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Trends in dissolved organic carbon in UK rivers and lakes

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Abstract. Several studies have highlighted an increase in DOC concentration in streams and lakes of UK upland catchments though the causal mechanisms controlling the increase have yet to be fully explained. This study, compiles a comprehensive data set of DOC concentration records for UK catchments to evaluate trends and test whether observed increases are ubiquitous over time and space. The study analysed monthly DOC time series from 198 sites, including 29 lakes, 8 water supply reservoirs and 161 rivers. The records vary in length from 8 to 42 years going back as far as 1961. Of the 198 sites, 153 (77%) show an upward trend in DOC concentration significant at the 95% level, the remaining 45 (23%) show no significant trend and no sites show a significant decrease in DOC concentration. The average annual increase in DOC concentration was 0.17 mg C/l/year. The dataset shows: (i) a spatial consistent upward trend in the DOC concentration independent of regional effects of rainfall, acid and nitrogen deposition, and local effects of land-use change; (ii) a temporally consistent increase in DOC concentration for period back as far as the 1960s; (iii) the increase in DOC concentration means an estimated DOC flux from the UK as 0.86 Mt C for the year 2002 and is increasing at 0.02 Mt C/year. Possible reasons for the increasing DOC concentration are discussed.

Key words: Climate change, DOC, Lakes, Rivers, Trends

Introduction

A limited number of studies have raised concern regarding observed increases in DOC concentrations in UK rivers. Freeman et al. (2001a) have shown increases of 65% for a series of 11 UK stream and 11 lake catchments over a period of 12 years. Worrall et al. (2003a) have shown long-term increases in dissolved organic matter of up to 100% for two catchments over timescales of up to 39 years for catchments up to 820 km^2 in size. Increases in river concentrations of carbon have important implications for water quality and climate change.

The removal of DOC from water sources represents one of the major costs to water treatment in large parts of Britain. Incomplete removal of DOC results in water of low aesthetic quality, increases the threat of biological contamination of the treated water as DOC consumes free residual chlorine used to protect water in transit, and can result in the formation of tri-halomethanes which are potential carcinogens and whose concentration in drinking water is limited by law in the UK. With respect to climate change, increasing DOC concentration in UK rivers is indicative of changes in terrestrial carbon reserves. High DOC concentrations in rivers are particularly associated with catchments where there is extensive peat (Aitkenhead et al. 1999). Increases in DOC concentrations in catchments could indicate either major changes in the carbon budget of these carbon reserves suggesting decreasing storage of carbon, or indicating an increased rate of carbon cycling in these stores.

Why then are these increases in DOC concentrations occurring? Several alternative explanations have been proposed to explain these observations. Firstly, Freeman et al. (2001a) have associated observed increases in DOC with rising temperature over the preceding decades. Worrall et al. (2003a) have correlated an observed 100% increase in DOC concentrations over a period of 30 years in the River Tees with an increase in summer temperatures of 0.6 °C over the same period. Increased temperature leads to greater microbial activity and enhanced decomposition of peat and thus increased production of DOC. Increases in temperature can also mean the greater draw-down of water tables in summer, increasing the depth of the zone of oxidation and production of DOC (Evans et al. 2002). The latter effect being extenuated by decreased summer rainfall over the last 40 years (Burt et al. 1998). However, Worrall et al. (in press) have shown that changes in temperature and consequent changes in water table depth are insufficient to explain the magnitude of the observed increases.

Increasing DOC production has been associated with decreasing mineral acidity (Krug & Frink 1983). The UK uplands are showing initial indications of recovering from acidification (Evans & Montieth 2001). Thus, observed increases in DOC could be correlated with recovery from acidification. Greive (1990a, b) has shown increases in DOC concentration followed liming in three Scottish catchments. Soulsby and Reynolds (1995) showed that increases in DOC concentrations following liming were short-lived. However, increases in DOC are widespread and even occur in catchments where no acidification has been observed (Freeman et al. 2001b). Equally, Kullberg and Petersen (1987) observed no change in DOC concentrations upon liming of a catchment.

Increasing DOC concentrations could result from changes in hydrology, that is, a decreasing discharge could result in increasing DOC concentrations (Tranvik & Jansson 2002). This mechanism has been proposed for increases in DOC concentrations in lakes and streams in Sweden during the 1970s and 1980s where increases in DOC concentrations coincided with decreases in temperatures and increased precipitation. Increasing precipitation during this period caused increased runoff from wetland areas and thus increased DOC flux to these catchments (Anderson et al. 1991; Forsberg 1992). Worrall and Burt (in press) have shown that for two long-term time series of increasing DOC concentration, the increase occurs equally for the baseflow as for the stormflow, suggesting that DOC has increased in general and that the overall increasing trend is not due to different flowpaths tapping different sources. Similarly, a decrease in discharge as opposed to a change in the balance of hydrological pathways could also explain increased DOC concentrations because of a decrease in dilution. Therefore, if changes in DOC concentration are to be interpreted as a concern for carbon storage, the increases must also be accompanied by a concomitant increase in carbon flux.

Changes in land management could also lead to increases in DOC concentrations. Most studies of the effect of land use upon the release of DOC have focused on forested catchments (e.g. Swank 1986). The pattern of carbon release is similar to that of other nutrients, that is, high values associated with any disturbance followed by a decline. Afforestation has been a common phenomenon in UK uplands, including afforestation of upland peat. The disturbance of peat caused by afforestation can cause significant loss of carbon storage even in comparison to increased primary productivity due to tree growth (Cannell et al. 1993). Afforestation is not the only management change that upland peat can undergo. To improve grazing large areas of upland peat were drained. Eight percent of the UK is covered with blanket peat moorland, most of which overlies headwater catchments, three quarters of which is estimated to have been drained (Ratcliffe & Oswald 1988). Drainage of peat could draw down water tables allowing ingress of oxygen and thus stimulating DOC production. The drainage of peat, which only ceased in 1995 when legislation and financial incentives changed, could have caused the number of trends already observed, however, a number of the catchments reported in Evans et al. (2002) have never been drained yet have shown a rising trend in DOC concentrations.

The hypothesis that drainage of peat could cause increasing trends in DOC concentrations in UK rivers and lakes is based on the idea that drainage lowers the water table. Implicit in this hypothesis is that DOC production is negligible below the water table. Anaerobic degradation, and therefore anaerobic production of DOC, does not appear to occur in peats whereas it does in other settings (Painter 1991). In peat bogs decomposition, and therefore DOC production, is restricted by repression of hydrolase enzymes are depressed in peatlands (Kang & Freeman 1999). Freeman et al. (2001b) have shown that hydrolase enzymes in peat bogs are inhibited by the presence of phenolic compounds. The phenolic compounds can build up in peat because of the activity of phenol oxidase is severely restricted in the absence of oxygen. Therefore, if the water table in peat bogs falls, the phenyl oxidase activity increases destroying the phenolic compounds that repress the hydrolase activity. A loss of phenolic compounds means that decomposition can continue after the water table has risen again. This has been referred to as an enzymic latch mechanism, that is, enzymes are switched on by water table drawdown but are not switched off as the water table rises again. This mechanism could cause the increased peat decomposition, and therefore increased DOC release, following periods of drought or water table drawdown. With several severe droughts occurring in the UK during the second half of the 20th century (e.g. 1976 and 1995) could it be that observed upwards trends are the result of blanket peats responding to an increased frequency of droughts?

The purpose of this study is to bring together a comprehensive set of DOC time series for the UK and to analyse them in a consistent manner in order to assess how ubiquitous is the increase in DOC concentrations in both time and space. The results of this review can then used to cast light upon mechanisms generating change in terrestrial carbon stores.

Methodology

Time series of DOC were compiled for 198 records. Only records longer than 8 years in length were considered. In practice, only data prior to 1993 were considered. This criterion was chosen for several reasons. Firstly, the summer of 1995 was a severe drought throughout the UK and this had a severe effect on the occurrence of DOC in UK rivers and lakes (Harriman et al. 2001). Therefore, records starting in 1995 or after largely reflect short-term consequences of the 1995 drought. It has been noted that the initial effect of a severe drought on DOC lasts not just for the year of the drought or for the subsequent year but for at least 3 years (Worrall et al. 2003a) and therefore records of less than 6 years would unduly reflect drought years rather than longer term processes. Secondly, a significant set of water quality records (Environmental Change Network (ECN)) only commenced in 1993. Owing to the outbreak of foot and mouth disease in Great Britain in 2001, many records experienced a significant break in monitoring at this time and so the majority of records are considered only up to the end of the year 2000. Records analysed come from a number of different agencies each of which is detailed below. All monitoring records were converted to a monthly time step and to be in units of mg C/l.

For the majority of sites the catchment size was recorded and the annual average DOC concentration calculated for the majority of the monitoring sites. The average annual DOC concentration was calculated for the year 2000.

Trend analysis

Trend analysis was performed using the seasonal Kendall test (Hirsch et al. 1982). The seasonal Kendall test is used to assess the significance of any trend in the data sets and used to estimate the slope of any trend expressed as median annual change in the DOC concentration. The seasonal Kendall test is robust against departures from normality and resistant to outliers. Esterby (1997) notes that this approach cannot simultaneously include a range of co-variates nor accommodate complex situations, but as this study is concerned only with DOC trends and not the correlation with other parameters, and since DOC time series are not complex, the seasonal Kendall test is considered appropriate. For some sites (Harriman et al. 2001) a Monte Carlo regression method was used to corroborate the results.

Sites used by FRS-Freshwater Laboratory (Harriman et al. 2001)

Catchments selected for a study of long-term acidification of lakes and stream waters in Scotland selected 37 sites (sites 1–37; Table 1, Fig. 1). These sites were selected for having at least 15 years of continuous monitoring and were unaffected by agricultural activity. However, sites included moorland areas, forested areas and areas that underwent both afforestation and deforestation during the period of the study. The sites were selected and grouped to cover the range of non-marine S deposition in Scotland and therefore represent both strongly and moderately acidifying sites (Table 1, Fig. 1). Subsequently some of these sites were incorporated into the UK Acid Waters Monitoring Network (UKAWMN). The majority of sties are concentrated in areas C (south central Scotland) and area D (south west Scotland) where the most serious biological consequences of acidification have been reported. Detailed site descriptions and results of acidification studies have been reported for area A (Patrick et al. 1995), area B (Harriman et al. 1990; Patrick et al. 1995), area C (Harriman & Morrison 1982; Harriman et al. 1995; Harriman & Miller 1996), and for area D (Harriman et al. 1987, 1995). The majority of sites are

Table 1. Details of sites used in this study. Catchment number refers to Fig. 1. Significance of the trend is assessed at the 95% level. The median slope of those trends which are significant at the 95% level are highlighted in italic.

Site	Catchment no.	National grid ref.	Type of site	Period of record	Significant upward trend	Median slope
Harriman et al. (1991)						
Strontian Burn	1	NM824652	Stream	1985–2000	Yes	*0.12*
Coire nan Con	2	NM793688	Stream	1985–2000	Yes	*0.10*
Coire nan Arr	3	NG808422	Lake	1985–2000	Yes	*0.08*
Allt a Mharcaidh	4	NH882043	Stream	1985–2000	Yes	*0.10*
Lochnagar	5	NO253863	Lake	1985–2000	Yes	*0.07*
Kirkton Control	6	NN524237	Stream	1985–2000	Yes	*0.08*
Kirkton Experimental	7	NN527231	Stream	1985–2000	Yes	*0.09*
Kirkton Gauge	8	NN533220	Stream	1985–2000	Yes	*0.17*
Chon	9	NN421051	Lake	1985–2000	Yes	*0.12*
Tinker	10	NN445068	Lake	1985–2000	Yes	*0.10*
Burn 2	11	NN388043	Stream	1985–2000	Yes	*0.19*
Burn 5	12	NS438992	Stream	1985–2000	Yes	*0.20*
Burn 6	13	NS438989	Stream	1985–2000	Yes	*0.17*
Burn 7	14	NS451985	Stream	1985–2000	Yes	*0.23*
Burn 9	15	NS466968	Stream	1985–2000	Yes	*0.40*
Burn 10	16	NS469988	Stream	1985–2000	Yes	*0.20*
Burn 11	17	NS470988	Stream	1985–2000	Yes	*0.53*
Corrie	18	NS485958	Stream	1985–2000	Yes	*0.40*

Dargall Lane	19	NX452787	Stream	1978–2000	Yes	*0.08*
Green Burn	20	NX478793	Stream	1978–2000	Yes	*0.26*
Enoch	21	NX444857	Lake	1978–2000	No	0.00
Arron	22	NX444837	Lake	1978–2000	Yes	*0.17*
Neldricken	23	NX443825	Lake	1978–2000	Yes	*0.14*
Valley	24	NX438818	Lake	1978–2000	Yes	*0.13*
Narroch	25	NX453815	Lake	1978–2000	Yes	*0.13*
Round Locj of Glenhead	26	NX448802	Lake	1985–2000	Yes	*0.02*
Long Loch of Glenhead	27	NX446806	Lake	1985–2000	Yes	*0.20*
Dry Loch of Dungeon	28	NX467858	Lake	1985–2000	Yes	*0.18*
Long Loch of Dungeon	29	NX467838	Lake	1985–2000	Yes	*0.17*
Round Loch of Dungeon	30	NX466848	Lake	1985–2000	Yes	*0.20*
Harrow	31	NX33867	Lake	1985–2000	Yes	*0.07*
Minnoch	32	NX533857	Lake	1985–2000	Yes	*0.10*
Dungeon	33	NX528842	Lake	1985–2000	Yes	*0.10*
Grannoch	34	NX548715	Lake	1985–2000	Yes	*0.86*
Riecawr	35	NX442937	Lake	1985–2000	Yes	*0.24*
Macaterick	36	NX478006	Lake	1985–2000	Yes	*0.25*
Doon	37	NX478006	Lake	1985–2000	Yes	*0.23*
Kin cardine region						
Carron Water – Tewel Ford	38	NO828853	Stream	1988–2001	No	0.08
Carron Water – Stonehaven	39	NO874857	Stream	1988–2001	No	0.07
Catterline Burn	40	NO868785	Stream	1988–2000	No	0.00

Table 1. (continued)

Site	Catchment no.	National grid ref.	Type of site	Period of record	Significant upward trend	Median slope
Berv. Water – Inverbervie GS	41	NO832729	Stream	1988–2001	Yes	*0.07*
Dee region						
River Dee – Linn of Dee	42	NO061897	Stream	1988–2001	Yes	*0.10*
River Dee – Ballater Brdige	43	NO372956	Stream	1988–2000	Yes	*0.11*
River Dee – Potarch Bridge	44	NO608974	Stream	1988–2000	Yes	*0.09*
River Dee – Park Bridge	45	NO982796	Stream	1988–2000	Yes	*0.10*
River Dee – Milltimber	46	NJ858004	Stream	1988–2001	Yes	*0.16*
River Dee – Bridge of Dee	47	NJ929035	Stream	1988–2000	Yes	*0.10*
Clunie Water – Braemar	48	NO151915	Stream	1988–2000	Yes	*0.09*
River Gairn – Bridge of Gairn	49	NO352971	Stream	1988–2000	Yes	*0.17*
River Muick – Bridgend	50	NO367948	Stream	1988–2000	Yes	*0.15*
Water of Tanar	51	NO505972	Stream	1988–2000	Yes	*0.14*
Dinnet Burn – Mill of Dinnet	52	NO468991	Stream	1989–2000	Yes	*0.24*
Tarland Burn – Aboyne	53	NO531982	Stream	1989 -2001	Yes	*0.12*
Water of Feugh – Bridge of Feugh	54	NO702950	Stream	1989–2000	Yes	*0.17*
Water of Dye – Bridge Bogandreip	55	NO663910	Stream	1989–2000	Yes	*0.30*
Sheeoch Burn	56	NO773961	Stream	1988–2001	Yes	*0.15*
Leuchar Burn	57	NJ783066	Stream	1988–2001	Yes	*0.18*
Culter Burn	58	NJ835005	Stream	1988–2000	Yes	*0.30*
Crynoch Burn	59	NJ858001	Stream	1988–2000	Yes	*0.24*
River Quoich – Quoich Water	60	NO118911	Stream	1983–2001	Yes	*0.07*

Clunie Water – Baddoch Burn	61	NO136832	Stream	1983–2001	Yes	*0.10*
River Muick – Loch Muick outlet	62	NO305853	Stream	1983–2001	Yes	*0.11*
River Muick – Allt Darrarie	63	NO309851	Stream	1983–2001	Yes	*0.15*
River Muick – Glas Allt	64	NO276824	Stream	1983–2001	Yes	*0.07*
Water Feugh	65	NO640924	Stream	1983–2001	Yes	*0.11*
River Lui	66	NO069898	Stream	1984–2001	Yes	*0.08*
Callater Burn	67	NO156882	Stream	1984–2001	Yes	*0.10*
Don region						
Cock Bridge	68	NJ257092	Stream	1988–2001	Yes	*0.10*
Glenkindie House	69	NJ418141	Stream	1988–2000	Yes	*0.10*
Bridge of Alford	70	NJ562172	Stream	1988–2000	Yes	*0.10*
Inverurie Brdige	71	NJ777207	Stream	1988–2000	Yes	*0.13*
Kinkell Church	72	NJ784193	Stream	1988–2000	No	0.10
Parkhill Bridge	73	NJ889141	Stream	1988–2000	Yes	*0.10*
Grandholm Bridge	74	NJ898113	Stream	1988–2001	Yes	*0.10*
Seaton Park	75	NJ941097	Stream	1988–2000	Yes	*0.09*
Deskry Water	76	NJ387123	Stream	1988–2000	Yes	*0.14*
River Urie – Balhalgardy	77	NJ721260	Stream	1988–2001	Yes	*0.08*
River Urie – Urie Cottage	78	NJ784205	Stream	1988–2001	Yes	*0.06*
River Ythan						
Auchterless	79	NJ713412	Stream	1988–2001	Yes	*0.05*
Tifty	80	NJ775408	Stream	1988–2001	Yes	*0.05*
Methlick	81	NJ856375	Stream	1988–2001	Yes	*0.10*

Table 1. (continued)

Site	Catchment no.	National grid ref.	Type of site	Period of record	Significant upward trend	Median slope
Ardlethen	82	NJ924308	Stream	1988–2001	Yes	*0.09*
Ellon	83	NJ956303	Stream	1988–2001	Yes	*0.09*
Fordoun Burn	84	NJ762377	Stream	1988–2001	Yes	*0.10*
Little Water	85	NJ842393	Stream	1988–2001	Yes	*0.10*
Ebrie Burn – Arnage	86	NJ837252	Stream	1988–2001	Yes	*0.13*
Bronie Burn	87	NJ837252	Stream	1988–2001	No	*0.10*
Bronie Burn – Hillhead	88	NJ923304	Stream	1988–2001	Yes	*0.07*
Forvie Burn	89	NK003292	Stream	1988–2001	No	0.10
Tarty Burn	90	NJ975269	Stream	1988–2001	Yes	*0.10*
Ugie Water						
North Ugie Water	91	NJ943555	Stream	1988–2000	Yes	*0.35*
North Ugie Water – Mill of Gaval	92	NJ995517	Stream	1988–2000	Yes	*0.31*
North Ugie Water – Millbank	93	NK0442494	Stream	1988–2000	Yes	*0.30*
South Ugie Water	94	NJ938482	Stream	1988–2000	Yes	*0.21*
South Ugie Water- Abbey Bridge	95	NJ965481	Stream	1988–2000	Yes	*0.10*
South Ugie Water – Mintlaw	96	NK002469	Stream	1988–2000	Yes	*0.10*
River Ugie – Inverugie	97	NK101482	Stream	1988–2000	Yes	*0.20*
Buchan region						
Tore Burn	98	NJ839657	Stream	1988–2000	Yes	*0.17*
Philorth Water 1	99	NJ997611	Stream	1988–2000	Yes	*0.18*

Philorth Water 2	100	NK018644	Stream	1988–2000	Yes	*0.22*
Burn Strathbeg	101	NK065598	Stream	1988–2001	Yes	*0.30*
Banff						
Buckie Burn	102	NJ419656	Stream	1989–2001	Yes	*0.24*
Rathven Burn	103	NJ437663	Stream	1989–2000	No	0.23
Deskford Burn	104	NJ507673	Stream	1989–2001	Yes	*0.30*
Scattery Burn	105	NJ555657	Stream	1989–2001	No	0.12
Durn Burn	106	NJ592658	Stream	1989–2001	Yes	*0.10*
Boyne Burn	107	NJ610654	Stream	1989–2001	Yes	*0.13*
Blyndie Burn	108	NJ668645	Stream	1989–2001	Yes	*0.08*
Deveron region						
Cairnford Bridge	109	NJ487406	Stream	1989–2000	No	0.14
Avochie	110	NJ533472	Stream	1989–2000	No	0.01
Marnoch	111	NJ605496	Stream	1989–2000	No	−0.01
Bridge Alvah	112	NJ680611	Stream	1989–2001	No	0.25
River Isla – Drummuir	113	NJ378441	Stream	1989–2000	Yes	*0.11*
River Isla – Montgrew	114	NJ449519	Stream	1989–2000	Yes	*0.20*
River Isla – Grange	115	NJ475516	Stream	1989–2001	Yes	*0.30*
River Isla – Birdge Isla	116	NJ520468	Stream	1989–2000	Yes	*0.23*
River Bogie	117	NJ502272	Stream	1989–2000	Yes	*0.23*
Burn Davidston	118	NJ410466	Stream	1989–2000	No	0.09
Forgue Burn	119	NJ611449	Stream	1989–2001	Yes	*0.10*
Idoch Water	120	NJ724494	Stream	1989–2000	No	0.15
Cairnie Burn	121	NJ518474	Stream	1989–2000	No	0.10

Table 1. (continued)

Site	Catchment no.	National grid ref.	Type of site	Period of record	Significant upward trend	Median slope
Priest's Water	122	NJ520358	Stream	1989–2000	Yes	*0.07*
Spey region						
Garva Bridge	123	NN522948	Stream	1989–2001	Yes	*0.19*
Kinguissie	124	NN759998	Stream	1989–2000	Yes	*0.22*
Fochabers	125	NJ341595	Stream	1988–2001	Yes	*0.23*
Dufftown	126	NJ324391	Stream	1989–2001	Yes	*0.14*
River Fiddich	127	NJ329408	Stream	1989–2000	Yes	*0.19*
River Livet – Downan	128	NJ185304	Stream	1989–2000	Yes	*0.13*
Conglass Water	129	NJ148222	Stream	1989–2000	No	0.10
River Avon – Tomintoull	130	NJ162174	Stream	1992–2000	Yes	*0.23*
River Avon – Deinasheigh	131	NJ183359	Stream	1989–2000	Yes	*0.18*
River Luineag	132	NH956096	Stream	1989–2000	Yes	*0.23*
Aberlour Burn	133	NJ264427	Stream	1989–2000	No	0.03
Rothes Burn – Broad Burn	134	NJ278492	Stream	1989–2000	No	0.44
Mulben Burn – Auchroisk	135	NJ335518	Stream	1992–2000	Yes	*0.28*
Mulben Burn – Spey confluence	136	NJ320518	Stream	1989–2000	Yes	*0.20*
River Tromie	137	NN789995	Stream	1989–2000	Yes	*0.13*
River Feshie	138	NH852043	Stream	1989–2000	No	0.08
Knockando Burn	139	NJ191419	Stream	1993–2000	No	0.30
River Calder	140	NN775987	Stream	1989–2000	Yes	*0.12*
Milton Burn	141	NH896127	Stream	1989–2000	Yes	*0.20*

River Gynack	142	NH749029	Stream	1983–2001	Yes	*0.15*
Allt Fheanagan	143	NH851971	Stream	1983–2001	Yes	*0.08*
Allt Rhuadh	144	NH859010	Stream	1983–2001	Yes	*0.07*
Allt an T'Slugain	145	NH865212	Stream	1983–2001	Yes	*0.19*
Lossie						
Torwinny	146	NJ133488	Stream	1984–2001	Yes	*0.29*
C–loddach	147	NJ201584	Stream	1989–2000	Yes	*0.50*
Sherrifhills	148	NJ194626	Stream	1989–2000	Yes	*0.46*
Arthu's Bridge	149	NJ253672	Stream	1990–2001	Yes	*0.30*
Blackburn	150	NJ194610	Stream	1989–2000	Yes	*0.20*
Linkwood Burn	151	NJ239623	Stream	1989–2000	Yes	*0.24*
Loch na Bo	152	NJ281592	Stream	1990–2001	No	0.01
Tycock Burn – Moycroft	153	NJ229627	Stream	1989–2000	Yes	*0.14*
North Pennines						
Broken Scar	154	NZ259139	Stream	1971–2000	Yes	*0.10*
Warkworth	155	NU234044	Stream	1962–2000	Yes	*0.03*
Wearhead	156	NY858395	Reservoir	1971–2000	No	0.00
Great Dun Fell X	157	NY701297	Lake	1991–2000	Yes	*1.52*
Great Dun Fell Y	158	NY701297	Lake	1991–2000	Yes	*1.48*
Troutbeck	159	NY756326	Stream	1993–2000	Yes	*0.62*
UKAWMN sites						
Scoat Tarn	160	NY159104	Lake	1988–2000	Yes	*0.08*

Table 1. (continued)

Site	Catchment no.	National grid ref.	Type of site	Period of record	Significant upward trend	Median slope
Burnmoor Tarn	161	NY184044	Lake	1988–2000	Yes	*0.15*
River Etherow	162	SK116996	Stream	1988–2000	Yes	*0.29*
Old Lodge	163	TQ456294	Stream	1988–2000	Yes	*0.28*
Llyn Llagi	164	SH649483	Lake	1988–2000	Yes	*0.08*
Afon Gwyi	165	SN842854	Stream	1988–2000	Yes	*0.10*
Beaghs Burn	166	D173297	Stream	1988–2000	Yes	*0.57*
Bencrum River	167	J304250	Stream	1988–2000	Yes	*0.27*
Blue Loough	168	J327252	Lake	1990–2000	Yes	*0.19*
Coneyglen Burn	169	H641884	Stream	1990–2000	Yes	*0.72*
Plynlimon						
Afon Hafren Lower	170	SN843877	Stream	1983–2001	Yes	*0.04*
Afon Hafren Upper	171	SN828892	Stream	1990–2001	No	0.00
Afon Hore Upper	172	SN831869	Stream	1984–2001	Yes	*0.07*
Afon Cyfi	173		Stream	1984–2001	Yes	*0.09*
Beddgelert						
D1	174	SH557513	Stream	1985–2000	No	
D2	175	SH555509	Stream	1985–2000	Yes	*0.04*
D4	176	SH552508	Stream	1985–2000	Yes	*0.02*
Forestry Commission						
Cefn Hendre	177	SN872808	Stream	1991–2001	Yes	*0.10*

Afon Nant yr Helyg	178	SN798285	Stream	1991–2001	No	0.20
Nant y Fedw	179	SN836556	Stream	1991–2001	Yes	*0.14*
Irton	180	SN833557	Stream	1991–2001	Yes	*0.17*
Afon Ceunant y Garnedd	181	SH704518	Stream	1991–2001	No	0.09
Nant Iago	182	SH691078	Stream	1991–2001	Yes	*0.10*
Llechwedd Mawr	183	SN753910	Stream	1991–2001	No	0.06
Nant Ceiswyn	184	SH778104	Stream	1991–2001	Yes	*0.10*
Crugnant	185	SN755640	Stream	1991–2001	No	0.11
Nant y Gerddinen	186	SN715469	Stream	1991–2001	Yes	*0.10*
Afon Colwyn	187	SH576508	Stream	1991–2001	Yes	*0.10*
Nant Milwyn	188	SN789737	Stream	1991–2001	Yes	*0.13*
Yorkshire Water reservoirs						
Scar House	189	SE069773	Reservoir	1980–2002	Yes	*0.09*
Angram	190	SE038765	Reservoir	1981–2002	Yes	*0.05*
Upper Barden	191	SE012608	Reservoir	1980–2002	Yes	*0.20*
Lower Barden	192	SE035569	Reservoir	1981–2002	No	0.02
Lower Laithe	193	SE038377	Reservoir	1980–2002	Yes	*0.05*
Thornton Moor	194	SE058338	Reservoir	1980–2001	No	0.00
Broomhead	195	SK269958	Reservoir	1961–2002	Yes	*0.06*
ECN sites						
Wytham	196	SP459094	Stream	1993–2001	No	0.01
Sourhope	197	NT867218	Stream	1993–2001	No	0.00
Glenshaugh	198	NO664799	Stream	1993–2001	Yes	*0.35*

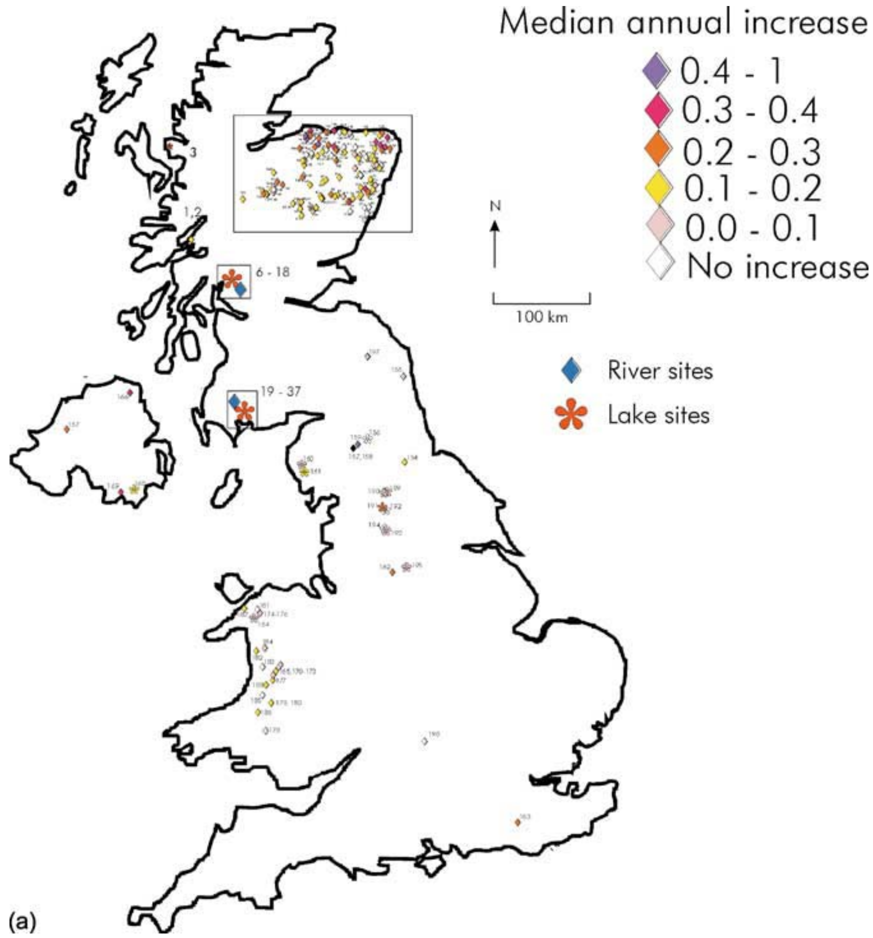

Fig. 1. (a) Location of sites used in this study. Site numbers refer to Table 1. Sites 6–37 are too close to be distinguished, but locality details are provided on Table 1. (b) Detailed location map of sites used in this study in north east Scotland. Site numbers refer to Table 1.

underlain by granites, schists and gneisses, one exception being sites within the Kirkton catchment where limestone bands are present in the catchment.

The temporal pattern of sampling at sites was variable, details of which can be found in Harriman et al. (2001). Methods for the initial period of study at the sites are described in Harriman et al. (1987); post-1988 methods accord with those of the UKAWMN.

Scottish Environmental Protection Agency (SEPA) monitoring sites

The one region of the SEPA does monitor regularly for DOC, unlike either other regions within SEPA nor the Environment Agency of England and

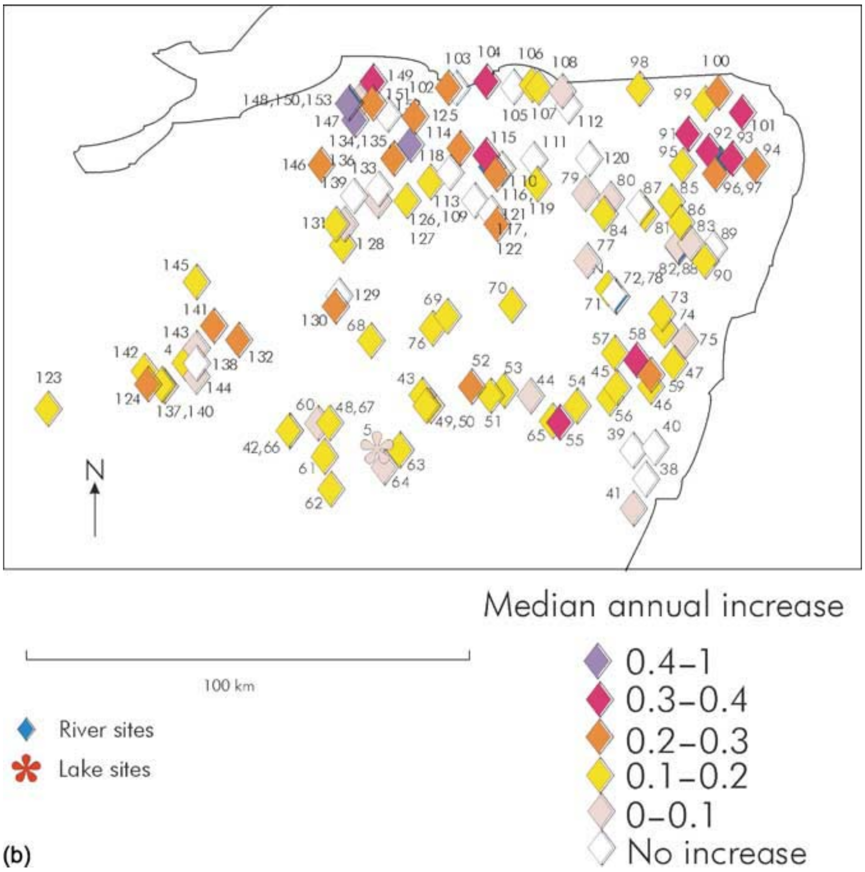

Fig. 1. (continued)

Wales. Data have been collated for SEPA monitoring sites in the north east of Scotland. Sites are sampled approximately monthly with most sampling going back to 1988 (sites 38–153). Several of the sites have been used in previous studies and further site details can be found in Aitkenhead et al. (1999), Aitkenhead and McDowell (2000), and Hope et al. (1997b). Analytical methods were the same as those of the FRS-Freshwater Laboratory.

North Pennines

These sites have been grouped together for geographical reasons sited as they are all around the three catchments of the Tees, Wear and Coquet and because they are sited around the particularly long water colour records for Broken Scar, Wearhead and Warkworth (sites 154–159; Table 1, Fig. 1). The long records of Broken Scar, Wearhead and Warkworth are river water treatment works operated by Northumbrian Water. At these sites water colour, as opposed to DOC measurements, are measured daily by spectrographic means and recorded as Hazen. These sites represent the longest, most-consistently sampled sites in the study. The calibration of colour against DOC in these catchments is outlined in Worrall et al. (2003b). Details of the time series for Warkworth, Wearhead and Broken Scar have been discussed in detail in Worrall et al. (2003a) and Worrall and Burt (in press).

Three other sites in the North Pennines have been included in the study, all of them in the headwaters of the Tees catchment – Troutbeck, and two sites on Great Dun Fell. The Troutbeck catchment is part of the Moor House National Nature Reserve and monitored as part of ECN (Sykes & Lane 1996). The behaviour of DOC in this catchment is described in Adamson et al. (2001), and Worrall et al. (in press). Two pool sites have been monitored monthly for DOC concentrations since 1991(Great Dun Fell X and Y – sites 157 and 158; Table 1, Fig. 1). The monitoring of these two pools has been described in Scott et al. (1998, 2001).

UKAWMN

Local monitoring of acidification has been ongoing in the UK since the 1970s (e.g. Harriman et al. 2001; Helliwell et al. 2001). An integrated national programme for acidification monitoring has been ongoing since 1988 at 21 acid-sensitive sites throughout the UK. These UKAWMN sites consist of 10 stream sites (stream sites 160–169) and 11 lakes. The sites are dominated by moorland grazing, but five catchments contain coniferous forests. Stream sites are monitored on a monthly basis and lake sites on a quarterly basis. Further details of sites can be found in Patrick et al. (1995) and details of analytical methodology can be found in Montieth and Evans (2000).

CEH monitoring sites

The Plynlimon catchment has long been used as an upland research catchment (Neal 1997). As a research catchment three sub-basins have been regularly monitored for their hydrochemistry including DOC. The catchment is divided into three sub-catchments (catchments 170–172; Fig. 1): the Lower Hafren has been subject to weekly DOC measurements since 1983; the Upper Hore since 1984; the Upper Hafren since 1990. The Lower Hafren is partly forested but has undergone felling during the period of the record. The Upper Hafren, in contrast, is dominated by moorland peat. The Upper Hore has remained forested throughout the period of the study. Analytical techniques are described in Neal et al. (1997). Fluvial flux of carbon from the Upper

Hafren has been discussed in Dawson et al. (2002) and the increasing trend in DOC noted in Neal et al. (2001). Two further Plynlimon catchments are included; Afon Gwy is the catchment to the south of the Hafren and Hore catchments and is one of the UKAWMN sites. The next catchment further south is Afon Cyff.

Five streams in Beddgelert Forest, North Wales, have been sampled at least fortnightly since 1984 by CEH Bangor. Four sites are forested with sitka spruce, which has been partially felled and replanted during the monitoring period. These sites have catchment areas ranging from 0.014 to 1.6 km^2. The fifth site is located on adjacent moorland, and has an area of 0.37 km^2. All sites are located on acid podzolic soils, underlain by Ordovician slates, shales and mudstone.

Yorkshire Water reservoirs

Records of water colour have been maintained for a series of Yorkshire Water water treatment works that receive water from seven reservoirs all situated in the Southern Pennines (sites 189–195). Water colour time series for each of these sites go back to at least 1981 and one case back to 1961. However, the sampling and measurement of water colour over the period has not been consistent. Watts et al. (2001) discuss the detail of the data collection and provide a quantitative description of the records. The calibration of water colour against DOC for these records was performed using the same approach as for the Northumbrian Water records (Worrall et al. in press).

ECN

The ECN monitors a range of lakes and catchments throughout the UK and a number of these sites are included in the study of Harriman et al. (2001); within the UKAWMN; discussed above as part of the North Pennine sites. However, three ECN monitoring sites have not been included in any previous grouping – Wytham, Sourhope and Glenshaugh (sites 186–188; Fig. 1, Table 1). These sites have been monitored on a weekly basis since 1993 for a comprehensive range of environmental parameters including DOC in stream water. Methodologies used throughout the ECN are detailed in Sykes and Lane (1996). The first 5 years DOC records from these sites are discussed in Miller et al. (2001).

Forestry Commission sites

The sites are distributed across the acid sensitive upland area of mid and North Wales and comprise 10 forest and 2 moorland streams. All forest streams drain catchments with at least 40% forest cover, much of which is located above 300 m elevation. Catchment area ranges from <1 to $15\,km^2$ and soils comprise a mixture of ferric stagnopodzols, brown podzolics, stagnohumic gleys, humic rankers and peat. Stream water samples have been collected monthly since 1991.

Results

In all, trends for 198 catchments were examined, of which, 29 are for lakes, 8 for water supply reservoirs and the remainder 161 sites, are for streams and rivers. Of these 198 sites, 153 sites (77%) show a significant upward trend, significant by the seasonal Kendall test at the 95% significance level. The remaining 45 sites do not show a significant increasing DOC trend at the 95% level, of these 45 sites, 2 show a downward trend, but neither of these measured downward trends are significant at the 95% level. Of the 29 lake sites, only 1 (3%) shows no significant (at the 95% level) upward trend; equally, 2 of the 8 reservoirs sites (25%) shows no significant upward trend. The average trend for all sites was 0.17 mg C/l/year, with a standard deviation of 0.19 mg C/l/year (Fig. 2). If it is assumed that the distribution can be approximated by a normal distribution it is possible to estimate that there is an 18% chance of a downward trend. However, no discrimination on the significance of these trends is made in the analysis of this distribution. For the

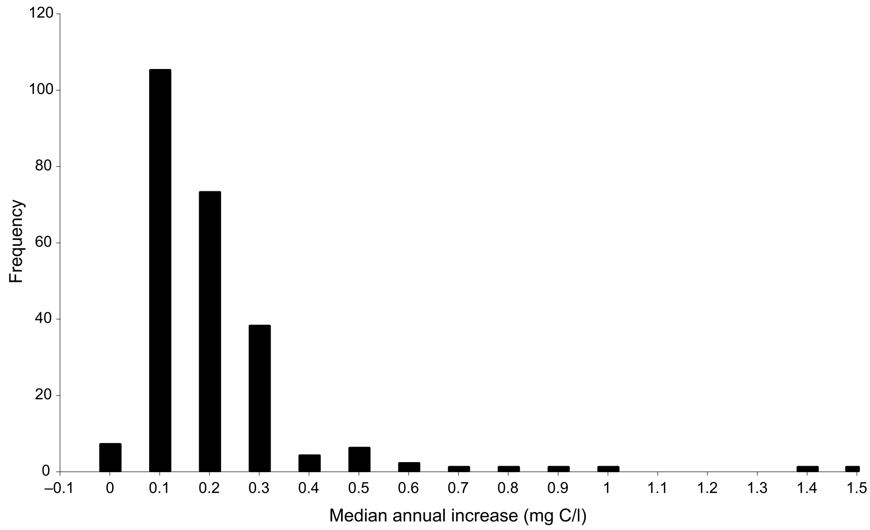

Fig. 2. Frequency distribution of calculated median annual increases for all 183 sites used in this study.

lakes sites only the average rise is 0.25 mg C/l/year, while that of reservoirs is 0.09 mg C/l/year. Based on the relationship found by Worrall et al. (2003b), a rise of 0.17 mg C/l/year is equal to approximately 4.5 Hazen/year.

The dataset presented here is dominated by shorter series, that is, those approximately 10 years in length. However, comparing the median annual increase of the those time series pre-1988 with post-1988 shows that the although the mean median annual increase increases from 0.145 mg C/l/year for pre-1988 sites to 0.185 mg C/l/year for post-1988 sites, there is no significant difference at the 95% level between the two sets of trends. The largest median annual increase was observed for the pools of Great Dun Fell (sites 157 and 158). The time series at Great Dun Fell shows a response to the severe drought of 1995 (Fig. 3) but the trend suggests that DOC concentrations were rising prior to 1995. Equally, to examine a series where there was no significant upward trend, the effect of the 1995 drought is less apparent, and the trend either side of the drought appears the same (Upper Hafren – site 171; Fig. 4). One of the longest of the time series (Warkworth – site 155; Fig. 5) shows that the severe drought of 1976 had a dramatic effect on the DOC trend. Prior to 1976 the trend through the 1960s is flat or downward, after 1976 the trend is steadily upward without further jumps despite there being further severe droughts in the mid-1980s and in 1995.

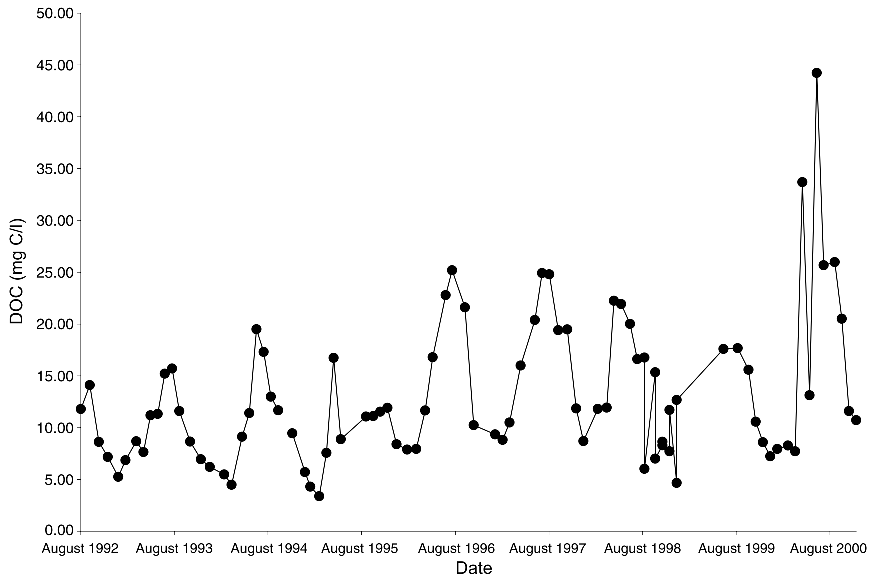

Fig. 3. Time series of DOC concentration from pool Y, Great Dun Fell.

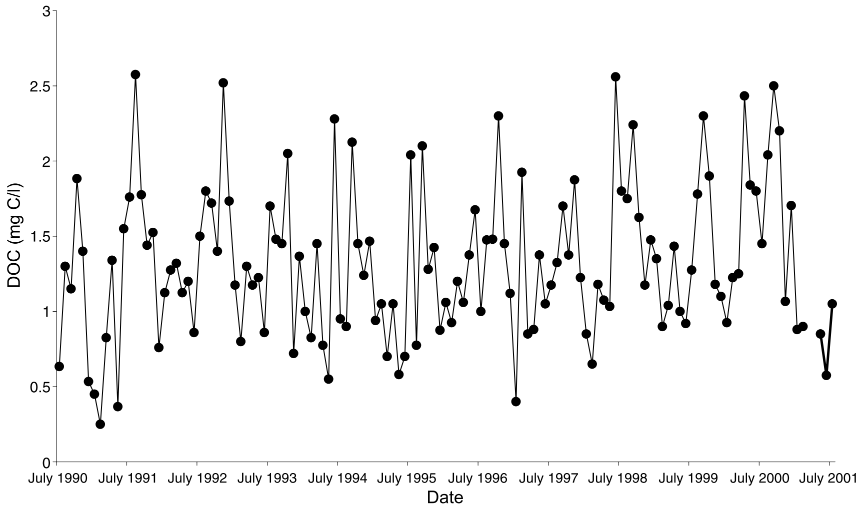

Fig. 4. Time series of DOC concentration from the Upper Hafron catchment, Plynlimon.

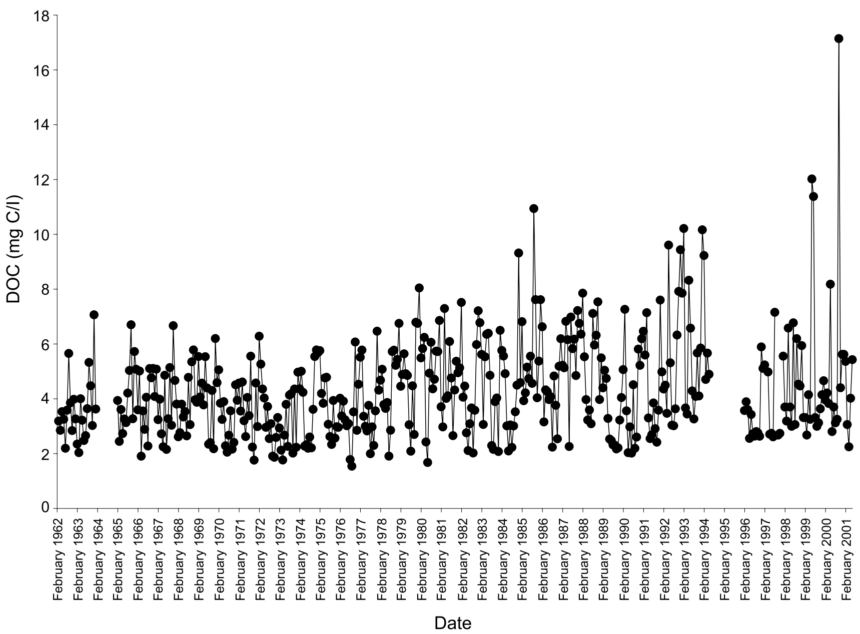

Fig. 5. Time series of DOC concentration from Warkworth.

A spatial analysis of the data is difficult because of the patchy distribution of the sites for which data were available (Fig. 1(a and b)). The majority of sites are concentrated in the north east of Scotland where intense sampling

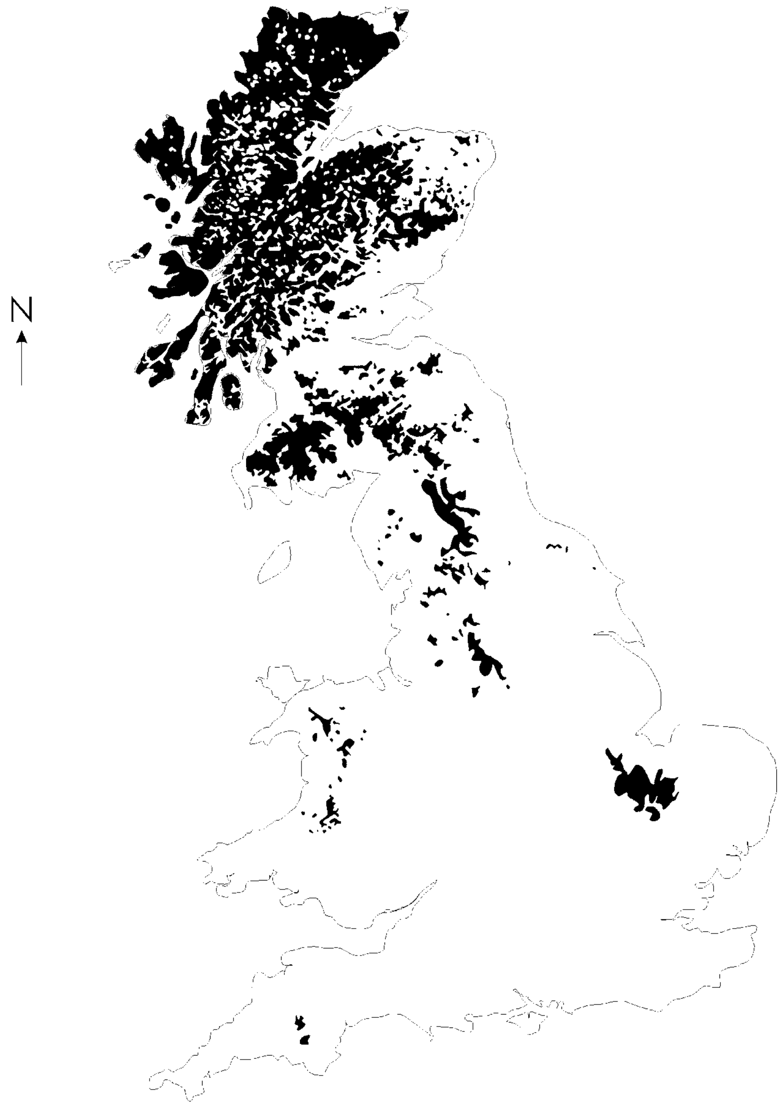

Fig. 6. Distribution of organic-rich soils in Britain, adapted from Milne and Brown (1997), based on soils >100 kt C/km^2.

has enabled analysis of local patterns of DOC trends. The 198 sites used in this study fall into 40 separate catchments, and of these separate catchments 36 show significant increases in DOC concentrations.

There is, unfortunately, insufficient spread of data to evaluate a north–south trend. Not surprisingly sites where long records of DOC concentrations exist are either where DOC is thought to be important in controlling water quality or biological change or acidification has been important. As a result most sites where DOC is monitored are associated with regions where soil carbon >100 kt/km^2 (Fig. 6). Indeed, DOC concentration in rivers is clearly associated with the percentage of peat cover within a catchment (Aitkenhead et al. 1999; Aitkenhead & McDowell 2000); however, two of the monitoring sites (sites 163 and 186) are in southern, lowland Britain and are not obviously associated with organic-rich soils. Old Lodge (site 163) shows a significant increasing trend in DOC concentrations, while Wytham (site 186) shows no significant trend. However, some sites (e.g. 19 and 21, Table 1) have shallow peaty soils and low DOC concentrations, but still show an increasing trend in those DOC concentrations. Of the remaining 196 sites where it is possible to believe that there are either peats, or at least organic-rich soils (soil carbon >100 kt/km^2; Fig. 3) are present somewhere within their catchment area, 40 show no significant trend. The reasons for a lack of significant increase are discussed below.

The majority of the sites are in the north east of Scotland, to test whether these sites distort the national picture, sites within the north east Scotland dataset (Fig. 1(b); sites 38–153) were compared with those sites from England, Wales and northern Ireland (sites 154–196; Fig. 1). The comparison shows that the mean median annual increase for the north east Scotland sites is 0.161 mg C/l/year while the mean median annual increase for the non-Scottish sites is 0.32 mg C/l/year; however, there is no significant difference between these two datasets at the 95% level.

The variation of the median annual increase in DOC with catchment size shows two possible trends in the data (Fig. 7). The first trend (Trend A; Fig. 7) is where the trend in DOC is independent of catchment size and is approximately constant at a median annual increase of 0.1 mg C/l. For the second trend (Trend B; Fig. 7) the median annual increase decreases with increasing catchment size. The smallest catchments in the data set have the greatest median annual increase (sites 157 and 158; Table 1). If the dominant or sole source of DOC within a catchment is the peats or organic-rich soils then the proportion of catchment that is covered by peat or organic-rich soils would be expected to decrease as the size of the catchment increases: thus, a negative correlation between median annual increase in DOC and catchment size would be expected. For the median annual increase to be independent of the catchment size, the proportion of the catchment area covered by DOC sources must increase in line with catchment size and the whole source must be undergoing a similar change leading to increased DOC release. The latter could well be true for some of the large Scottish catchments (e.g. site 47) where there are extensive organic-rich soils throughout the catchment (Fig. 6).

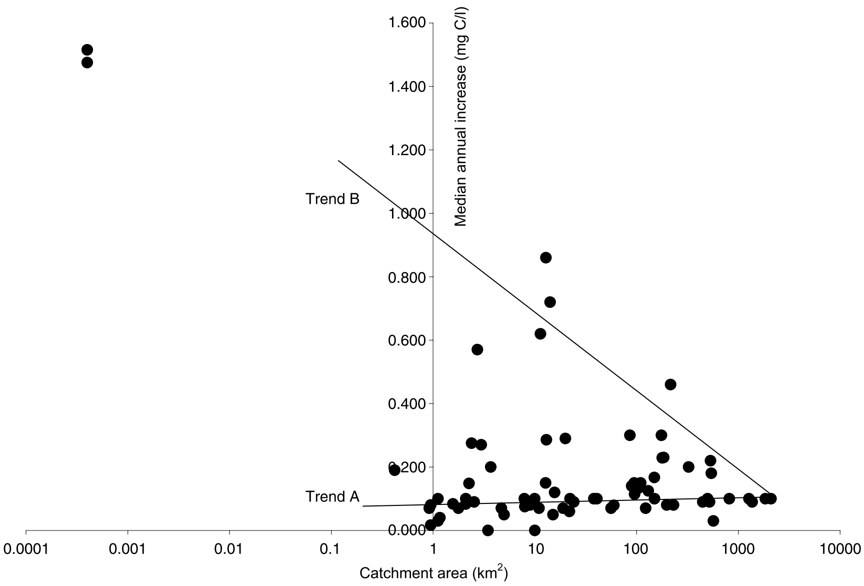

Fig. 7. Relationship between calculated median annual increase in DOC concentration and catchment size.

It is not possible to compare the trends calculated for all the 198 sites to the proportion of peats or organic-rich soils in their catchment. However, it is possible to compare the median annual increases to the annual average DOC concentration calculated for the year 2000. As the annual average DOC concentration is closely related to the percentage of the catchment area that is peat it can provide an index of the relationship between median annual increase of DOC and properties of the soil organic reserves within a catchment (Aitkenhead et al. 1999; Aitkenhead & McDowell 2000; Fig. 8). This comparison shows a general increase in median annual increase in the DOC concentration and the annual average DOC concentration at a monitoring site in the final complete year of monitoring. This relationship is significant at the 95% level and suggests that the larger the percentage of peat in the catchment the larger the increase in DOC concentration per year. However, the comparison between annual average and annual increase shows that even when average annual DOC concentration is as high as 13.9 mg C/l, no significant trend might still be observed. When the annual average DOC concentration is as high as 13.9 mg C/l the catchment would be expected to have a very high proportion of organic-rich soils in the catchment area suggesting that some peatlands are not undergoing increased loss of DOC.

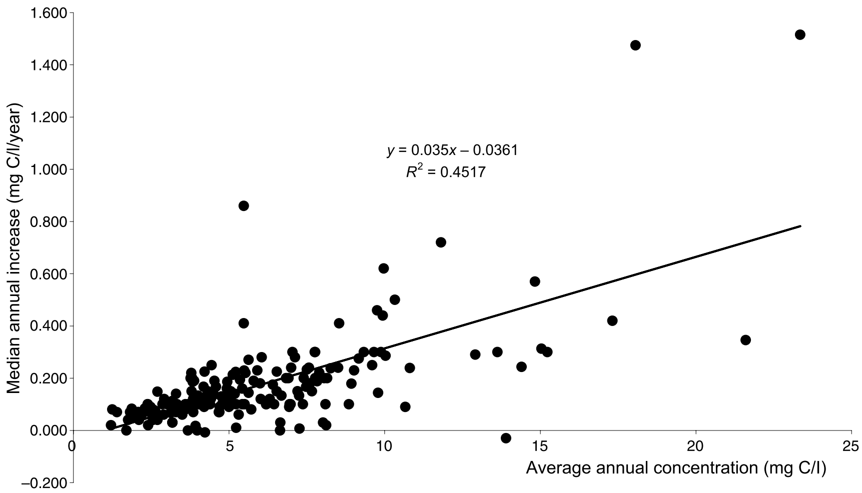

Fig. 8. The calculated median annual increase in DOC concentration in comparison to the average annual concentration of DOC in the year 2000 at each site included in the study.

Trends in DOC from outside the UK

The best comparisons with UK sites are those of similar latitude with similar peat catchments. Very few studies exist that are of similar length to those used in the study of the UK (e.g. Scarsbrook et al. 2000) or are cover a large spatial dataset but do not report figures for DOC (e.g. Alexander et al. 1998). Skjelkvåle et al. (2001) report trends in lakes in Finland, Norway and Sweden and show significant increases in 12% of the 344 monitored lakes over the period 1990–1999, and only 0.9% (4 sites) showed a significant decrease. There is a significant geographical contrast between sites, with the majority of sites that show an increasing trend in their DOC concentration situated south of 63 degrees north and dominantly in the west of the region, that is, where snow cover in winter is less.

Bouchard (1997) in a study of acidification of lakes in Quebec found that between 1985 and 1993, 17 out of 51 lakes showed statistically significant increases in DOC concentration with no lakes showing a significant decrease. In this study, the lakes that were recovering from acidification had the lowest DOC concentrations and the lowest increases in DOC concentration. Bouchard (1997) does not suggest a reason for this observation of increased DOC. However, they show that it was not caused by increased rainfall in the region leading to increased leaching of organic soils. Driscoll and Van Dreason (1993) found that decreases in DOC in lakes of the Adirondacks could be related to increasing availability of N leading to the mineralisation of organic N.

Asite and Klavins (1998) examined a 20-year record of monthly water colour and chemical oxygen demand (COD) for nine sites across Latvia; all these time series showing decreasing levels of colour and COD due to decreases in anthropogenic pollution and improved land-use practices. A similar cause but different outcome is noted by Siepak (1999) where increasing trends in DOC were noted due to increasing anthropogenic pollution and land-use change especially sewage treatment.

Export of DOC from UK rivers

Hope et al. (1997a) gave an estimate of DOC fluxes for British rivers as 0.688 Mt C for 1993. However, with significant increases in DOC concentration recorded for rivers draining peat catchments this must now be considered to be an underestimate. Given that this study and that of Hope et al. (1997a) share several rivers in common it is possible to update their estimate. An estimate of the DOC flux for the UK is based on the following assumptions. Firstly, that there has been no significant trend in river flow over the period 1993–2000. Secondly, the average annual increase in DOC concentration is linearly related to average annual DOC concentration, that is, those rivers with a higher flux will have a higher increase in flux and that this can be linearly related to linear increase already demonstrated (Fig. 5). Given these assumptions, the flux of DOC from UK rivers in 2002 is 0.86 Mt C and that the average annual increase in flux for the UK is 0.02 Mt C/year.

Discussion

What possible explanations have been proposed for rising DOC concentrations and does this review of trends lend credence for one mechanism over any other? The important feature of the trends in DOC concentrations examined in this study is their ubiquitous nature in both time and space. Any causative factor must be true for the whole of UK uplands and to have been operating since the 1960s.

Changing discharge could alter the concentration such that increases in DOC are observed. An overall decrease in the volume of discharge without a concomitant decrease in supply of labile carbon would result in an increase in DOC concentration. If the flux of carbon and the DOC concentration have both risen then there must be increased supply of carbon. Worrall et al. (2003a) have shown that, for two long-term DOC time series, not only have there been long term increases in DOC concentration but also long-term increases in carbon flux. Equally, no decreasing trend in river flows across the UK has been reported; indeed, the reverse might actually be the case as Werrity (2002) shows that, for 38 gauging stations across Scotland, 12 showed statistically significant increased runoff between 1970 and 1996 while none of the remaining 26 sites showed a significant decline in runoff. A similar result has been found for the North Pennines rivers included in this study, that is, that discharge either increased or showed no significant change (Worrall & Burt, in press). Future predictions of runoff suggest increases on the order of 10% by 2050 in Scotland and northern England, that is, regions of blanket peat, while parts of southern England may experience decreased river discharge (Arnell et al. 1997). The implication of increasing runoff is that increases in DOC concentrations may be buffered by increases in river discharge and that increases in DOC concentration alone may well underestimate the increase in carbon flux from UK rivers.

It is not necessary to decrease the total mean annual flow for flow to cause an increase in DOC concentration, that is, some change in a component of the flow could have caused a change in concentration. Such changes could include changes in the seasonal pattern of the flow, for example, a decrease in flow when the supply of mobile carbon is at its highest. For the UK there has been a recent trend for wetter winters and drier summers (Burt et al. 1998). Using the outputs from global circulation models, Conway (1998) and Hulme and Jenkins (1998) have shown that in Scotland and northern England, increases in runoff will be concentrated in the autumn and the winter (September–February). The early autumn period is of course the period of maximum DOC availability and thus increasing runoff at this time would mean that any increases in DOC concentration would be furthered masked. Furthermore, the same analysis of likely future changes suggests reductions in summer flows that could be indicative of lower water tables in blanket peats. Lower water tables in blanket peats would allow greater ingress of oxygen into the peat and lead to increased decomposition and enhanced DOC production.

Change in the source of the flow or some component of the flow as opposed to increases in overall flow could cause a rise in DOC concentrations. In a large catchment increased rainfall in the headwaters relative to the middle or lower reaches of the river could cause increases in DOC, or alternatively, the nature of the rainfall may changing causing increased storm runoff relative to baseflow without necessarily changing overall discharge. Tranvik and Jansson (2002) have suggested that change between runoff dominated by flow through subsoil horizons and flow through surface, organic-rich peat would result in increased DOC concentrations. This is true where the sub-soil horizons are mineral as opposed to organic layers, but in this dataset upward trends are observed for deep peats where runoff does not interact with any mineral horizons. This study cannot provide evidence on this possible mechanism.

When discussing whether changes in river chemistry have caused the observed increases, consideration of pH must be included. Increasing DOC production has been associated with decreasing mineral acidity (Krug & Frink 1983), but evidence from field observations is at best equivocal (Kullberg & Petersen 1987; Greive 1990a, b; Bouchard 1997). Hedin et al. (1990) and Wright (1989) have both shown that changes in DOC related to acidification are small or non-existent. A significant proportion of the sites included in this study are primarily monitored for purposes of assessing acidification of natural waters (sites 1–37 and 160–169) and as such it is easy to assess whether pH changes correlate with DOC changes. The ubiquitous nature of significant increases in DOC concentration would require an equally ubiquitous increase change in pH of streams and lakes. Indeed, UK uplands are showing initial indications of recovering from acidification (Evans & Montieth 2001). The observation that UK uplands are at least no longer acidifying means that over the time span covered by increases in DOC concentration found in this study UK uplands have both been going through acidification and recovering from it, that is, there is no consistent trend in acidification comparable to the trend observed in DOC concentration. Furthermore, not all catchments covered in this study have been subject to acidification (Evans et al. 2002; Worrall & Burt, in press). However, changes in acidity may result in changes in the composition of the DOC for which there is no evidence here.

Another possible component of water chemistry could be the nutrient status of the source areas. Nitrogen in UK upland streams does show some evidence of increasing over the same period of the increases observed in DOC concentrations even though N-deposition was not observed to change (Jenkins et al. 2001). The amount of stream nitrate in upland, non-forested catchments is not closely related to N-deposition and there is evidence of extensive N-saturation in upland environments (Harriman et al. 1998; Kernan & Allott 1999). Significant correlations have been found between DOC concentration and nitrate concentrations in some upland streams (Harriman et al. 1998). Eutrophication from N-deposition of uplands may be driving changes in the upland that are releasing DOC. Cole et al. (2000) have shown that the increasing activity of enchytraeid worms (the dominant invertebrate in upland peats) increases microbial activity in peat which in turn enhances nutrient mineralisation. Enchytraeid worm activity increases with temperature (Cole et al. 2002) and so as the climate warms enchytraeid worm activity would increase with consequences for microbial activity and N-mineralisation leading to increased losses of nitrate and DOC (Cole et al. 2002), however, the scale of increase observed by this study is too small compared to the changes in DOC observed in this study. Equally, Harriman et al. (1998) concluded that increases in nitrate concentration were the result of increasing DOC concentrations and not vice versa. Hence it is uncertain whether increased nitrate levels in upland streams are related to increased DOC levels or whether they are in fact separate consequences of a common cause namely temperature increase.

Over the period of the records that could be included in this study temperatures in the UK have been rising (Parker et al. 1992), with increases of the order of 1 °C over the period of this study (Worrall et al. 2003a). Temperature could have two effects on release of DOC. Firstly, increasing rates of decomposition either directly making decomposition reactions faster or indirectly via stimulating faunal activity (e.g. Cole et al. 2002). Secondly, increases in temperature could lead to increased drawdown of water tables leading to increases in the depth of oxidation. However, predictions of only a 1 °C rise must be matched against approximate 100% increases over the same period in the DOC concentrations, that is, temperature changes appear too small unless such temperature changes are amplified by other mechanisms to give very large effects on reaction rates or water tables.

One possible accentuating factor is the existence of enzymic latch mechanisms as discussed above (Freeman et al. 2001a, b). Such a mechanism means that, as a consequence of periods of drought DOC production in wetlands can be turned on without being turned off as water tables recover. During the period covered by the records in this study, two severe droughts occurred throughout the UK – 1976 and 1995. Although estimating return periods is notoriously uncertain, the severe drought has a return period of 75 years and 1995 of 28 years in the Northern Pennines (Burt et al. 1998). The trends reported upon in this study may reflect recovery from two severe droughts. Indeed, long term Yorkshire water colour records also provide some evidence of recovery from both the 1976 and 1995 droughts, and of step-change increases in water colour at one reservoir following the droughts of 1976 1990 and 1995 (Watts et al. 2001).

Changes in land management have been linked to observed changes in DOC concentrations. Changes in land management could also have the same effect. Afforestation has been common practice in UK uplands and this disturbance has led to patterns of carbon release similar to that of other nutrients, that is, high values post-disturbance leading to a new equilibrium position. Afforestation is not the only management change that upland peat can undergo, afforestation is often preceded by drainage of the peat and large areas of upland peat were drained in order to improve grazing. Ratcliffe and Oswald (1988) have estimated that 75% of UK peat has been affected by some form of drainage. Drainage of peat could draw down water tables in the immediate area of the drain, allowing ingress of oxygen and thus stimulating DOC production. There is no published information on the effect of gripping (artificial drainage) *per se* on DOC production in UK peat, although several studies in the UK report increased runoff and peak flows even after 30 years (Robinson 1986; Robinson & Newson 1986). However, land-use change has not been as extensive as the observed increase in DOC concentration and so peat drainage and afforestation can at best only be accentuating factors.

Finally, it must be pointed out that 24 of the sites were identified as being in catchments with significant coverage of organic-rich soils yet showed no significant upward trend in DOC concentration. This must mean that some catchments are well buffered against changes which elsewhere seem to have been effective drivers of increases in DOC concentration.

Conclusions

This study has examined the monthly trend of DOC concentrations for 198 sites across the UK, including stream, lakes and water supply reservoirs draining catchments that vary in size between 400 m^2 and 2100 km^2. The records examined were all over 8 years in length, including some going back as far as 1961. The seasonal Kendall test was used to test significance and magnitude of the trend at these sites, with 153 (77%) showing an upward trend in DOC concentration significant at the 95% level, the remaining 45 (23%) show no significant trend. No site showed a significant decrease in DOC concentration. The average annual increase in DOC for the examined sites is 0.17 mg C/l. The greatest annual increases in DOC concentration were found for those sites with the largest average DOC concentration and there is some suggestion that the largest annual increases are observed for the smallest catchments. These increases in DOC concentration means that DOC flux from UK rivers for 2002 is approximately 0.86 Mt C/year, and increasing at 0.02 Mt C/year. Increases in river discharge in northern Britain means that increases in DOC concentration may be being hidden. The increase in DOC concentrations is sufficiently ubiquitous in time and space to discount several possible explanations for its occurrence. Changes in acidification and pH are not sufficiently widespread in time or space. The most likely driver for increasing DOC concentrations is temperature increase and the frequency of severe droughts, have occurred over a sufficient area and over the correct time span to provide an explanation. However, changes driven by climate change might be accentuated by land-use changes and by eutrophication of the uplands.

References

Adamson JK, Scott WA, Rowland AP & Beard GR (2001) Ionic concentrations in a blanket peat bog in northern England and correlations with deposition and climate variables. Eur. J. Soil Sci. 52: 69–80

Aitkenhead JA & McDowell WH (2000) Soil C:N ratio as a predictor of annual riverine DOC flux at local and global scales. Global Biogeochem. Cy. 14: 127–138

Aitkenhead JA, Hope D & Billet 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

Alexander RB, Slack JR, Ludtke AS, Fitzgerald KK & Schertz TL (1998) Data from selected US Geological Survey national stream water quality monitoring networks. Water Resour. Res. 34: 2401–2405

Arnell NW, Reynard N, King R, Proudhomme C & Branson J (1997) Effects of climate change on river flows and groundwater recharge: guidelines for resource assessment. Environment Agency Technical Report W82, Bristol, UK

Asite E & Klavins M (1998) Assessment of the changes of COD and color in rivers of Latvia during the last twenty years. Environ. Int. 24: 637–643

Bouchard A (1997) Recent lake acidification and recovery trends in southern Quebec, Canada. Water Air Soil Pollut. 94: 225–245

Burt TP, Adamson JK & Lane AMJ (1998) Long-term rainfall and streamflow records for north central England: putting the Environmental Change Network site at Moor House, Upper Teesdale, in context. Hydrol. Sci. J. 43: 775–787

Cannell MGR, Dewar RC & Pyatt DG (1993) Conifer plantations on drained peatlands in Britain: a net gain or loss of carbon? Forestry 66: 353–369

Cole L, Bardgett RD & Ineson P (2000) Enchytraeid worms (oligochatea) enhance mineralisation of carbon in upland soils. Eur J. Soil Sci. 51: 185–192

Cole L, Bardgett RD, Ineson P & Adamson JK (2002) Relationships between enchytraeid worms (Oligochaeta), climate change, and the release of dissolved organic carbon from blanket peat in northern England. Soil Biol. Biochem. 34: 599–607

Conway D (1998) Recent climate variability and future climate change scenarios for Great Britain. Prog Phys Geog 22: 350–374

Dawson JJC, Billet MF, Neal C & Hill S (2002) A comparison of particulate, dissolved and gaseous carbon in two contrasting upland streams in the UK. J. Hydrol. 257: 226–246

Esterby SR (1997) Review of methods for detection and estimation of trends with emphasis on water quality applications. In: Peters NE, Bricker OP & Kennedy MM (Ed) Water Quality Trends and Geochemical Mass Balance (pp 3–26) John Wiley and Sons, Chichester, UK

Evans CD & Montieth DT (2001) Chemical trends at lakes and streams in the UK Acid Waters Monitoring Network, 1988–2000: evidence for recent recovery at a national scale. Hydrol. Earth Sys. Sci. 5(3): 351–366

Evans CD, Freeman C, Monteith DT, Reynolds BR & Fenner N (2002) Climate change – terrestrial export of organic carbon – reply. Nature 415: 862–862

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

Freeman C, Ostle N & Kang H (2001b) An enzymic ‘latch’ on a global carbon store – a shortage of oxygen locks up carbon in peatlands by restraining a single enzyme. Nature 409: 149

Greive IC (1990a) Variations in the chemical composition of the soil solution over a four year period at an upland site in southwest Scotland. Geoderma 46: 351–362

Greive IC (1990b) Soil and soil solution chemical composition at three sites within the Loch Dee catchment, SW Scotland. J. Soil Sci. 41: 269–277

Harriman R & Miller JD (1996) The effects of forestry practices on water quality and biota in the Balquidder catchments, 1983–1993. Foundation Water Research, Marlow, UK, 73 pp

Harriman R & Morrison BR (1982) The ecology of streams draining forested and non-forested catchments in an area of central Scotland subject to acid precipitation. Hydrobiologia 88: 251–253

Harriman R, Morrison BRS, Caines LA, Collen P & Watt AW (1987) Long term changes in fish populations of acid streams in Galloway, south-west Scotland. Water Air Soil Pollut. 32: 89–112

Harriman R, Gillespie E, King D, Watt AW, Christie AEG, Cowan AA & Edwards T (1990) Short-term ionic responses as indicators of hydrochemical processes in the Allt a'Mharcaidh catchment, western Cairngorms, Scotland. J. Hydrol. 116: 267–285

Harriman R, Curtis C & Edwards AC (1998) An empirical approach for assessing the relationship between nitrogen deposition and nitrate leaching from upland catchments in the United Kingdom using runoff chemistry. Water Air Soil Pollut. 105: 193–203

Harriman R, Watt AW, Christie AEG, Collen P, Moore DW, McCartney AG, Taylor EM & Watson J (2001) Interpretation of trends in acidic deposition and surface water chemistry in Scotland during the past three decades. Hydrol. Earth Sys. Sci. 5: 407–420

Helliwell RC, Ferrier RC, Johnson L, Goodwin J & Doughty R (2001) Land-use influences on acidification and recovery of freshwaters in Galloway, south-west Scotland. Hydrol. Earth Sys. Sci. 5: 451–458

Hirsch RM, Slack JR & Smith RA (1982) Techniques of trend analysis for monthly water quality data. Water Resour. Res. 18: 107–121

Hope D, Billett MF & Cresser MS (1994) A review of the export of carbon in river water: fluxes and processes. Environ. Pollut. 84: 301–324

Hope D, Billett MF, Milne R & Brown TAW (1997a) Exports of organic carbon in British rivers. Hydrol. Process. 11: 325–344

Hope D, Billett MF & Cresser MS (1997b) Export of organic carbon in two river systems in NE Scotland. J. Hydrol. 193: 61–82

Hulme M & Jenkins CJ (1998) Climate change scenarios for the UK: scientific report. UKCIP Technical Report No. 1. Climate Research Unit, Norwich, UK

Jenkins A, Ferrier RC & Helliwell RC (2001) Modelling nitrogen dynamics at Lochnagar, NE Scotland. Hydrol. Earth Sys. Sci. 5: 519–527

Kernan MR & Allott THE (1999) Spatial variability of nitrate concentration in lakes in Snowdonia, North Wales, UK. Hydrol. Earth Sys. Sci. 3: 395–408

Krug EC & Frink CR (1983) Acid rain on acid soil: a new perspective. Science 211: 520–525

Miller JD, Adamson JK & Hirst D (2001) Trends in stream water quality in Environmental Change Network upland catchments: the first 5 years. Sci. Total Environ. 265: 27–38

Milne R & Brown TA (1997) Carbon in the vegetation and soils of Great Britain. J. Environ. Manage. 49: 413–433

Montieth DT & Evans CD (2000) The UK Acid Waters Monitoring Network: 10 Year Report. ENSIS Publishing, London

Neal C (1997) Water quality of the Plynlimon catchments. Hydrol Earth Sys. Sci. 1: 381–764

Neal C, Wilkinson J, Neal M, Harrow M, Wickham H, Hill L & Morfitt C (1997) The hydrochemistry of the River Severn, Plynlimon, mid-Wales. Hydrol. Earth Sys. Sci. 1: 583–618

Neal C, Reynolds B, Neal M, Pugh B, Hill L & Wickham H (2001) Long-term changes in the water quality of rainfall, cloud water and stream water for the moorland, forested and clear-felled catchments at Plynlimon, mid-Wales. Hydrol. Earth Sys. Sci. 5: 459–476

Parker DE, Legg TP & Folland CK (1992) A new daily central England temperature series, 1772–1991. Int. J. Climatol. 12: 317–342

Patrick ST, Monteith DT & Jenkins A (1995) UK Acid Waters Monitoring Network: The First Five Years (April 1988–March 1993). ENSIS publishing, London, 364 pp

Ratcliffe DA & Oswald PH (1988) The Flow Country. Nature Conservancy Council, Peterborough, UK

Robinson M (1986) Changes in catchment runoff following drainage and afforestation. J. Hydrol. 86: 71–84

Robinson M & Newson M (1986) Comparison of forest and moorland hydrology in an upland area with peat soils. Int. J. Peat 1: 49–68

Scarsbrook MR, Boothroyd IKG & Quinn JM (2000) New Zealand's national river water quality network: long-term trends in macroinvertebrate communities. NZ J. Marine Freshwater Res. 34: 289–302

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

Scott MJ, Jones MN, Woof C, Simon B & Tipping E (2001) The molecular properties of humic substances isolated from a UK upland peat system: a temporal investigation. Environ. Int. 27: 449–462

Siepak J (1999) Total organic carbon (TOC) as a sum parameter of water pollution in selected Polish rivers (Vistula, Odra, and Warta). Acta Hydrchimica et Hydrobiol. 27: 282–283

Skjelkvåle BL, Mannio J, Wilander A & Andersen T (2001) Recovery from acidification of lakes in Finland, Norway and Sweden 1990–1999. Hydrol. Earth Sys. Sci. 5(3): 327–338

Soulsby C & Reynolds B (1995) Impact of source area liming on the hydrochemistry of an acidic headwater stream in upland Wales. In: McGregor DFM & Thompson DA (Ed) Geomorphology and Land Management in a Changing Environment (pp 121–138). John Wiley and Sons, Chichester, UK

Sykes JM & Lane AMJ (1996) The United Kingdom Environmental Change Network: Protocols for Standard Measurements of Terrestrial sites. Natural Environment Research Council, London, 220 pp

Tranvik LJ & Jansson M (2002) Terrestrial export of organic carbon. Nature 415: 861–862

Watts CD, Naden PS, Machell J & Banks J (2001) Long term variation in water colour from Yorkshire catchments. Sci. Total Environ. 278: 57–72

Werrity A (2002) Living with uncertainty: climate change, river flows and water resource management in Scotland. Sci. Total Environ. 294: 29–40

Worrall F & Burt TP Time series analysis of long term river DOC records. Hydrol. Process. (in press)

Worrall F, Burt TP & Shedden R (2003a) Long terms records of riverine carbon flux. Biogeochemistry 64: 165–178

Worrall F, Burt TP, Jaeban RY, Warburton J & Shedden R (2003b) Release of dissolved organic carbon from upland peat. Hydrol. Process. 16: 3487–3504

Worrall F, Burt TP & Adamson J Can climate change explain increases in DOC flux from upland peat catchments? Sci. Total Environ. (in press)