).

In 1986, Yorkshire Water commissioned research to investigate the factors controlling water colour (McDonald et al. 1991) that included monitoring the water colour of the sub-catchments feeding Angram and Scar House reservoirs, in the River Nidd catchment (Fig. 1), northeast England. This work showed that apparently similar sub-catchments, often adjacent to each other, produced marked differences in water colour. The reason for this was unclear, although higher coloured waters were observed in catchments that had a southerly aspect, leading McDonald et al. (1991) to suggest that colour generation is driven by moisture deficit. Over the last 20 years, water colour in Scar House and Angram reservoirs has increased (Fig. 2), particularly since 1990. However, it is not known whether the rate of increase in water colour has (i) been the same for all sub-catchments feeding the reservoirs and (ii) occurred throughout the year (i.e. has colour increased mainly in the autumn or throughout the year). The aim of this study was to re-visit fifteen sub-catchments in the upper Nidd catchment, which were sampled in 1986, to determine (i) whether the timing and/or magnitude of colour release has changed between 1986 and 2006/2007, and (ii) if the magnitude of increase in water colour has been the same for all the sub-catchments.

Methods

Study area

The upper Nidd catchment is located on the eastern slopes of the North Pennines in northeast England (Fig. 1). The River Nidd feeds directly into Angram and Scar House reservoirs, which were constructed in the 1930s to supply drinking water to Bradford, northeast England. In the 1960s, water from two neighbouring catchments, How Stean and In Moor, was diverted via an intake system and aqueduct to Scar House reservoir to augment the supply (Fig. 1). Of the two intake systems, by far the larger contribution of water is from the fifteen How Stean sub-catchments, which are the focus of this study.

The underlying geology of the upper Nidd catchment is comprised of alternating bands of sandstone and shale of the Millstone Grit series which forms a gently rolling landscape known as the Nidderdale plateau. This area is overlain by a range of poorly drained, acid soil types ranging from organo-mineral (histic mineral soils) soil on the lower slopes to deep peat (~1–2 m) (histosols) on the upper slopes and plateau. The soils support dwarf-shrub vegetation such as heather (*Calluna vulgaris*), cotton grass (*Eriophorum vaginatum*), bilberry (*Vaccinium myrtillus*) and *Sphagnum* moss. Although the area is of poor agricultural value, supporting low intensity sheep grazing and grouse moors, it supports important heath and blanket bog habitats of conservation value.

As in other upland areas of the UK, agricultural improvement of the land, often via the provisions of grants, has occurred. In the 1960s, 1970s and early 1980s networks of drainage ditches were introduced with the purpose of lowering the water table to improve the quality of vegetation for grazing and game and hence the agricultural production of upland areas. The other major land management activity that occurs in the area is controlled, rotational (10–15 years) patch burning of the heather to produce stands at different ages, which increase habitat structural diversity predominantly for grouse (*Lagapus lagapus* L.).

Between 1980 and 1999, annual rainfall at Scar House reservoir ranged from a minimum of 1,100 mm in 1995 to a maximum of 1,731 mm in 1986. The annual mean rainfall is 1,393 mm (1980–1999).

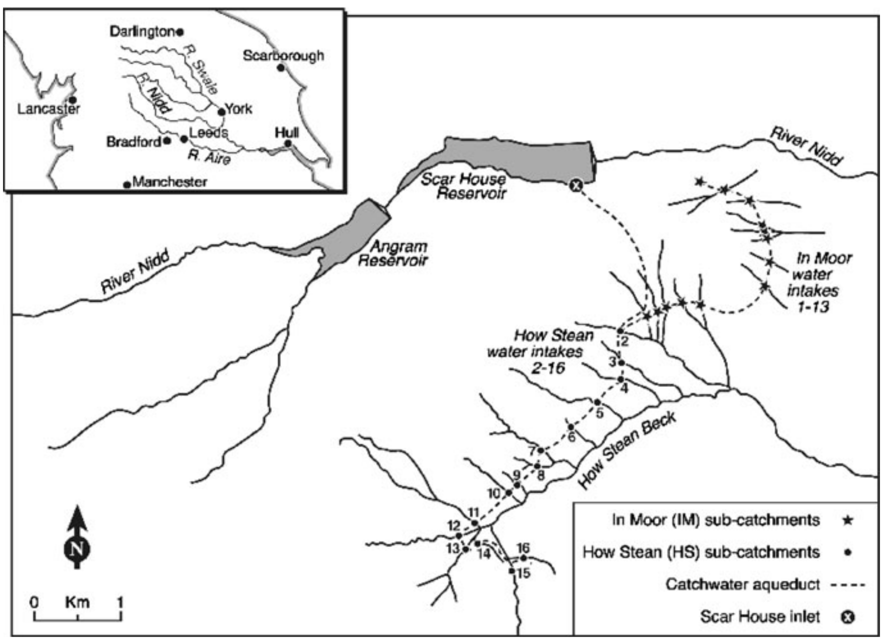


Fig. 1 Map showing the location of the How Stean sub-catchments, Scar House Reservoir and Angram Reservoir in the Upper Nidd Catchment, northeast England

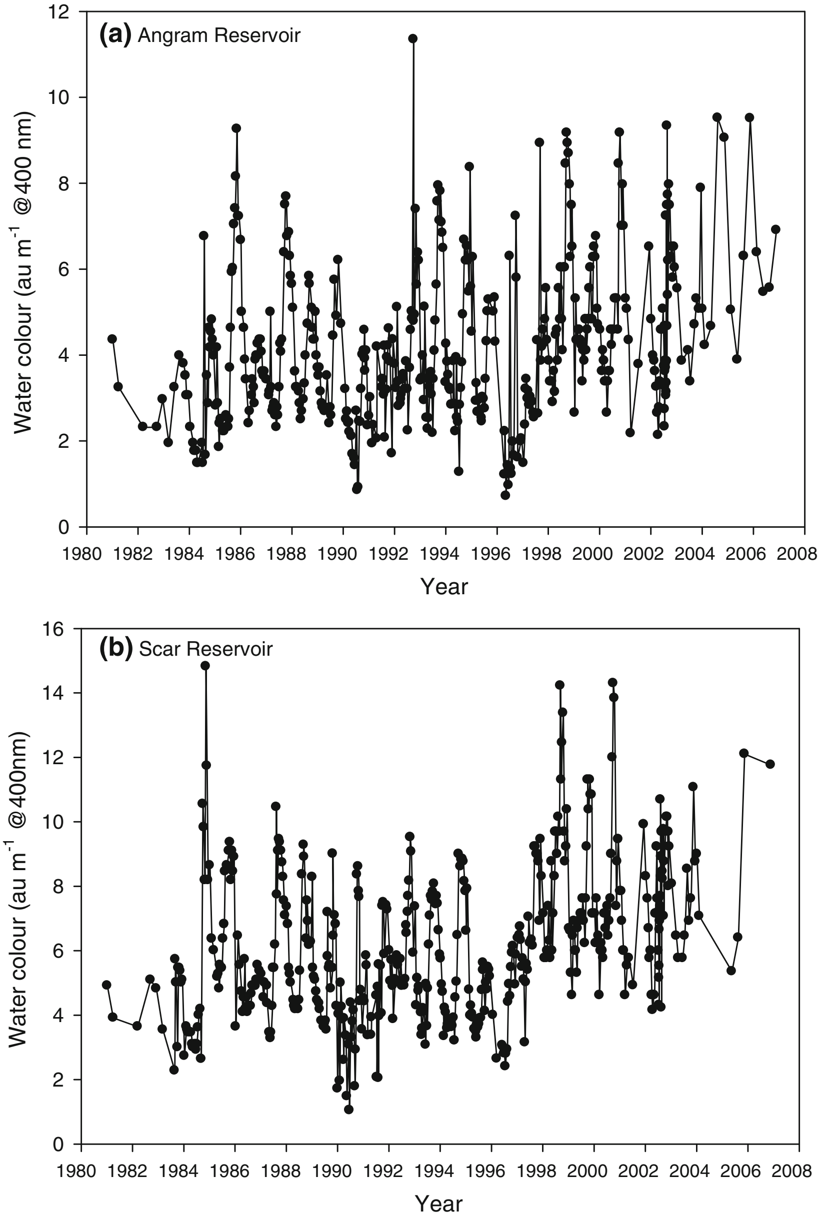


Fig. 2 Water colour in spot samples collected from **a** the outlet of Angram Reservoir and **b** the outlet of Scar Reservoir over the period January 1981 to November 2006 (note sampling frequency varied between years from a maximum of every 2 weeks to a minimum of a few times a year)

Characteristics of the How Stean sub-catchment

The How Stean sub-catchments cover an area of 15.67 km^2 and an altitude range of 342–575 m above mean sea-level and the characteristics of each sub-catchment (HS2–16) are presented in Table 1. Catchment boundaries provided by Yorkshire Water were used as a mask to extract the following information for each catchment; catchment area, coverage of the main soil types (NatMap Vector, NSRI), coverage of the major vegetation cover (LCM2000) and land management practices such as area of heather burning and drainage. Information on the extent of drainage and burning were obtained from aerial photographs. For the burning data, each 1 km^2 grid cell was assigned a percentage of burnt area.

There are no records of when the drainage ditches were dug, although ditching is known to have occurred in HS14, 15 and 16 in 1986. It is very

Table 1 Distribution (%) of the major soil types, vegetation covers and land management practices in the How Stean (HS) sub-catchments

Catchment	Area(km^2)	Soil type		Vegetation cover				Land management	
		Peat	Organo-mineral	Neutral grass[a]	Acid grass[a]	Dwarf shrub[b]	Bog	Drained	Burnt
HS2	2.00	79	21	0.5	0	87	12	21	77
HS3	0.11	0	100	73	0	18	0	47	56
HS4	0.17	0.5	99.5	5.5	0	79	0	46	56
HS5	0.47	48	52	6	0	64	21	59	59
HS6	0.05	48	52	34	0	66	0	43	56
HS7	1.48	92	8	28	0	62	9	11	49
HS8	0.13	34	66	21	0	79	0	69	0
HS9	0.08	45	55	43	0	57	0	97	0
HS10	0.19	77	23	72	1	27	0	96	1
HS11	0.62	100	0	58	1	26	14	61	11
HS12	2.85	100	0	37	6	40	17	33	9
HS13	3.67	100	0	22	24	41	12	32	1
HS14	0.16	100	0	90	10	0	0	96	0
HS15	3.59	100	0	14	6	32	42	63	16
HS16	0.17	100	0	72	23	0	0	57	9

[a] Unimproved and unmanaged grassland, [b] dominated by *Calluna vulgaris*, *Erica* spp. and *Vaccinium* spp.

likely that this was the last digging of drainage ditches to occur in the How Stean catchment as financial assistance stopped shortly after this. Heather burning currently occurs predominantly in sub-catchments HS2–7 (Table 1). In 1986, McDonald et al. (1991) noted that burning was mainly being carried out in sub-catchments HS2–6. Hence it seems likely that heather burning has continued to occur in sub-catchments HS2–6 while little burning has occurred in sub-catchments HS8–16 over the 20 year period.

Sample collection and analysis

In 1986, stream water samples were collected approximately every 2 weeks between 1st March and 24th November from the How Stean sub-catchments and the catchwater aqueduct inflow to Scar House reservoir (known hereafter as Scar inflow). In 2006/2007, the How Stean sub-catchments and the Scar inflow were sampled monthly between May 2006 and April 2007. In addition, samples were collected on two occasions in October in an attempt to determine peak water colour. On some occasions during both 1986 and 2006/7, it was not possible to collect water samples from all of the sub-catchments on every trip due to either severe weather conditions (snow or high winds) or lack of flowing water during very dry periods.

In 1986, colour measurements were made on filtered samples of stream water that had passed through Whatman 0.45 μm membrane filters. A range of methods are used to determine water colour but absorbance per meter at a wavelength of 400 nm is the preferred method (Mitchell and McDonald 1991) and was used in 1986. In 2006/2007, pH measurements were taken in the field using a hand-held Mettler Toledo meter which was calibrated prior to each visit. On return to the laboratory, samples were filtered through Whatman 0.45 μm cellulose nitrate membrane filters. Highly coloured samples were pre-filtered through Whatman GF/C 1.2 μm glass microfibre filters. Samples were stored in a refrigerator and all chemical analysis was carried out as soon as possible and usually within 2–3 days. Colour measurements were taken at 400 nm using a UV-3101PC UV–VIS NIRS Scanning Spectrophotometer. In 2006, all samples were also analysed for DOC using a Thermalox Total Carbon Analyser, major anions using a Dionex DX-500 High Performance Liquid Chromatography, and major cations and silicon using a Perkin Elmer 5300DV ICP Optical Emission Spectrophotometer.

Data and statistical analysis

In 1986, samples were only collected between March and November as water colour is low during the winter months, whereas in 2006/2007 samples were collected monthly from May 2006 until April 2007. In order to compare water colour between 1986 and 2006/2007, data from only those months that were sampled in both years were used.

Other studies have used the relationship between water colour and DOC concentration to derive DOC concentrations (e.g. Worrall et al. 2003). In this study, the relationship (Eq. 1) observed between water colour and DOC concentration in the 2006/2007 water samples was used to calculate DOC concentrations for corresponding water colour values in 2006/2007. DOC concentrations were not calculated for 1986 using Eq. 1 as we do not know whether the composition of DOC, and hence the relationship between water colour and DOC concentrations, has changed over the 20 year period.

$$\mathrm{DOC}\left(\mathrm{mg\,l^{-1}}\right) = 1.06 * \text{water colour} + 6.14\left(r^2 = 0.79, P < 0.001, n = 133\right) \quad (1)$$

Similarities in water colour between individual sub-catchments in 1986 were explored by correlation analysis. The results of these correlations indicated two distinct groups of sub-catchments and subsequently repeated measures ANOVA (SAS v9) was used to determine whether there was a statistically significant effect of catchment type on mean monthly water colour in both years of sampling. Relationships between mean annual water colour in 2006 and catchment attributes were examined by correlation analysis.

Rainfall

Daily tipping bucket records of rainfall for 1980 to 2007 were available from the Environment Agency from a rain gauge situated at Scar House reservoir (NGR SE 066766).

Results

Rainfall in 1986 and 2006–2007

Overall, 1986 was a very wet year with an annual rainfall of 1,731 mm compared to 1,510 mm in 2006. This difference was mainly due to very wet months in January and April 1986 (Fig. 3). In both years, June and July were very dry and were followed by a wet August, but in 1986 September was extremely dry, receiving only 17 mm of rainfall in comparison to 111 mm in 2006.

Water colour in 1986

In 1986, a total of 259 water samples were collected from the How Stean sub-catchments and water colour ranged from a minimum of 0.3 absorbance units per metre (au m^{-1}) to a maximum of 32 au m^{-1}, with a mean of 6.41 au m^{-1} (Table 2). In comparison, water colour in the samples from Scar inflow ranged between 3.0 and 8.7 au m^{-1} with a mean of 4.9 au m^{-1} (Table 2). A wide range in water colour was observed between sub-catchments, with largest water colour values observed in HS2 and HS14 (Fig. 4a). Mean water colour in HS2 and HS14 was two to three times greater than in seven of the sub-catchments and Scar inflow.

The results of correlation analysis of all water colour data in 1986 exhibited two distinct groups with: (i) significant and positive correlations ($P < 0.05$) between HS2, 4, 5, 6, 8, 9, 11 and 14 (hereafter referred to as type 1 catchments); and (ii) significant and positive correlations ($P < 0.05$) between HS12, 7, 13, 15 and 16 (type 2 catchments). Water colour in HS10 was positively correlated ($P < 0.05$) with that in HS5, 8 and 9. In HS3, where water originates from a ground water spring close to the sampling point, water colour was consistently low and showed no relationship with colour in any of the other sub-catchments which are not spring fed. The two types of sub-catchment (type 1 and type 2) were significantly different at $P < 0.05$ (Repeated Measures ANOVA).

Water colour at Scar inflow was positively correlated with HS12, 13, 15 and 16, which reflects the fact that these catchments represent the majority of the How Stean catchment area (see Table 1).

The type 1 catchments displayed a strong seasonal cycle in water colour, with largest values observed in

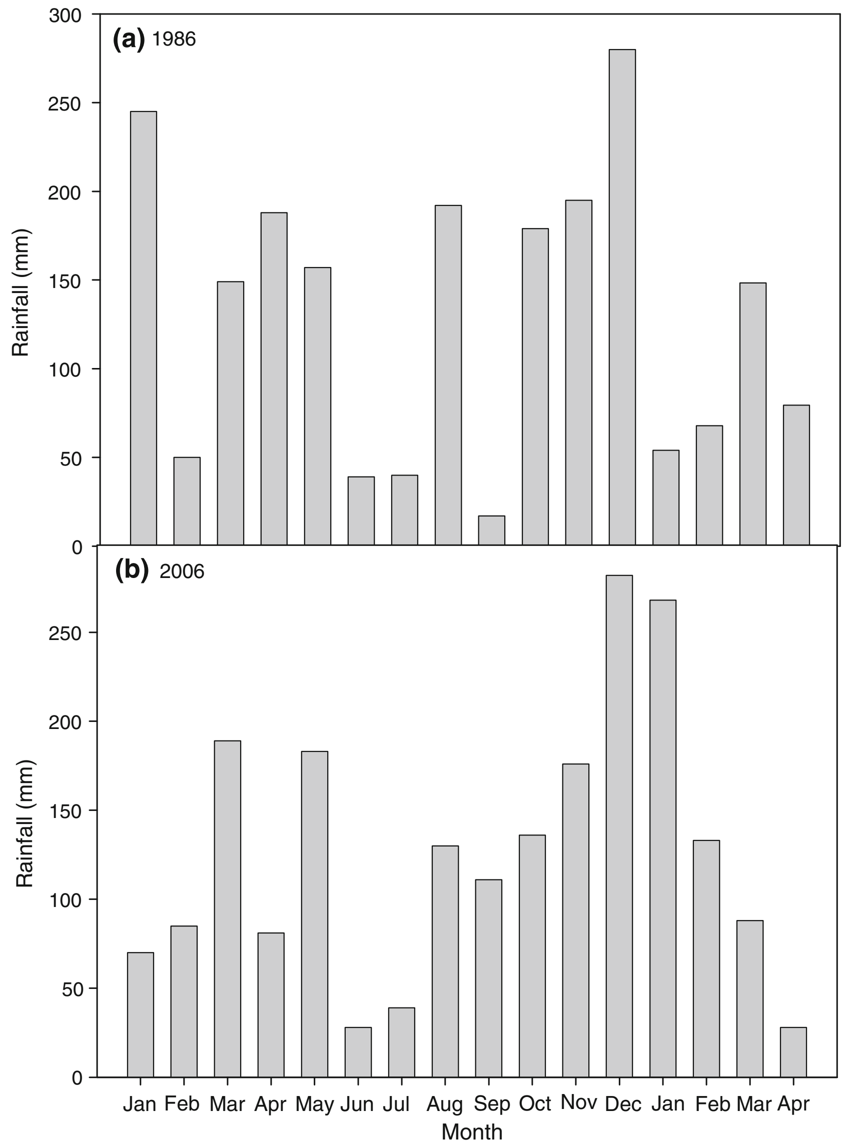


Fig. 3 Monthly rainfall during the period **a** January 1986 to April 1987 and **b** January 2006 to April 2007

July (Fig. 5a). The peak in water colour in these sub-catchments coincided with the end of a particularly dry period in June and July. In contrast, water colour in the type 2 catchments, HS3 and Scar inflow displayed little variability in water colour over the period February to November 1986 (Fig. 5a, b) and showed no immediate response to the dry period in June and July.

Water colour in 2006/2007

In 2006/2007, a total of 133 water samples were collected from the How Stean sub-catchments and water colour ranged from a minimum of 1.3 au m^{-1} (7.5 mg DOC l^{-1}) to a maximum of 57 au m^{-1} (66.6 mg DOC l^{-1}), with a mean of 12.5 au m^{-1} (19.4 mg DOC l^{-1}) (Table 2). In comparison, water colour in the samples from Scar inflow ranged between 3.2 and 23.3 au m^{-1} (9.5–30.8 mg DOC l^{-1}) with a mean of 12.9 au m^{-1} (19.8 mg DOC l^{-1}) (Table 2). Compared to 1986, there was considerably less variation in water colour between sub-catchments, although water colour was significantly lower in HS3 compared to all the other sub-catchments and water was still most coloured in HS2 and HS14 (Fig. 4b). There was no statistical effect of catchment type on monthly mean water colour in 2006/2007.

Table 2 Summary statistics for water colour (au m^{-1} at 400 nm) in each of the How Stean (HS) sub-catchments and the inflow to Scar House reservoir for the period March to November, 1986 and 2006/2007

Catchment	1986				2006/2007			
	Mean	CV%	Minimum	Maximum	Mean	CV%	Minimum	Maximum
HS2	10.72[a]	43	5.0	22.5	20.89[f]	47	8.7	34.7
HS3	2.87[a]	67	0.3	8.3	3.92[f]	64	2.7	10.4
HS4	4.74[a]	42	1.4	9.0	10.31[f]	74	2.4	27.1
HS5	6.38[b]	95	1.8	29.0	9.03[f]	66	1.7	15.9
HS6	3.82[c]	95	1.1	11.5	7.93[g]	58	2.7	15.9
HS7	6.71[d]	44	2.3	13.0	16.32[f]	51	4.1	29.4
HS8	9.47[d]	81	2.3	32.0	13.92[f]	51	3.4	24.2
HS9	8.16[d]	83	1.9	30.0	17.57[g]	94	4.2	56.9
HS10	6.01[d]	46	2.9	13.0	12.37[f]	55	3.2	20.7
HS11	7.69[d]	40	2.6	13.0	14.82[f]	40	5.5	22.2
HS12	4.55[d]	44	2.4	8.5	13.37[f]	50	2.4	20.4
HS13	3.73[d]	43	1.9	6.5	10.66[f]	63	3.5	20.3
HS14	12.29[c]	51	2.6	27.0	15.97[f]	44	8.4	24.5
HS15	5.00[d]	56	1.6	12.5	11.72[f]	71	1.9	25.3
HS16	4.12[c]	53	1.6	8.5	8.04[f]	70	1.3	14.8
Mean	6.41 (n = 259)				12.46 (n = 133)			
Scar Inflow	4.91[e]	35	3.00	8.7	12.92[f]	55	3.2	23.2

[a] n = 19, [b] n = 18, [c] n = 16, [d] n = 17, [e] n = 15, [f] n = 9, [g] n = 8

All of the sub-catchments and Scar inflow displayed a strong seasonal pattern, rising from a minimum in January and February to a maximum in October (Fig. 5c, d). However, those catchments designated as type 1 in 1986 also displayed a peak in water colour in June 2006, which coincided with a dry period. As observed in 1986, the seasonal pattern in water colour at Scar inflow displayed a strong relationship with the type 2 catchments that did not respond to the dry period in June (Fig. 5c, d).

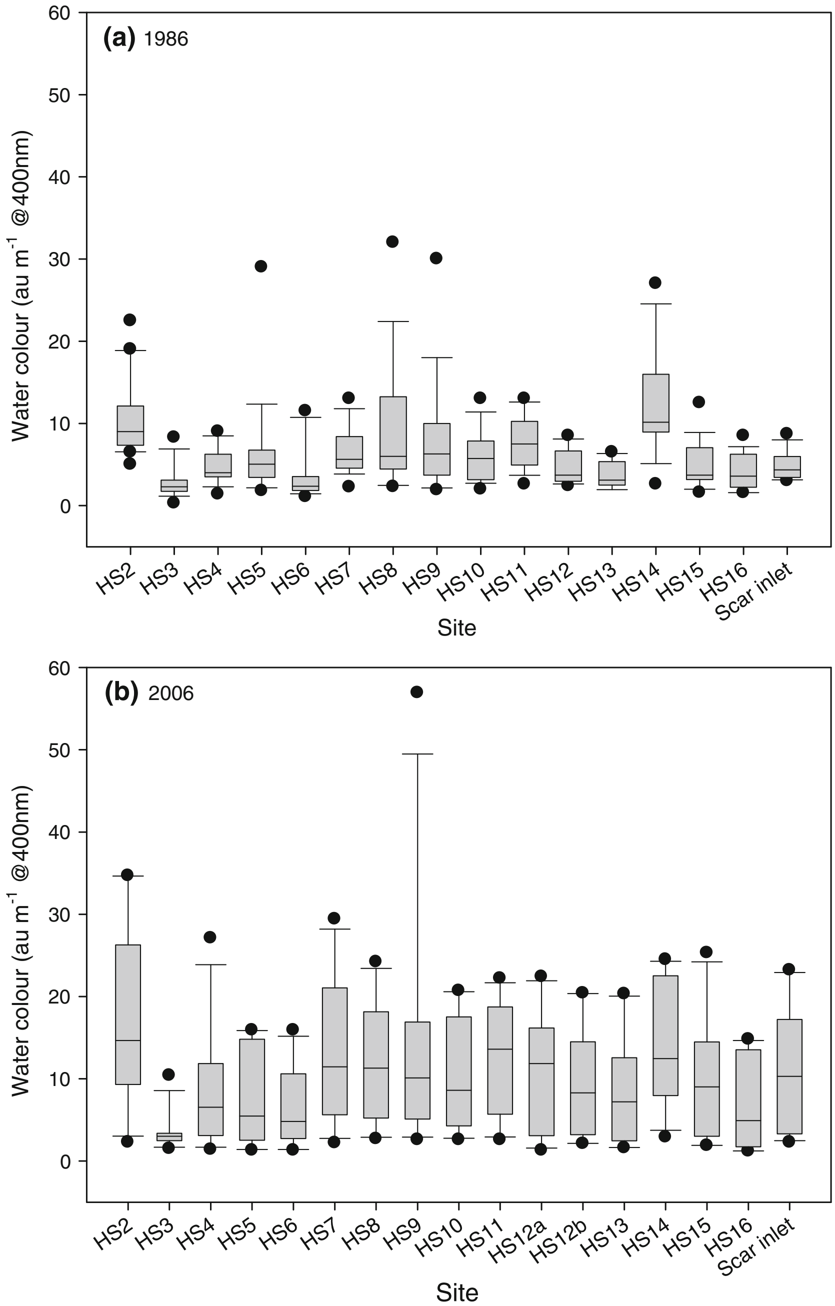
Comparison between 1986 and 2006/2007

The mean water colour of all samples collected from the How Stean sub-catchments increased by 94% from 6.4 au m^{-1} in 1986 to 12.5 au m^{-1} in 2006. In comparison, the average water colour at Scar inflow increased by 163% from 4.9 au m^{-1} in 1986 to 12.9 au m^{-1} in 2006. Between 1986 and 2006, mean annual water colour increased in all of the How Stean sub-catchments. However, there was considerable variation in the increase, which ranged from 22 to 155% (Table 3). The sub-catchments that have shown the greatest increase in water colour, had some of the lowest mean annual water colour values in 1986 while the sub-catchments that displayed the smallest increase in water colour, excluding HS3, had some of the highest mean annual water colour values in 1986 (Table 3). Hence, in 2006 considerably less variation in water colour was observed between sub-catchments than in 1986 (see Table 2 and cf. Fig. 4a, b). The results also show that it is the bigger sub-catchments that have shown the largest increase in water colour and that these sub-catchment waters are also less acidic and have higher concentrations of base cations (Table 3).

Relationships between catchment characteristics and the increase in water colour were examined further by correlation analysis (Table 4). The analysis showed that the percentage increase in water colour displayed a positive significant relationship with catchment area (Fig. 6a), pH, silicon and magnesium concentrations and a significant negative relationship with colour in 1986 (Fig. 6b) and area drained by ditches (Fig. 6c).

In 1986 water colour in the type 1 sub-catchments increased from April to a peak in late July, after

Fig. 4 Box and whisker plots summarising water colour values (au m^{-1} at 400 nm) in samples of stream water collected from the How Stean sub-catchments (HS2–HS16) and Scar inflow in **a** 1986 and **b** 2006/2007. The *middle horizontal line* of the *box* represents the median values and 50% of the data points lie within the box. The ends of each box delineate the upper and lower quartiles and the whiskers show the spread of data and closed circles represent outliers



which values rapidly declined to those observed in the other sub-catchments and Scar inflow (Fig. 5a). In 2006/2007, water colour in the type 1 catchments displayed a peak in June that was not observed in the type 2 catchments or Scar inflow (Fig. 5c, d). Thus in both 1986 and 2006/2007, the type 1 and 2 catchment displayed contrasting seasonal patterns.

Discussion

Between 1986 and 2006/2007, the annual mean water colour increased in all of the How Stean sub-catchments, as observed in other upland catchments in the UK (e.g. Worrall et al. 2003, 2004; Evans et al. 2006). While most other studies that have reported

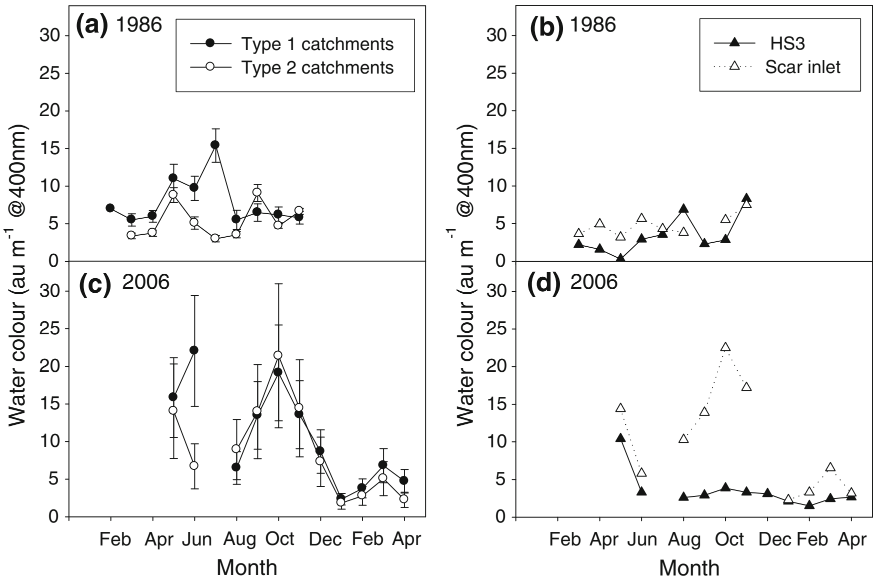


Fig. 5 Seasonal trend in water colour in **a** type 1 (n = 9) and type 2 (n = 5) sub-catchments in 1986, **b** HS3 and Scar inflow in 1986, **c** type 1 (n = 9) and type 2 (n = 5) sub-catchments in 2006/2007 and **d** in HS3 and Scar inflow in 2006/2007

Table 3 Percentage increase in water colour based on change in mean (March to November) water colour (au m^{-1} at 400 nm) between 1986 and 2006/2007 plus annual mean values for pH, Mg, Ca and Si in 2006/2007 for each of the How Stean sub-catchments

	Increase in colour (%)	Area (km^2)	1986	2006/2007				
			Water colour	Water colour	pH	Si[a] (mg l^{-1})	Mg (mg l^{-1})	Ca (mg l^{-1})
HS14	22	0.16	12.29	14.94	4.06	1.17	0.56	0.61
HS8	35	0.13	9.47	12.80	3.97	0.67	0.63	1.31
HS3	37	0.11	2.87	3.93	6.63	2.23	3.99	9.33
HS5	39	0.47	6.38	8.88	4.34	0.92	0.82	1.47
HS16	76	0.17	4.12	7.23	5.82	2.05	1.68	2.31
HS2	79	2.00	10.72	19.18	4.49	0.94	0.93	1.86
HS11	82	0.62	7.69	14.01	6.20	1.38	1.68	3.35
HS10	89	0.12	6.01	11.35	4.11	0.89	0.68	1.03
HS6	104	0.05	3.82	7.79	5.10	0.62	1.04	2.58
HS15	105	3.59	5.00	10.25	6.35	1.79	2.29	4.43
HS4	115	0.17	4.74	10.21	4.17	1.44	0.77	1.33
HS9	117	0.08	8.16	17.67	4.64	0.76	1.27	2.87
HS7	123	1.48	6.71	14.94	5.46	1.38	1.32	2.40
HS12	126	2.85	4.55	10.29	5.91	1.89	1.37	2.62
HS13	155	3.67	3.73	9.50	5.33	1.64	1.18	1.83

[a] Mean value based on four measurements only (January–April 2007)

increases in water colour and/or DOC have focussed on DOC/water colour time series data at the outlet of an individual catchment, this study has looked at the change in water colour for fifteen adjacent sub-catchments and observed that while the annual mean water colour increased in all of the sub-catchments, there was considerable variation in the magnitude of increase, which ranged from 22 to 155%. Evans et al. (2006) also observed a wide range in the increase of DOC concentrations, of between 31 and 140%, in 11 lakes and 11 streams across the UK over the period 1988–1993 to 1998–2003. They showed, for the

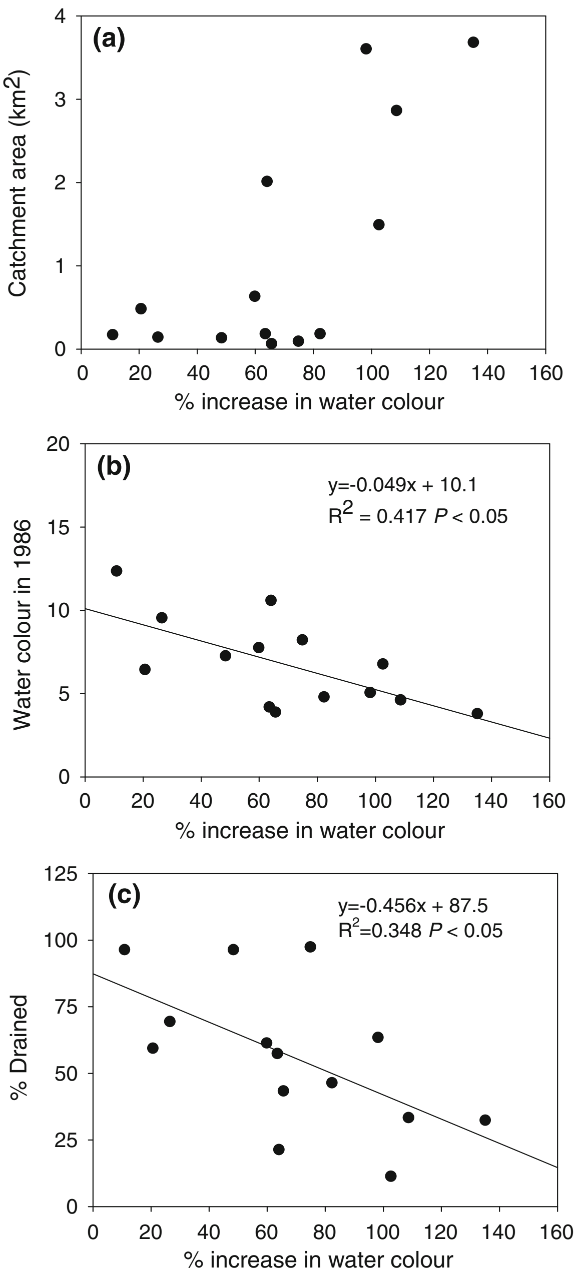


Fig. 6 Relationship between percentage increase in water colour between 1986 and 2006/2007 and **a** catchment area, **b** mean water colour in 1986 and **c** percentage of catchment drained for each How Stean sub-catchment

lakes, that the majority of the variation in DOC trend could be accounted for by variability in temperature and sulphur and seasalt deposition at the sites. However, the results from this study highlight that even within small adjacent catchments which experience the same climate and atmospheric deposition chemistry, the spatial variability in the rate of water colour increase can be very large.

So what factors may account for the large spatial variability in water colour increase in the How Stean catchments? All catchments have experienced the same climate and acid rain deposition over the 20 year period. The land is predominantly used for grazing sheep, the number of which may have changed over the 20 year period, but as there is open access across the land then any change in grazing intensity is likely to have been the same across all sub-catchments. In addition, the few studies that have investigated the impact of grazing intensity on soil solution DOC concentration have found either small inconsistent differences (Ward et al. 2007) or no significant difference between grazed and ungrazed plots (Worrall et al. 2007). Heather burning has occurred in some of the catchments, but there has been no large change in burning, with those catchments that showed signs of burning in 1986, still showing signs of burning 2006/2007. Hence, in contrast to other studies (e.g. Yallop and Clutterbuck 2009) no relationship between the proportion of catchment burnt and water colour or the increase in water colour was observed (Table 4). If we assume that no new drainage ditches have been dug since 1986, then there was a positive, but not significant relationship, between proportion of sub-catchment influence by drainage ditches and water colour in 1986 (Table 4). However, it is the catchments that contain the least drainage ditches that have shown the largest increase in water colour resulting in no relationship being observed between water colour and drainage in 2006/2007 (Table 4).

It is the catchments that had the smaller mean annual water colour values in 1986 that have shown the largest increase in water colour. In general, these catchments have larger Si and base cation concentrations and pH values, suggesting greater connectivity between the organic horizon and the mineral horizons beneath and thus a greater contribution of flow from depth (see Tables 3, 4). Hence dominant soil type and flow of water through the catchment appears critical in controlling the rate of increase in water colour, with water colour increasing at a greater rate in catchments with greater flow from the mineral horizons.

Table 4 Correlation coefficients calculated between annual mean water colour in 1986 and 2006/2007 and % increase in colour and catchment characteristics and water quality parameters sampled in 2006/2007 for the 15 study catchments

Characteristic	Colour 1986	Colour 2006/2007	% Increase in colour
Area (km^2)	−0.32	0.03	0.74**
% Peat	0.02	0.14	0.27
% Bog vegetation	−0.23	−0.05	0.33
% Drained	0.39	0.05	−0.59*
% Burnt	−0.07	0.03	−0.02
Colour in 1986		0.81***	−0.65**
DOC		0.80***	−0.51
Sulphate		−0.47	0.13
Iron		0.85***	−0.40
pH		−0.24	0.60*
Silicon		−0.30	0.56*
Calcium		−0.07	0.50
Magnesium		−0.15	0.54*

* $P < 0.01$, ** $P < 0.05$, *** $P < 0.001$

Worrall et al. (2004) compiled monthly DOC time series for 198 sites across the UK and observed that 153 of them showed a significant upward trend in DOC. They also observed that, in general, the larger the proportion of peat in a catchment, the greater the increase in DOC. However, they also noted that some catchments with high annual mean DOC concentrations, and therefore large areas of peat, showed no increase in DOC while other catchments that contained a large proportion of organo-mineral soils had low DOC concentrations showed an increasing trend in DOC. In our study, soil type appeared to have no influence on water colour or the increase in water colour (Table 4). However, it is likely that the soil map is not accurate at the scale of these small sub-catchments and in fact mineral soil has been observed in many of the sub-catchments beneath an organic horizon of 40 to 60 cm.

As water moves down the soil profile in organo-mineral soils the amount and composition of DOC may undergo substantial modification due to the ability of mineral horizons to adsorb and store carbon. Hence, adsorption in the mineral soil regulates the amount and composition of DOC reaching surface waters (Mcdowell and Wood 1984; Vance and David 1991) resulting in a negative relationship often being observed between catchment area and DOC (e.g. Palmer et al. 2005). The capacity of the mineral soil to adsorb DOC is related to the soil organic matter content, mineralogy and pH of the B horizon. Maximum adsorption of DOC in mineral soils has been observed to occur at pH 4.5 (Jardine et al. 1989; Kennedy et al. 1996), and at higher pHs a reversal of charge can occur, leading to the release of DOC (Kennedy et al. 1996).

Of the three main factors controlling DOC adsorption, only the soil organic matter content and pH of the mineral soil could have changed over the 20 year period. Although mineral horizons are known to adsorb DOC, little is known about whether they naturally reach a saturation point under field conditions, although field and modelling experiments suggest that this is likely, particularly for organic-rich soils (Chung et al. 2010; Stewart et al. 2007). If the mineral horizons in this catchment have reached saturation this may account for the larger rate of increase in water colour from the type 2 catchments where it appears that a larger proportion of water has had contact with mineral soil. Alternatively the pH of the mineral soil may have changed. Over the last 20 years there has been a considerable reduction in acid deposition across the UK (Fowler et al. 2005) and there is evidence from a number of recent studies that this has lead to a faster increase in soil pH in the mineral B horizon than the organic horizon (RoTAP 2010). Such an increase in the pH of mineral soil may lead to the release of DOC. Without further research it is not possible to determine whether either or both of these factors are important in controlling stream water DOC and hence water colour in the How Stean sub-catchments, but both hypotheses would account for why it is that type 2 catchments have shown the larger rate of increase in water colour over the 20 year period in comparison to the type 1 catchments which are dominated by surface runoff from peat.

To date, research on water colour and DOC concentrations in surface waters has focussed on the factors controlling DOC production in, and export from, peat soils. In many upland catchments in the UK, peat dominates the upper plateaus whereas organo-mineral soils predominate on the slopes. These organo-mineral soils are likely to have a large influence on the amount and composition of DOC reaching UK upland surface waters and, therefore, warrant further investigation given that the results from this study suggest that it is the catchments with a larger proportion of flow coming from the mineral horizons that have shown the largest increase in water colour over the last 20 years. Without a better understanding of the processes controlling DOC retention and release within organo-mineral soils, it is not possible to predict or model the future trajectory of DOC change and hence water colour, and its subsequent impact on drinking water treatment and quality, freshwater biota and the carbon cycle. For example, McDonald et al. (1991) proposed sub-catchment exclusion on a permanent and on a dynamic basis to Yorkshire Water as a strategy to reduce the colour of water reaching the water treatment works. This assumed that the relative differences in water colour between the sub-catchments would remain the same over time. The evidence presented in this paper indicates that the strategy would have worked initially but would have become less effective with time as the sub-catchments with low water colour in 1986 began to merge with the sub-catchments which had high water colour in 1986.

Acknowledgments This research was supported by Yorkshire Water, the Natural Environment Research Council via grant NE/D005973/1 and a Rural Economy and Land Use programme grant (RES-227-30-2001) co-sponsored by ESRC, NERC BBSRC, DEFRA and SEERAD. We would like to thank Doug Tyson, Alona Armstrong and Joseph Holden for their assistance with field work; David Ashley, Rachel Gasior and Holly Mottershead for their assistance with the chemical analysis of the water samples; David Higgins, University of Durham, for digitising the area of drainage ditches from aerial photographs and Fred Worrall, University of Durham, for classifying the percentage of burning at a 1 km^2 resolution from air photographs taken in 2000/2001.

References

Aitkenhead JA, Hope D, Billett MF (1999) The relationship between dissolved organic carbon in stream water and soil organic carbon pools at different spatial scales. Hydrol Process 13:1289–1302

Barr CJ, Bunce RGH, Clarke RT, Fuller RM, Furse MT, Gillespi MK, Groom GB, Hallam CJ, Hornung M, Howard DC, Ness MJ (1993) Countryside survey 1990 main report. Report to the DOE. Institutes of Terrestrial Ecology and Freshwater Ecology, UK

Bishop KH, Pettersen C, Allard B, And Lee YH (1994) Identification of the riparian sources of dissolved organic carbon. Environmental International 20:11–19

Chapman PJ, Edwards AC, Cresser MS (2001) The nitrogen composition of streams in upland Scotland: some regional and seasonal differences. Sci Total Environ 265:65–83

Chung H, Ngo KJ, Plante AF, Six J (2010) Evidence for carbon saturation in a highly structured and organic-matter-rich soil. Soil Sci Soc Am J 74:130–138

Clair TA, Pollock TL, Ehrman JM (1994) Exports of carbon and nitrogen from river basins in Canada's Atlantic Provinces. Global Biogeochem Cycles 8:441–450

Clark JM, Botrell SH, Evans CD, Monteith DT, Bartlett R, Rose R, Newton RJ, Chapman PJ (2010) The importance of the relationship between scale and process in understanding long-term DOC dynamics. Sci Total Environ 408:2768–2775

Dawson JJC, Soulsby C, Tetzlaff D, Hrachowitz M, Dunn SM, Malcolm IA (2008) Influence of hydrology and seasonality of DOC exports from three contrasting upland catchments. Biogeochemistry 90:93–113

Driscoll CT, Fuller RD, Schecher WD (1989) The role of organic acids in the acidification of surface waters in the Eastern US. Water Air Soil Pollut 43:21–40

Erlandsson M, Buffam I, Folster J, Laudon H, Temnerud J, Weyhenmeyer GA, Bishop K (2008) Thirty-five years of synchrony in the organic matter concentrations of Swedish rivers explained by variation in flow and sulphate. Glob Chang Biol 14:1191–1198

Evans CD, Chapman PJ, Clark JM, Monteith DT, Cresser MS (2006) Alternative explanations for rising dissolved organic carbon export from organic soils. Glob Chang Biol 12:2044–2053

Findlay SEG (2005) Increased carbon transport in the Hudson River: unexpected consequence of nitrogen deposition? Front Ecol Environ 3:133–137

Forsberg C (1992) Will an increased greenhouse impact in Fennoscandia give rise to more humic and coloured waters? Hydrobiologia 229:51–58

Fowler D, Smith RI, Muller JBA, Hayman G, Vincent KJ (2005) Changes in the atmospheric deposition of acidifying compounds in the UK between 1986 and 2001. Environ Pollut 137:15–25

Freeman C, Evans CD, Monteith DT, Reynolds B, Fenner N (2001) Export of organic carbon from peat soils. Nature 412:785

Freeman C, Fenner N, Ostle NJ, Kang H, Dowrick DJ, Reynolds B, Lock MA, Sleep S, Hughes S, Hudson J (2004) Export

of dissolved organic carbon from peatlands under elevated carbon dioxide levels. Nature 430:195–198
Grieve IC (1990a) Variations in chemical composition of the soil solution over a four year period at an upland site in Scotland. Geoderma 46:351–362
Grieve IC (1990b) Seasonal, hydrological, and land management factors controlling dissolved organic carbon concentrations in the Loch Fleet catchments, southwest Scotland. Hydrol Process 4:231–239
Heino J, Muotka T, Mykrä H, Paavola R, Hämäläinen H, Koskenniemi E (2003) Defining macroinvertebrate assemblage types of headwaters: implication for bioassessment and conservation. Ecol Appl 13:842–852
Hongve D, Riise G, Kristianse JF (2004) Increased colour and organic acid concentrations in Norwegian forest lakes and drinking water—a result of increased precipitation? Aquat Sci 66:231–238
Hope D, Billett MF, Cresser MS (1997) Exports of organic carbon in two river systems in NE Scotland. J Hydrol 193:61–82
Jardine PM, Weber NL, McCarthy JF (1989) Mechanisms of dissolved organic carbon adsorption on soil. Soil Sci Soc Am J 53:1378–1385
Kennedy J, Billett MF, Duthie D, Fraser AR, Harrison AF (1996) Organic matter retention in an upland humic podzol: the effect of pH and solute type. Eur J Soil Sci 47:615–625
Lepistö A, Kortelainen P, Mattsson T (2008) Increased organic C and N leaching in a northern boreal river basin in Finland. Global Biogeochem Cycles 22:GB3029. doi: 10.1029/2007GB003175
McDonald AT, Mitchell GN, Naden PS, Martin DSJ (1991) Discoloured water investigations. Final report to Yorkshire Water plc
McDowell WH, Wood T (1984) Podzolization: soil processes control dissolved organic carbon concentrations in stream water. Soil Sci 137:23–32
Mitchell G, McDonald AT (1991) The relationship between different methods of colour measurement in potable water. Trans Inst Meas Control 24:306–309
Mitchell G, McDonald AT (1992) Discoloration of water by peat following induced drought and rainfall simulation. Water Res 26:321–326
Mitchell G, McDonald AT (1995) Catchment characterization as a tool for upland water-quality management. J Environ Manage 44:83–95
Monteith DT, Stoddard JL, Evans CD, de Wit HA, Forsius M, Hogasen T, Wilander A, Skjelkvale BL, Jeffries DS, Vuorenmaa J, Keller B, Kopacek J, Vesely J (2007) Dissolved organic carbon trends resulting from changes in atmospheric deposition chemistry. Nature 450: 537–541
Naden PS, McDonald AT (1989) Statistical modelling of water colour in the Uplands: the Upper Nidd catchment 1979–1987. Environ Pollut 60:141–163
Nikolaou AD, Golfinopoulos SK, Lekkas TD, Kostopoulou MN (2004) DBP levels in chlorinated drinking water: effect of humic substances. Environ Monit Assess 93: 301–319
Palmer SJ, Wellington BI, Johnson CE, Driscoll CT (2005) Landscape influences on aluminium and dissolved organic carbon draining the Hubbard Brook valley, New Hampshire, USA. Hydrol Process 19:1751–1769
Rook JJ (1977) Chlorination reactions of fulvic acids in natural-waters. Environ Sci Technol 11:478–482
RoTAP (2010) Review of Transboundary Air Pollution (RoTAP): acidification, eutrophication and ground level ozone and heavy metals in the UK. Report to the Department for Environment, Food and Rural Affairs, Centre for Ecology and Hydrology, Edinburgh, UK
Roulet N, Moore TR (2006) Environmental chemistry—browning the waters. Nature 444:283–284
Skjelkvåle BL, Stoddard J, Jeffries D, Tørseth K, Høgåsen T, Bowman J, Mannio J, Monteith DT, Mosello R, Rogora M, Rzychon D, Vesely J, Wieting J, Wilander A, Worsztynowicz A (2005) Regional scale evidence for improvements in surface water chemistry 1990–2001. Environ Pollut 137:165–176
Stewart CE, Paustian K, Conant RT, Plante AF, Six J (2007) Soil carbon saturation: concept, evidence and evaluation. Biogeochemistry 86:19–31
Tipping E, Hilton J, James B (1988) Dissolved organic matter in Cumbrian lakes and streams. Freshw Biol 19:371–378
Tipping E, Smith EJ, Lawlor AJ, Hughes S, Stevens PA (2003) Predicting the release of metals from ombrotrophic peat due to drought induced acidification. Environ Pollut 123:239–253
Tranvik LJ, Jansson M (2002) Terrestrial export of organic carbon. Nature 415:861–862
Vance GF, David MB (1991) Chemical characteristics and acidity of soluble organic substances from a northern hardwood forest floor, Central Maine, USA. Geochim Cosmochim Acta 55:3611–3625
Vuorenmaa J, Forsius M, Mannio J (2006) Increasing trends of total organic carbon concentrations in small forest lakes in Finland from 1987 to 2003. Sci Total Environ 365:47–65
Wallage ZE, Holden J, McDonald AT (2007) Drain blocking: an effective treatment for reducing dissolved organic carbon loss and water discolouration in drained peatland. Sci Total Environ 367:811–821
Ward SE, Bardgett RD, McNamara NP, Adamson JK, Ostle NJ (2007) Long-term consequences of grazing and burning on northern peatland carbon dynamics. Ecosystems 10:1069–1083
Watts CD, Naden PS, Machell J, Banks J (2001) Long term variation in water colour from Yorkshire catchments. Sci Total Environ 278:57–72
Worrall F, Burt T, Shedden R (2003) Long term records of riverine dissolved organic matter. Biogeochemistry 64: 165–176
Worrall F, Harriman R, Evans CD, Watts CD, Adamson J, Neal C, Tipping E, Burt T, Grieve I, Monteith D, Naden PS, Nisbet T, Reynolds B, Stevens P (2004) Trends in dissolved organic carbon in UK rivers and lakes. Biogeochemistry 70:369–402
Worrall F, Armstrong A, Adamson JK (2007) The effects of burning and sheep-grazing on water table depth and soil water quality in an upland peat. J Hydrol 339:1–14
Yallop AR, Clutterbuck B (2009) Land management as a factors controlling dissolved organic carbon release from uplands soils 1: spatial variation in DOC production. Sci Total Environ 407:3803–3813