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Report summarising statistical analysis of controls on DOC variations at UK long-term monitoring sites

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Introduction

This deliverable takes the form of a paper published in Environmental Pollution in June 2005, which is appended. The paper presents the most recent DOC trend data for UK Acid Waters Monitoring Network (AWMN) sites, reviews the possible causes of rising DOC, and identifies the potential consequences of these changes. A statistical analysis was undertaken for the 11 lakes in the network, in which DOC time series were compared to a range of potential driving variables including temperature, rainfall, and lake acidity, non-marine sulphate concentration and ionic strength. Within-year DOC variations appear to be most strongly linked to temperature. Long-term trends are more difficult to attribute to particular drivers, but positive correlations were found with temperature, and negative correlations with non-marine sulphate and the sum of acid anions. The initial conclusion from this assessment is that both climate (temperature) and deposition chemistry (a combination of pollutant sulphate and natural seasalt deposition) have contributed to DOC trends in the UK. Temperature appears to influence the rate of potential dissolved organic carbon production, while deposition chemistry influences its solubility through its influence on soil water acidity and ionic strength. These findings indicate that changes in climate and acid deposition will need to be considered together in order to model future changes in surface water DOC, and its ecological effects.

Further statistical analysis of DOC data for the UK and other partners in the project is ongoing, and will contribute to the development of a final spatial/temporal model of DOC for Task 5.2

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Long-term increases in surface water dissolved organic carbon: Observations, possible causes and environmental impacts

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Large increases in dissolved organic carbon concentrations across the UK may be a combined response to climate change and decreasing acid deposition.

Abstract

Dissolved organic carbon (DOC) concentrations in 22 UK upland waters have increased by an average of 91% during the last 15 years. Increases have also occurred elsewhere in the UK, northern Europe and North America. A range of potential drivers of these trends are considered, including temperature, rainfall, acid deposition, land-use, nitrogen and CO_2 enrichment. From examination of recent environmental changes, spatial patterns in observed trends, and analysis of time series, it is suggested that DOC may be increasing in response to a combination of declining acid deposition and rising temperatures; however it is difficult to isolate mechanisms based on monitoring data alone. Long-term DOC increases may have wide-ranging impacts on freshwater biota, drinking water quality, coastal marine ecosystems and upland carbon balances. Full understanding of the significance of these increases requires further knowledge of the extent of natural long-term variability, and of the natural "reference" state of these systems.

Keywords: Dissolved organic carbon; UK Acid Waters Monitoring Network; Long-term trends; Climate change; Acid deposition

1. Introduction

Dissolved organic matter (DOM) is a ubiquitous component of natural waters, operationally defined as comprising any organic compound passing through a 0.45 μm filter. The number of such compounds is effectively limitless, and it is thus impossible to provide a general chemical description of DOM. However, in general it includes a small proportion of identifiable, low-molecular weight compounds such as carbohydrates and amino acids, and a larger proportion of complex, high-molecular weight compounds collectively termed humic substances. Humic substances have a medium to high molecular weight, and are a complex mixture of aromatic and aliphatic hydrocarbon structures with attached amide, carboxyl, ketone and other functional groups (Leenheer and Croué, 2003). Humic substances absorb visible light, most strongly at the blue end of the spectrum, giving high-DOM water a characteristic brown colouration.

DOM is generated by the partial decomposition of, or exudation from, living organisms including plants, animals, and soil microorganisms. The organic matter generated by these processes may be stored in the soil for a varying length of time (e.g. as peat) before decomposition processes render a part of this material soluble. The compounds comprising DOM in natural waters may therefore range in age from relatively recent

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to thousands of years (Raymond and Bauer, 2001). DOM affects the functioning of aquatic ecosystems through its influence on acidity (Eshleman and Hemond, 1985), trace metal transport (Lawlor and Tipping, 2003), light absorbance and photochemistry (Schindler, 1971; Zafariou et al., 1984), energy supply (Wetzel, 1992), and nutrient supply (Stewart and Wetzel, 1981). It also affects water treatment processes (Alarconherrera et al., 1994) and, as a transfer of carbon from terrestrial to aquatic and ultimately marine ecosystems, forms a significant component of the global carbon cycle (Hope et al., 1994).

In most studies concerning DOM, the DOC component is quantified. The organic nutrients, DON and DOP, are also widely measured. Concentrations of DOC in natural waters vary widely, from <1 to >50 mg l^{-1} (Thurman, 1985), with the lowest values observed in the oceans, groundwater, and "clearwater" lakes and rivers draining bare rock or thin, organic-poor soils. Concentrations are highest in organic soil porewaters, and freshwaters draining wetlands and peatlands, especially where runoff is low. In a number of studies (e.g. Curtis, 1998; Xenopoulos et al., 2003) positive spatial relationships have been demonstrated between DOC export and wetland area. In the UK, Hope et al. (1997) demonstrated a correlation between riverine DOC flux and the amount of organic matter (predominantly peat) in catchment soils. While controls on spatial DOC variations among freshwaters can be considered reasonably well understood, the causes of temporal change in DOC at a particular site remain more uncertain. The aim of this paper is to: (i) evaluate the changes in DOC concentration observed over the last 15 years among the lakes and streams of the UK Acid Waters Monitoring Network; (ii) consider these trends in the context of other observations in the UK, Europe and North America; (iii) identify the possible drivers of observed trends; (iv) analyse the monitoring data relative to these potential drivers; and (v) assess the significance of observed trends in terms of local biological impacts and larger-scale environmental change.

2. Observed trends in DOC

2.1. Trends in the UK Acid Waters Monitoring Network

The UK Acid Waters Monitoring Network (AWMN) comprises 11 lakes and 11 streams, at which coordinated chemical and biological monitoring has been undertaken according to consistent measurement protocols since 1988 (Patrick et al., 1991). Lakes are sampled quarterly, whilst streams, due to their greater short-term variability, are sampled monthly. Catchments are located across the main acid-sensitive regions of the UK, and mostly comprise moorland, with land-use limited to rough grazing by sheep, deer or red grouse. Five catchments contain significant areas of coniferous plantation forestry. Soils include peats, peaty podzols, peaty gleys, and thin ranker soils in montane areas. Sites, measurements and analytical techniques are described by Patrick et al. (1991), and by Monteith and Evans (2005, this issue).

Trends at AWMN sites have been assessed using the Seasonal Kendall Test (SKT), a non-parametric method that is robust against seasonality, missing values and autocorrelation. The methods used are described in detail by Evans et al. (2001a). Analysis of trends after 10 years (Monteith and Evans, 2000) identified significant ($p<0.05$) increases in DOC for 17 out of 22 sites, at a time when few sites showed decreases in non-marine sulphate (xSO_4), or increases in alkalinity or pH, associated with recovery from acidification. Following a further 5 years of monitoring, clear evidence of recovery from acidification has emerged within the AWMN, with 17 sites now showing significant xSO_4 decreases, and 8 sites showing increases in pH (Davies et al., this issue). Over the same period, trends in DOC have been sustained, with all 22 sites now showing significant increases. Trend magnitude, calculated using the Sen slope estimation method (Evans et al., 2001a) ranges from 0.06 to 0.51 mg l^{-1} $year^{-1}$. With few exceptions, trend magnitudes over 15 years have remained similar to those observed after 10 years, and trend significances have increased or remained constant at 21 of the 22 sites. In percentage terms, DOC concentrations have increased on average by 91% relative to 1988–1993 means.

Individual time series (Fig. 1) do show some variability in the temporal pattern. At some sites (e.g. Loch Coire nan Arr, Allt na Coire nan Con, Loch Chon, Round Loch of Glenhead) increases appear approximately linear, and are evident in both minimum and maximum concentrations. At others, notably the River Etherow and Old Lodge, increases are most apparent in episodic maxima. At Dargall Lane, Scoat Tarn and Burnmoor Tarn, initially linear increases appear to have levelled off from the mid-1990s, whilst at Lochnagar, the Afon Hafren, and three of the Northern Ireland sites, there are indications that increases occurred as a step change around 1996. The fourth Northern Ireland site, Bencrom River, is the only site in the network where the trend appears to have reversed in recent years, with trend significance having decreased since 1998 as a result.

Variations in temporal pattern suggest that, at least to some extent, local factors have contributed to observed DOC variations. Nevertheless, all 22 sites have shown significant DOC increases, and the ubiquity of these trends suggests the presence of one or more underlying drivers of change, operating in a uniform and, over the timescale of monitoring, essentially unidirectional manner across the whole acid-sensitive area of the UK.

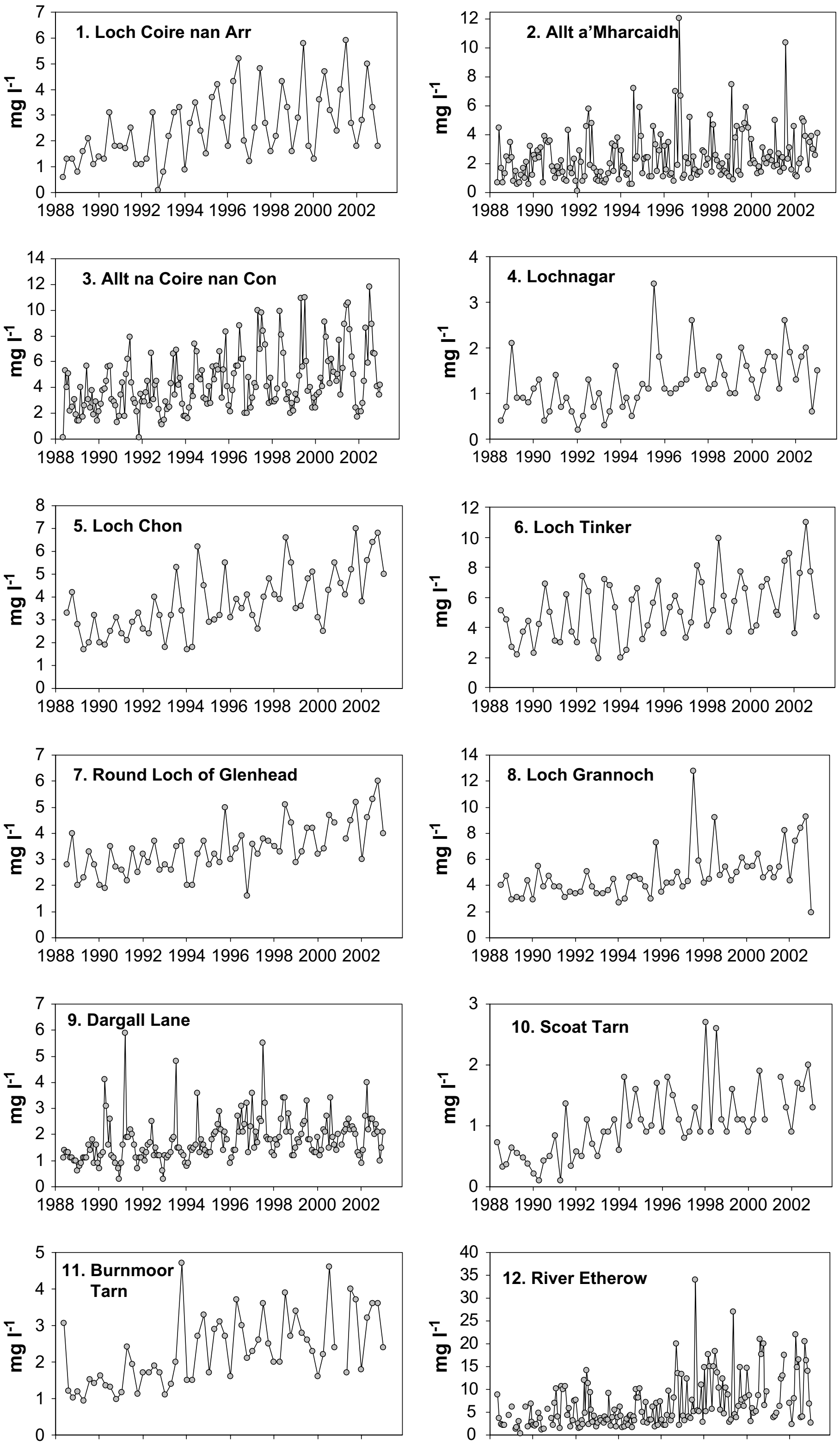

Fig. 1. Time series of dissolved organic carbon concentrations at all UK (space) AWMN sites.

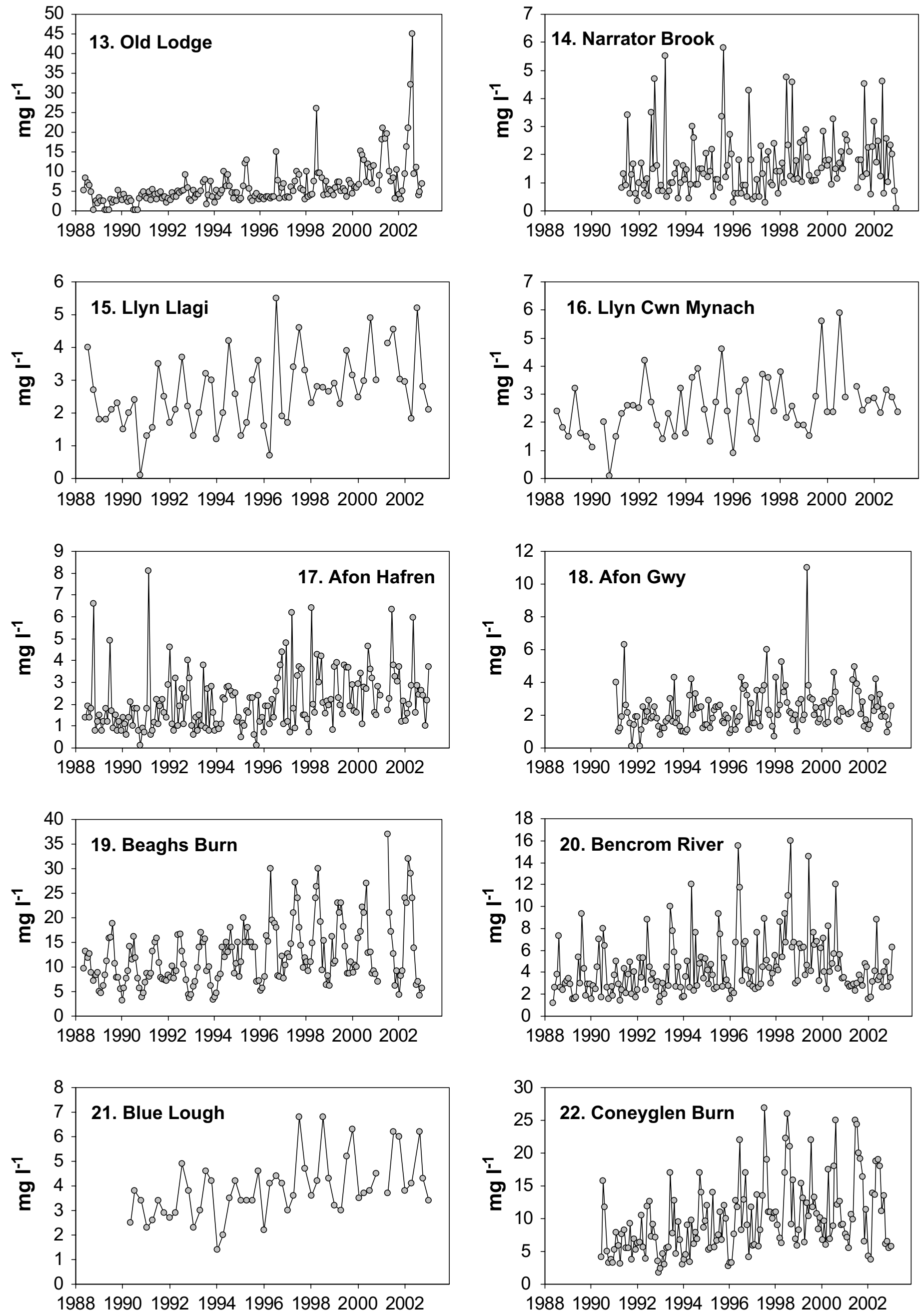

Fig. 1. (*continued*)

2.2. Trends in other UK datasets

The possibility of increasing DOC, as reflected in increases in water colour, was first raised in the 1980s with regard to impacts on water supply (e.g. McDonald et al., 1989; Kay et al., 1989). Prior to the late 1980s, however, systematic DOC monitoring of upland waters was limited to a small number of sites, notably the Plynlimon and Beddgelert catchments in North Wales (Reynolds et al., 1997; Robson and Neal, 1996; Stevens et al., 1995) and the Galloway Lochs and Loch Ard streams in Scotland (Harriman et al., 2001). In almost every case, these datasets also show rising DOC, and suggest that increases were occurring from at least the early 1980s. Longer-term data extending back into the 1960s and 1970s are limited to water colour records from water supply companies for peaty upland areas of northeast England (Watts et al., 2001; Worrall et al., 2003). Trends in these records are variable, but several show significant increases, while none show decreases. All of these datasets, plus others including the AWMN, Forestry Commission monitoring sites in Wales

(Forestry Commission, unpublished data), and Scottish Environmental Protection Agency monitoring sites in northeast Scotland, were collated by Worrall et al. (2005, in press). Of a total of 198 sites, 153 (77%) showed significant increases when analysed using SKT, and none showed significant decreases. Overall, therefore, it appears that the AWMN is representative of the wider situation in UK upland waters; that DOC increases have been near-ubiquitous in these systems; and therefore that the driving mechanism for these increases must have operated across the whole country and over a prolonged period.

2.3. Trends in Europe and North America

The most extensive trend analysis for acid-sensitive European surface waters has been undertaken by the UNECE ICP Waters programme. A review after 15 years of monitoring (Skjelkvåle et al., this issue) suggests that DOC concentrations have increased widely across the Nordic Countries and British Isles (data include six AWMN sites), with no overall trends in central Europe. Other studies have shown somewhat differing patterns; Hejzlar et al. (2003) report increasing DOC for a river in the Czech Republic since the mid-1980s, whereas Forsius et al. (2003) found few DOC trends in the 1990s for a large Finnish lake dataset. However, more intensive data for Finnish streams do now show evidence of rising DOC (Finnish Environment Institute (SYKE), unpublished data).

In a large-scale study of trends in the northern and eastern US from 1990 to 2000, four out of five areas studied showed regionally significant increases in DOC (Stoddard et al., 2003). On average, concentrations increased by 10% over the 10 years. The authors suggest that observed DOC increases across much of Europe and North America must indicate a large-scale cause. Other data from northeastern North America show similar trends, with DOC increases observed at 8 out of 17 lakes monitored since 1982 in the Adirondacks (Driscoll et al., 2003), and 17 out of 51 lakes in southern Quebec between 1985 and 1993 (Bouchard, 1997). However an assessment of lake DOC in Ontario and Quebec during the 1990s found few significant trends (Jeffries et al., 2003). Schindler et al. (1997) reported a decrease in DOC for lakes in northwestern Ontario between 1970 and 1990, linked to changes in climate.

3. Potential drivers of change in DOC

3.1. Recovery from acidification

It has been suggested that, in response to increasing inputs of mineral acids, soils may release lower quantities of organic acids, thereby buffering the impact of acid deposition on runoff acidity (Rosenqvist, 1978; Krug and Frink, 1983). Surface water DOC concentrations would thus be depressed when acid anion concentrations are high, and would increase as acid anion concentrations are reduced. Palaeolimnological evidence has been used to support this hypothesis, with lake cores showing diatom assemblages characteristic of less coloured waters during the period of maximum acidification (Davis et al., 1985; Dixit et al., 2001). Laboratory experiments on organic soils suggest that DOM release is positively related to pH (e.g. Tipping and Hurley, 1988; Kennedy et al., 1996) although studies of podzolic mineral horizons have shown inverse relationships (e.g. David et al., 1989). Clark et al. (in press) have found that acidification caused by oxidation of reduced S to SO_4 under experimental and field drought conditions was associated with large reductions in soil solution DOC (up to 60%). With regard to biological processes controlling DOM production, however, Cronan (1985) concluded pH effects were minor.

Field-scale experiments provide equivocal evidence for the role of pH. Schindler et al. (1992, 1997) showed large DOC decreases due to enhanced in-lake removal at experimentally acidified lakes, and a temporary decline in bog pools within an acidified peatland. Catchment-scale acidification experiments at Lake Skjervetjem, Norway (Hessen et al., 1997) and Bear Brook, Maine (David et al., 1999) showed no clear changes in surface water DOC, although some evidence of decreasing organic anion concentrations was observed at Bear Brook. Similarly, a catchment acid-exclusion experiment at Risdalsheia, Norway (Wright et al., 1993) found no DOC change, but increased organic acid dissociation. Stoddard et al. (2003) suggest an inverse correlation between DOC and $x\text{SO}_4$ trends in US surface water monitoring data, consistent with an acidification control on DOC, although correlations were weak, and only observed when waters were subdivided into low- and high (>5 mg l^{-1}) DOC classes. Using the same approach, somewhat stronger relationships were noted for European sites in the ICP Waters network (Skjelkvåle, 2003; J. Stoddard personal communication). Since emissions and deposition of acidifying compounds have decreased in the UK since 1988, changes in acidity may have contributed to observed DOC trends, and are considered in the analysis below.

Soil solution ionic strength has also been proposed as a control on DOC mobilisation. Laboratory studies show fairly consistent reductions in DOC release with increasing ionic strength in both organic and mineral soils (e.g. Tipping and Hurley, 1988; Evans et al., 1988; Vance and David, 1989). Since acid deposition raises ionic strength, any ionic strength effects are difficult to distinguish from those of acidity in the field. In this respect, the absence of DOC response to pH change in the field manipulation experiments described above also implies a lack of response to ionic strength change. It is worth noting, however, that for most UKAWMN sites, the dominant ions are sodium (Na) and chloride (Cl), associated with high sea salt deposition. Climatic fluctuations cause large, cyclical variations runoff seasalt ion concentrations (Evans et al., 2001b), and consequently ionic strength variations in these waters are partially decoupled from those in acid deposition. Since sea salt concentrations were higher during the early years of monitoring, this mechanism could also contribute to observed DOC trends.

3.2. Temperature change

Spatially, there is generally a negative relationship between DOC and temperature, with maximum concentrations observed in waters draining peatlands characteristic of cold, northern latitudes (Meybeck, 1982). However, the influence of temperature on temporal variations at an individual site appears very different. Laboratory studies have consistently shown a positive influence of temperature on soil DOC production (e.g. Christ and David, 1996; Andersson et al., 2000; Moore and Dalva, 2001; Fenner, 2002; Clark et al., in preparation), and positive within-year correspondence between DOC and temperature has been observed in field studies of a range of soil waters (e.g. Cronan and Aiken, 1985; Liechty et al., 1995; Chapman et al., 1995; Michalzik and Matzner, 1999). A translocation study by Tipping et al. (1999) also showed increased DOC leaching from peaty soils moved to warmer, dryer locations. A 4°C catchment-scale warming experiment at Risdalsheia, Norway produced an apparent increase in runoff DOC concentrations (Wright and Jenkins, 2001).

Enzymatic hydrolysis of high molecular weight organic matter, into smaller molecules utilisable by micro-organisms, is widely considered the rate-limiting step for organic matter decomposition (Hoppe et al., 1988; Chróst, 1991). High levels of recalcitrant phenolic compounds in peaty soils can inhibit enzyme activity (Wetzel, 1992; Kang and Freeman, 1999) and the phenol oxidase enzyme, which degrades these compounds, is sensitive to climatic conditions (Freeman et al., 2001a,b; Fenner, 2002). Laboratory peat warming experiments showed increased phenol oxidase activity, DOC, and proportion of phenolic compounds within this DOC (Freeman et al., 2001b; Fenner, 2002), implying both a temperature effect on DOC production, and increased recalcitrance of that DOC, likely to limit further degradation of DOC to CO_2. This mechanism was proposed as a cause of DOC increases by Freeman et al. (2001b). Enchytraeid worms (Oligochaeta), which form the dominant soil fauna in UK upland soils, increase in abundance at higher temperatures and, by influencing microbial activity, litter fragmentation and soil aeration, may also significantly enhance DOC production (Briones et al., 1998; Cole et al., 2002).

The central England Temperature Record (CET) (Parker et al., 1992), considered representative of temperature trends across the UK as a whole, shows that the 15 years of AWMN monitoring (1988–2002) were on average 0.75 °C warmer than the period 1960–1987. Five of the six warmest years in the CET, which began in 1659, have occurred since 1989. Although temperature trends since 1988 are less apparent (Fig. 2), potential delays between DOC production in the soil, and subsequent washout to surface waters (e.g. Mitchell and McDonald, 1992), means that any DOC-temperature response may be fairly lagged and damped.

3.3. Hydrological change

Three possible mechanisms by which hydrological processes could affect surface water DOC may be identified:

(a) In the absence of any change in the DOC flux entering the stream network, a decrease in discharge should lead to increased DOC concentrations.
(b) Conversely, increased flow may increase both DOC flux and concentration by altering water flowpath, with more runoff routed through shallow, organic-rich soil horizons, relative to deeper mineral horizons in which DOC adsorption is high (Cronan and Aiken, 1985; McDowell and Likens, 1988). Flowpath-related hydrological changes have been associated with lake DOC variations in Sweden (Forsberg, 1992; Tranvik and Jansson, 2002) and Ontario (Schindler et al., 1997), whilst neural network modelling by Clair et al. (1999) showed a positive relationship between runoff and DOC in Canadian surface waters.
(c) Within-year changes in rainfall and runoff distribution may affect both DOC production and transport processes. Drought-rewetting cycles have been identified as a major influence on DOC production in the UK, characterised by (i) enhanced organic

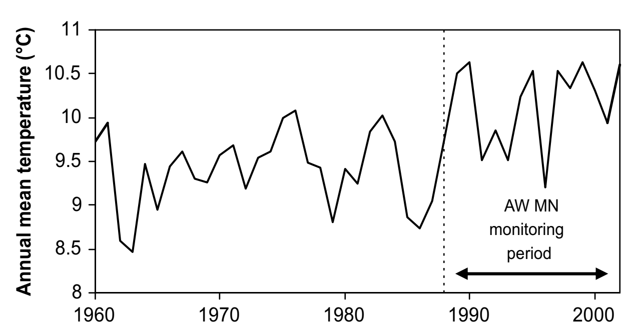

Fig. 2. Annual mean central England temperatures, 1960–2002. Data provided by the Hadley Centre (www.met-office.gov.uk/research/hadleycentre) (Parker et al., 1992).

matter decomposition due to aeration of normally saturated peaty soils; and (ii) flushing of accumulated DOM into streamwaters upon rewetting (McDonald et al., 1991). Freeman et al. (2001a) argue that, since phenol oxidase activity is inhibited under anaerobic conditions, peat decomposition may be highly sensitive to aeration. Clark et al. (in preparation) have observed significantly increased peat DOC production in response to warming under aerobic versus anaerobic conditions. It is worth noting, however, that aerobic conditions may favour CO_2 rather than DOC production, and that breakdown of DOC is itself moisture dependent (Kalbitz et al., 2000). Therefore, DOC response to drought is not straightforward, and may depend on initial moisture conditions in the soil. Nevertheless, field studies of dry–wet cycles have typically shown DOC increases following rewetting (Mitchell and McDonald, 1992; Hughes et al., 1998; Tipping et al., 1999; Lundquist et al., 1999), often with DOC concentrations suppressed during the drought period itself (Mitchell and McDonald, 1992; Hughes et al., 1998; Clark et al., in press). A wetland manipulation by Hughes et al. (1998) suggested that repeated droughts might generate long-term DOC increases, although subsequent data for the same site indicate that this increase was not sustained (Freeman et al., 2004). Watts et al. (2001) noted step-change increases in water colour for several northern England reservoirs after natural droughts in 1976, 1984 and 1995, with colour levels apparently not returning to pre-drought levels between each drought.

Over the AWMN monitoring period, available data do not show flow decreases consistent with hypothesis (a), and DOC fluxes estimated for the Afon Hafren AWMN site (Cooper and Watts, 2002) and for two rivers in northeast England (Worrall et al., 2003) indicate that fluxes have increased in line with concentrations. There is some evidence of long-term increasing river flows in northwest Britain from 1961 to the early 1990s (Cannell et al., 1999a; Werrity, 2002), but these have not been sustained during the 1990s (DEFRA, 2003). Discharge data for several AWMN rivers (Fig. 3) do not show clear or consistent trends. Overall, therefore, there is little evidence that long-term runoff changes have contributed to DOC trends.

Regarding the role of drought/re-wetting cycles, there is evidence of a recent trend towards wetter winters and drier summers in the UK (Burt et al., 1998). Again this trend is not clear within the AWMN monitoring period (e.g. Fig. 4), but the majority of sites were affected by the severe drought of 1995. Although droughts form part of the natural hydrologic variation of these systems, the recent sequence of three severe droughts could potentially have affected long-term DOC trends. Apparent step change increases in DOC following the 1995 drought at a number of sites (e.g. sites 17–22, Fig. 1) lend some support to this hypothesis.

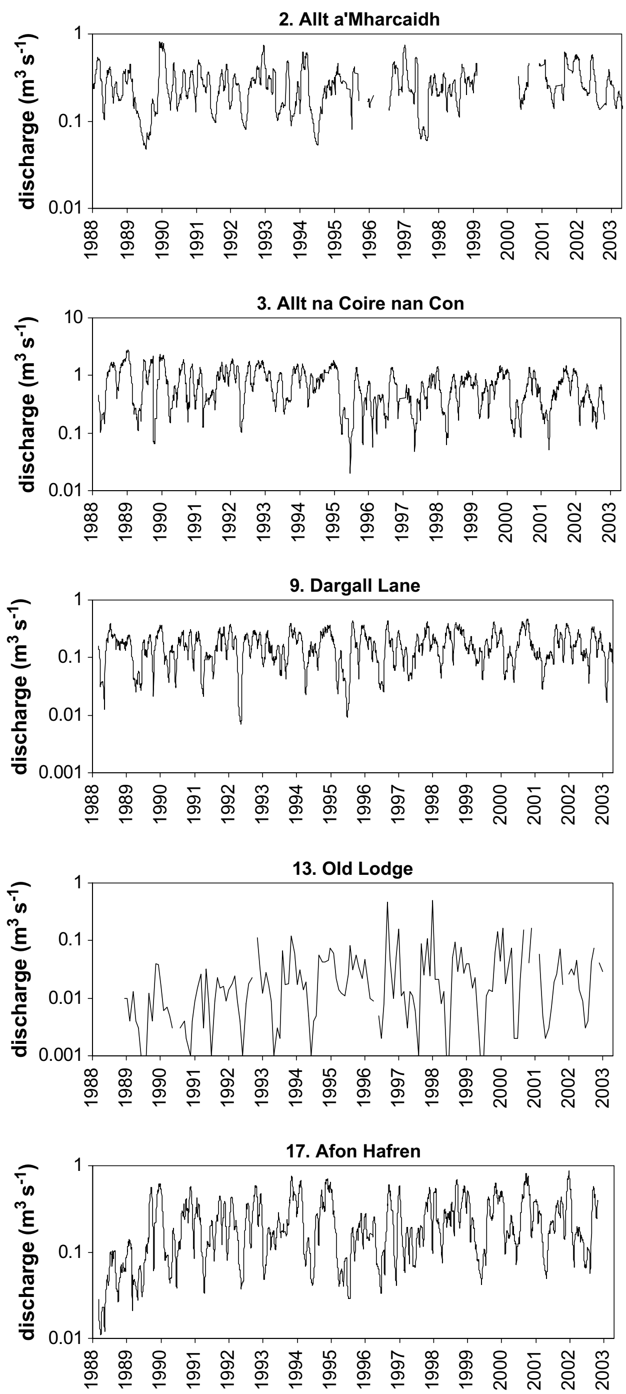

Fig. 3. Daily mean discharge records for five UK AWMN streams.

3.4. Land-use change

UK semi-natural ecosystems are subject to a range of land-use practices that may influence DOC. Much of the UK uplands are grazed, primarily by sheep, affecting vegetation cover, soil compaction and drainage (Milne,

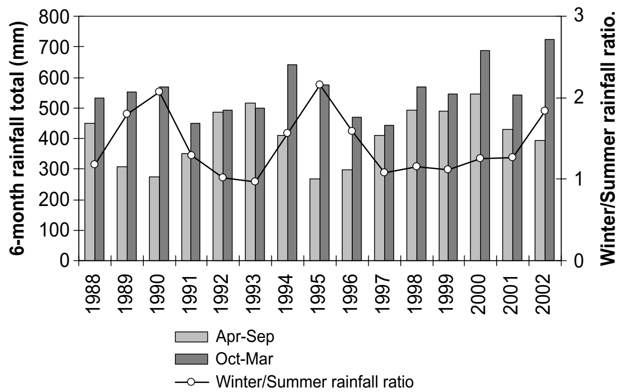

Fig. 4. Six-monthly rainfall totals and winter/summer rainfall ratios from the England and Wales Precipitation Series, during the UKAWMN monitoring period. Data provided by the Hadley Centre (www.met-office.gov.uk/research/hadleycentre) (Alexander and Jones, 2000).

1996; Holman et al., 2002). Census data show that overall stocking levels in upland England have increased since 1980 (English Nature, 2001). Conifer afforestation has been extensive during the last century, and may have influenced DOC generation, for example through increased litter production and mineralisation; forestry effects on DOC appear most significant following felling (Hughes et al., 1990; Neal et al., 1998). Peatland drainage was widespread during the last century, and has been identified as a possible contributor to DOC trends by Worrall et al. (2003), whilst managed heather burning has been shown to profoundly impact on peatland carbon cycling (Garnett et al., 2000).

Of the 22 AWMN catchments, 17 are moorland (acid grassland or heathland), but the nature and intensity of land-use vary, with several sites largely or entirely ungrazed. There are no indications of extensive drainage or burning at most sites. The five forested sites contain plantations of varying age, with harvesting having occurred since 1988 in three catchments. Despite the potential for forests to impact on DOC export, trends for forested sites show no systematic deviation from nearby moorland sites (Fig. 5). A larger set of monitored Welsh forest catchments (Forestry Commission, unpublished data) also show similar DOC trends to the Welsh AWMN sites. In Scotland, although Grieve and Marsden (2001) found higher DOC concentrations in forest versus moorland soil solutions, Harriman et al. (2003) found similar DOC trends in waters draining forests and moorlands, and concluded that forest impacts on DOC export were relatively minor.

On the evidence available, there do not appear to have been any systematic trends in land-use affecting all AWMN catchments. Although one or more land-use factors could have influenced DOC at individual sites, then, it appears unlikely that any single land-use factor could explain trends across the entire network.

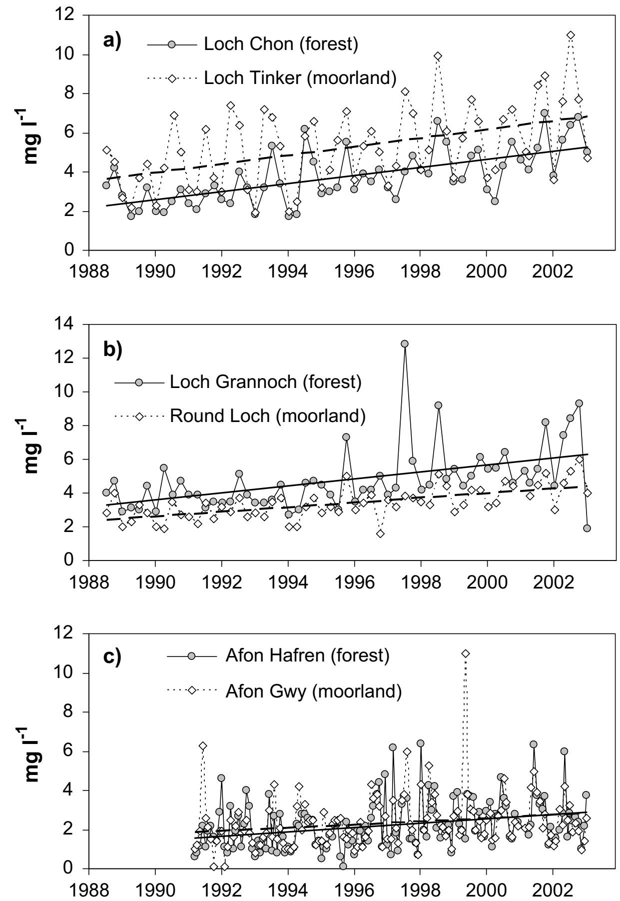

Fig. 5. DOC trends at three UKAWMN paired moorland and forest catchments.

3.5. In-lake and in-stream removal

In-lake processes affecting DOC have received considerable attention in North America and Scandinavia, where microbial utilisation and photo-oxidation have been shown to significantly reduce DOC concentration (e.g. Hongve, 1994; Granéli et al., 1996; Schindler et al., 1997; Dillon and Molot, 1997). Both lake acidification and longer water residence times (associated with climatic factors) tend to decrease lake DOC. In-stream DOC removal, for example due to utilisation by biofilms, has also been demonstrated (e.g. Freeman et al., 1990). However, the quantitative importance of these processes in UK waters is questionable, due to the relative recalcitrance of DOC from peaty soils, and typically short residence times due to a combination of high rainfall, and large catchment area:lake volume ratios (mean residence time of AWMN lakes is 2 months, range <1–8 months). Although inflow data are unavailable for AWMN lakes, 2 years of data for similar lakes (Curtis et al., 1998) show no consistent differences between main inflows and outflows for a range of DOC levels (Fig. 6), suggesting that in-lake processing is minor. Short water residence times

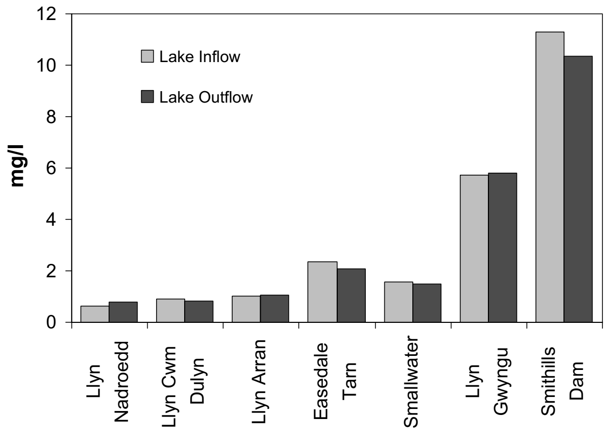

Fig. 6. Two-year mean inflow and outflow DOC concentrations for a range of UK lakes (data from Curtis et al., 1998).

in rivers, and the persistence of both high DOC levels and temporal patterns into the lower reaches of rivers draining peaty uplands (Eatherall et al., 1998; Worrall et al., 2003) suggest that in-stream removal is also quantitatively minor.

3.6. Nitrogen enrichment

Nitrogen enrichment has been proposed as a potential influence on DOC through its role as a limiting nutrient in terrestrial ecosystems, and due to the role of labile organic matter in N immobilisation (Aber, 1992; Zech et al., 1994). Pregitzer et al. (2004) showed dramatically increased DOC export from a North American forest soil following long-term N additions, but other studies have shown little or no response (Gundersen et al., 1998, McDowell et al., 1998; McDowell et al., 2004). Neither N deposition (Fowler et al., this issue) nor surface water NO_3 (Davies et al., this issue) have shown clear trends in the UK that might support N as a driver of DOC increases, although these observations do not exclude the possibility that long-term soil N-enrichment could impact on DOC production.

3.7. Atmospheric CO_2 enrichment

Atmospheric CO_2 increases have recently been proposed as an alternative explanation for rising surface water DOC in the UK. Freeman et al. (2004) found that experimentally increasing atmospheric CO_2 by 235 ppm led to increases in soil solution DOC ranging from 14% in blanket peats to 61% in more nutrient-rich riparian wetland peats. The increase was attributed to enhanced primary production and DOC exudation by plants, possibly associated with increased vascular plant cover. Since atmospheric CO_2 increases since 1988 have been around 10% of the experimental increase, this suggests that around a 1–6% DOC increase may be explained by this mechanism, considerably smaller than the actual increases observed.

4. Analysis of AWMN data

Previous research, and environmental changes over the last 15 years, suggest several drivers with the potential to explain observed UK DOC increases. Those considered here are (i) decreasing soil acidity; (ii) decreasing soil solution ionic strength; (iii) increasing temperature; and (iv) dry–wet cycles. The relative role of these drivers is examined firstly with regard to spatial patterns in observed chemical trends. Secondly, a stepwise regression analysis of raw DOC data is undertaken for lake sites, using a range of potential chemical and climatic predictors.

4.1. Spatial variations in chemical trends

Comparing DOC trends between sites, there is a strong correlation ($R^2 = 0.71$) between the rate of annual DOC increase, and mean DOC concentrations for the first 5 years (Fig. 7). This implies that *proportional* DOC increases have been fairly similar between sites: on average 6.1% per annum, i.e. 91% over 15 years. This correlation is replicated for a larger dataset by Worrall et al. (2005, in press). Since mean DOC concentrations largely reflect organic carbon stores in catchment soils (Hope et al., 1997), this suggests that DOC release per unit of soil organic carbon has increased, and done so fairly uniformly across the UK. This implies a driving mechanism which has operated consistently at the same spatial scale.

If decreases in acid (primarily S) deposition have driven DOC increases, a correlation might be expected between the magnitude of trends in DOC and xSO_4, as suggested by Stoddard et al. (2003). This is considered

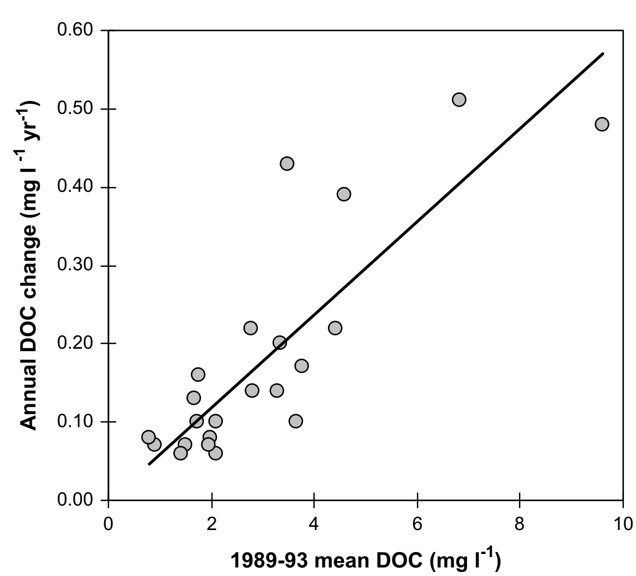

Fig. 7. Relationship between the magnitude of trends in DOC, and mean DOC during the first 5 years of monitoring, UKAWMN sites.

appropriate for AWMN catchments since SO_4 appears approximately conservative (Cooper et al., this issue), whilst few sites show NO_3 trends, and any trends in base cations appear correlated to those in xSO_4 (Davies et al., this issue). The correlation between DOC and xSO_4 for the AWMN sites is significant ($p=0.01$) but relatively weak ($R^2=0.29$, Fig. 8a), and reliant on two sites with large DOC increases and xSO_4 decreases (River Etherow, Old Lodge). The correlation is not improved by subdividing sites into low- (mean <5 mg l^{-1}) and high-DOC classes. The two sites with the largest DOC increases (Coneyglen Burn, Beaghs Burn) are located in the low-deposition region of northwest Northern Ireland, and exhibit relatively small xSO_4 decreases. Similarly, the northwest Scotland sites (Loch Coire nan Arr, Allt na Coire nan Con) show some of the clearest DOC increases (Fig. 1) but are located in a region of very low S deposition, with only minor changes in xSO_4 observed. These observations suggest that acid deposition can provide only a partial explanation for DOC trends.

Trends in the sum of mineral acid anion concentrations ($SAA=SO_4+Cl+NO_3$) were taken to be indicative of ionic strength trends (based on the mobile anion concept, changes in overall ionic strength should be driven by changes in SAA). In addition to decreases in xSO_4, SAA has also been influenced by a reduction in sea salt deposition from high levels in the early 1990s. Correlations between SAA and DOC trend slopes are again fairly weak ($p=0.01$, $R^2=0.30$, Fig. 8b), suggesting that changes in ionic strength alone are also unlikely to account for all observed DOC increases.

4.2. Stepwise regression analysis

DOC time series were analysed using three simple statistical models:

- *Model 1*: a simple stepwise regression, whereby DOC time series were analysed against a range of chemical and climatic variables. Chemical predictor variables used were pH, xSO_4, Cl and SAA. Climatic predictor variables were rainfall measurements from nearby meteorological stations (totals for 1, 2, 3, 6, 12 and 24 month antecedent periods) and temperatures from the CET (averages for 3, 6, 12, 24 and 36 month antecedent periods). The CET was considered suitable for all sites, given high correlations with water temperature records for all AWMN lakes (D. Monteith, unpublished data). Stepwise regressions were undertaken using a standard selection procedure (forward selection and backward elimination with a 0.15 significance threshold) in Minitab statistical software. Variable selection was constrained such that (i) a maximum of one short-term (<1 year) and one long-term (≥ 1 year) variable was included for rainfall and temperature; (ii) only the most significant of SAA and Cl were included (since Cl is the dominant acid anion at all sites). In practice, these constraints were not required in most analyses.
- *Model 2*: a baseline model, in which a linear trend and four-level seasonal component were fitted to DOC concentrations based simply on year and time of year. The extent to which this non-causal model is able to represent the variability in the time series provides a basis for assessing the quality of fit of any proposed causal model. A causal model would be expected to be at least comparable in predictive power with this baseline model.
- *Model 3*: a strong stepwise elimination model using Model 2 trend and seasonal variables, plus all climatic and chemical variables included in Model 1. Variable selection constraints were as in Model 1. The stepwise elimination procedure was weighted in favour of low-dimensional models, so that a sub-model with fewer parameters may be selected over one with a lower residual standard error (RSE).

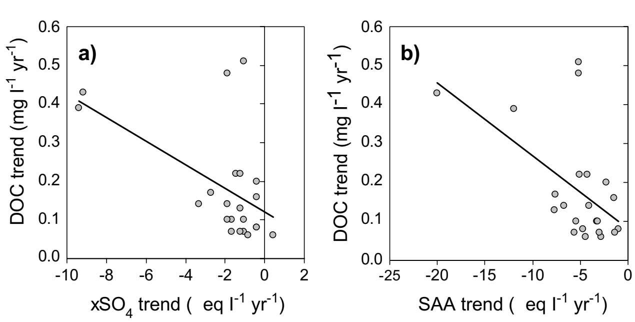

Fig. 8. Relationship between the magnitude of trends in DOC, and trends in (a) non-marine sulphate and (b) sum of acid anions, UKAWMN sites.

The analysis was limited to the 11 lake sites, which show greater short-term chemical stability than streams, where episodic DOC variations tend to partly obscure long-term patterns. In this exploratory analysis the data were not transformed; generally proportional changes in concentrations suggest a log transformation might also be considered.

The simple stepwise regression, Model 1, gave R^2 values ranging from 0.21 to 0.72 among sites. Although the selected predictor variables varied (Table 1), some general observations may be made:

- At all sites except Scoat Tarn, at least one temperature variable was selected, with a long-term temperature variable selected at seven sites. In all cases, regression coefficients were positive.
- Rainfall and pH were selected less frequently, and regression coefficients showed both positive and negative values.

Table 1
Variables selected in stepwise regression, Model 1

Site	Seasonal climatic	Long-term climatic	Chemical
1	CET_{3month} (+), $Rain_{1month}$ (−)	CET_{3year} (+), $Rain_{1year}$ (−)	pH (−)
4	$Rain_{1month}$ (+)	CET_{1year} (+), $Rain_{2year}$ (+)	
5	$Rain_{2month}$ (+)	CET_{2year} (+)	pH (+)
6	CET_{3month} (+)	CET_{2year} (+)	SAA (−)
7		CET_{2year} (+)	SAA (−)
8	CET_{3month} (+), $Rain_{1month}$ (−)	CET_{1year} (+)	Cl (−), xSO_4 (−), pH (−)
10			SAA (−)
11	$Rain_{6month}$ (−)	CET_{2year} (+)	Cl (−), pH (−)
15	CET_{3month} (+)		SAA (−)
16	CET_{3month} (+)		SAA (−)
21	CET_{6month} (+)		SAA (−)

- Either SAA or Cl was selected at eight sites. In all cases, regression coefficients were negative. The three sites in which neither variable was selected were in the relatively low deposition area of northern/central Scotland.
- xSO_4 was selected only at Loch Grannoch. However, changes in SO_4 were incorporated within SAA at six sites.

These observations appear to support both a positive association between DOC and temperature, and a negative association between DOC and ionic strength, at most AWMN lakes. Any relationship to recovery from acidification, as distinct from reduced ionic strength, is unclear. Association between DOC and rainfall is also hard to detect. Modelled time series based on the regression equations (Fig. 9) show that, at most sites, much of the observed rising trend in DOC is successfully reproduced, indicating that correlations are not simply seasonal.

While these results appear consistent with temperature and ionic strength as driving variables, this conclusion is subject to several major caveats. First, the linear predictor variables used are fairly crude, and may not adequately reflect the conditions affecting DOC production. For example, antecedent rainfall totals provide only a weak indicator of soil moisture status and drought occurrence. Additionally, surface water DOC is a function both of the DOC composition of source waters, and of the proportion of water from different sources. Thus, while dry conditions and high pH might increase DOC concentrations in soil waters, short-term variations in lake chemistry might be more related to the proportion of water from shallow (acid, high-DOC) versus deep (less acid, lower DOC) soil horizons. Although these flowpath variations may not explain long-term trends, they may be sufficient to confound correlations between DOC and either lake pH or rainfall.

Second, all lakes show some seasonality. DOC is typically highest in September, when temperatures are high, and lowest in March, when seasalt concentrations, and hence ionic strength, are typically at a maximum. Observed correlations must therefore to some extent reflect seasonal, rather than long-term, correlations. This is particularly true for sub-annual rainfall and temperature, which essentially account for seasonal variability, and may be independent of any mechanism influencing long-term trend. Finally, there is a risk that any variable with a long-term trend will, to some extent, correlate with the trend in DOC; again, this does not necessarily demonstrate a causative relationship.

Model 2 demonstrates the extent to which observed DOC variations can be explained fitting simple seasonal and linear trend components. A comparison of RSE values (Table 2) shows that in only three cases does Model 1 provide a better fit than Model 2. While this does not invalidate the relationships observed in Model 1, it suggests that the variables selected provide at best only a first approximation of a causal mechanism.

Model 3 condenses the contributions from a comprehensive candidate causal model and Model 2. The selected variables in this model (Table 3) generally include 3 components: a descriptor of seasonality, a descriptor of trend, and one or more chemical variables (which may incorporate both seasonal and long-term variation). This model provided the lowest RSE values of the three models applied for 7 of the 11 lakes. General observations that may be made are:

- Sub-annual temperature and rainfall appear more successful in describing within-year variability than a seasonal factor, which was not selected at any site. However, since a seasonal factor effectively uses 3 parameters in contrast to the single parameter used by a seasonal variable, it tends to be excluded in stepwise regression.
- The descriptor of DOC trend selected was generally the simple linear trend, rather than longer-term climate variables.
- An acid anion (Cl, SO_4) was selected at six sites. This may explain in part both trend and seasonality. Selection of Cl suggests a possible ionic strength effect, selection of SO_4 either an ionic strength or acidity effect.

From this exploratory analysis, it has not been possible to identify any single simple linear predictor of DOC increases in the AWMN lakes. Results lend some support to the hypotheses that DOC concentrations are affected positively by temperature and negatively soil solution ionic strength, but variability between sites, and the failure of any long-term variable to perform significantly better than a simple linear trend, suggest

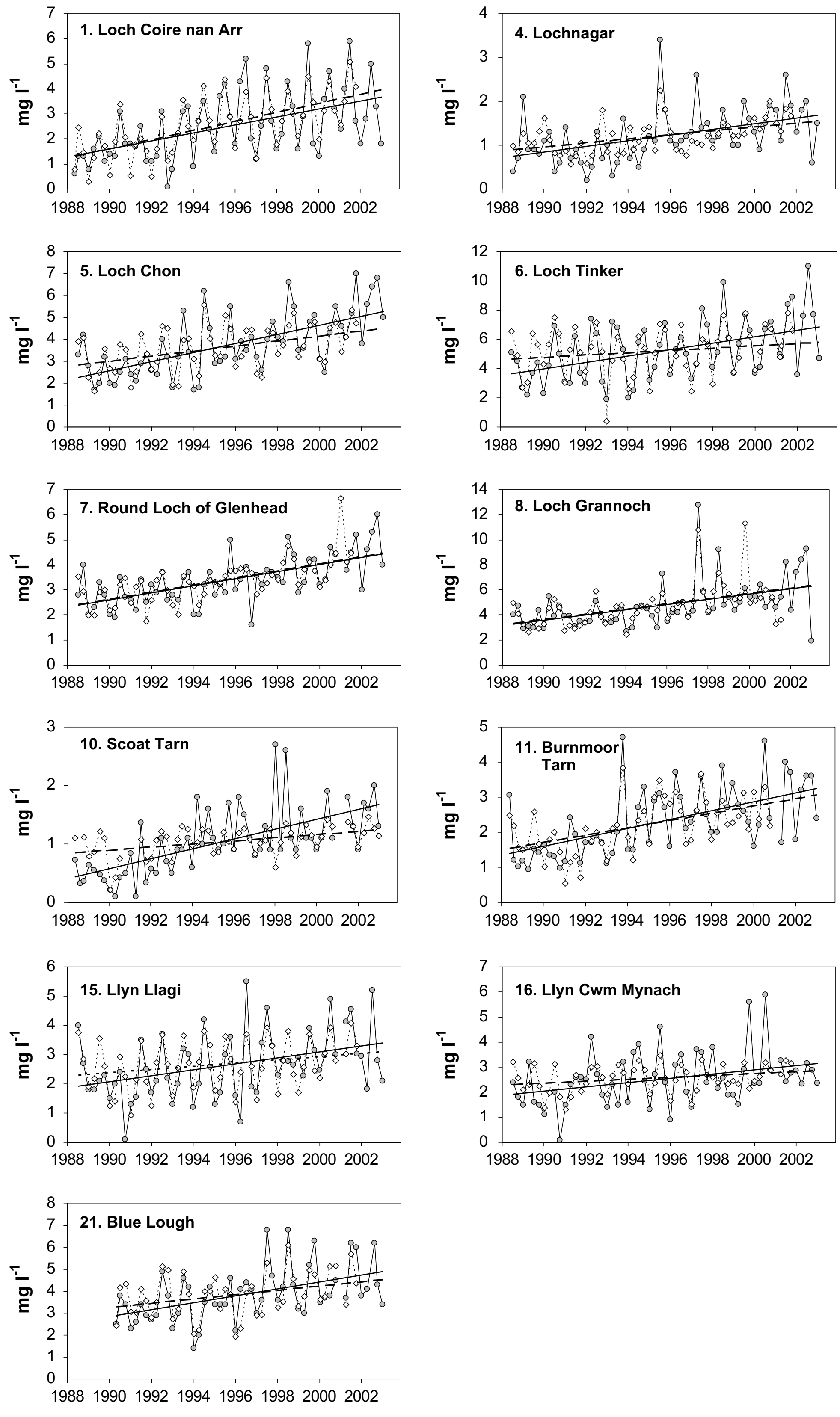

Fig. 9. Observed DOC for UKAWMN lakes, compared to predicted DOC from stepwise regressions (Model 1).

Table 2
Residual standard error (RSE) and R^2 values for each statistical model

Site	Model 1		Model 2		Model 3	
	RSE	R^2	RSE	R^2	RSE	R^2
1	0.71	0.74	0.71	0.74	0.71	0.74
4	**0.51**	0.36	0.55	0.25	0.56	0.18
5	0.83	0.60	0.79	0.70	**0.70**	0.76
6	1.30	0.62	1.18	0.69	**1.05**	0.72
7	0.65	0.55	**0.59**	0.63	0.61	0.60
8	0.95	0.71	1.10	0.53	**0.85**	0.55
10	0.50	0.22	**0.43**	0.46	0.44	0.41
11	**0.60**	0.61	0.73	0.46	0.61	0.58
15	0.76	0.55	0.71	0.62	**0.69**	0.64
16	0.95	0.24	0.93	0.28	**0.81**	0.52
21	0.74	0.66	0.72	0.67	**0.59**	0.78

The model with the lowest RSE for each site is highlighted in bold.

that other or more complex (e.g. non-linear) mechanisms may be required. Nonetheless, the consistent pattern of rising DOC at all sites does suggest one or more common drivers.

5. Environmental impacts of rising DOC

The lakes and streams of the AWMN have clearly undergone major chemical change during the last 15 years, and increased concentrations of DOC are likely to have significantly affected other chemical variables. In particular, metal transport may have increased due to increased complexation by organic compounds. Organic Al concentrations have increased widely (significant at eight sites) whereas concentrations of toxic inorganic Al have decreased (significant at ten sites). Total iron concentrations have increased significantly at 13 sites, reflecting the importance of organic complexes for iron transport. Other, unmonitored, trace metals forming organic complexes may also have increased with DOC.

Table 3
Variables selected in stepwise regression, Model 3

Site	Seasonal	Long-term	Chemical
1	CET_{3month} (+), $Rain_{6month}$ (−)	Trend	
4		Trend	
5	CET_{6month} (+)	Trend	Cl (−)
6	CET_{3month} (+)	Trend, $Rain_{1year}$ (+)	Cl (−)
7	CET_{6month} (+)	Trend	
8	CET_{6month} (+), $Rain_{2month}$ (−)		SO_4 (−), pH (−)
10		Trend	
11	$Rain_{6month}$ (−)	Trend	Cl (−)
15	CET_{3month} (+),	Trend, CET_{2year} (−)	
16	CET_{3month} (+), $Rain_{2month}$ (−)	Trend	SO_4 (−), pH (−)
21	CET_{6month} (+)	Trend	Cl (−)

DON monitoring began in 1995, so trends are not yet apparent, but again a correlation with DOC would be expected. Additionally, increases in organic acidity have clearly, to some extent, offset decreases in mineral acid anions since monitoring began, so that pH and alkalinity increases are generally weaker than those in ANC (Davies et al., this issue). However, the impact of DOC changes on runoff may be complicated by changes in soil solution DOC; a modelling study for the Afon Gwy (Evans, 2005, in press) suggested that suppression of soil water pH by increasing organic acids could cause displacement of base cations from soils to runoff, reducing the impact of DOC increases on runoff pH, but also leading to a reduction in soil base saturation.

Given the influence of DOC on light regime, energy and nutrient supply, and metal toxicity, observable biological responses to large DOC increases might be expected. These include transparency effects, for example on maximum depth of macrophytes within lakes, and indirect effects on the toxicity of Al to fish and other biota (Roy and Campbell, 1997; McCartney et al., 2003). While the former have not yet been observed in the AWMN, Monteith et al. (2005, this issue) have shown that faunistic changes are largely occurring at sites with rising ANC. This may simply represent an acidity response, but changes in Al complexation associated with an exchange of mineral for organic acidity could also contribute. Where DOC is rising in the absence of declines in mineral acidity, as in northern Scotland, these biological changes are absent. Given the complexity of factors influencing aquatic biota, clear identification of biological responses to changing DOC may require further monitoring.

Downstream effects of DOM increases may also be significant. High levels of humic substances, although not directly harmful, are generally removed from drinking water for aesthetic reasons. It has been suggested that humic substances in water during the chlorination process may (i) reduce residual chlorine levels leading to increased risk of bacterial contamination; and (ii) produce carcinogenic organo-chlorine compounds (Alarconherrera et al., 1994). Since humic substances are considered fairly unreactive on the timescale of most river (and small lake) residence times in the UK, much of the DOM released from upland regions is transported to estuaries, and into the oceans. Significant inputs of terrestrially-derived DOM to coastal waters, noted by Raymond and Bauer (2001), may significantly affect their energy, nutrient, and light regimes.

Regardless of the direct short-term consequences of rising DOC, their fundamental significance depends greatly on the driving mechanism. Because pre-industrial, reference conditions for UK surface waters are essentially unknown, and natural variability not well quantified, it remains unclear whether recent changes represent (i) a return to reference conditions following anthropogenic perturbation; (ii) fluctuations within natural ranges, or (iii) an increase towards "new" levels. If DOC increases are driven by declining acid deposition, then resulting biologic changes can be considered part of a return to the pre-industrial state. If increases are related to natural climate variability, they can in turn be considered natural. However, given current projected climate changes for the UK, notably increases in temperature and in winter/summer rainfall ratio (Hulme et al., 2002), even "natural" changes observed to date may be indicative of future responses to climate change. Furthermore, the recent succession of warm years in the UK has been attributed to human perturbation of the climate system (Hulme et al., 2002), and it is therefore possible that observed DOC trends already represent a response to this climate change.

If DOC increases in surface waters are attributable to warming, or to other meteorological factors associated with climate change, the potential consequences in terms of carbon cycling may be significant. DOC fluxes from UK rivers were estimated at 0.69 Mt year^{-1} in 1995 (Hope et al., 1997), comparable in magnitude to the UK C sink associated with peat accumulation (Cannell et al., 1999b). Worrall et al. (2005, in press) have recalculated the UK DOC flux for 2000 at 0.86 Mt year^{-1}. Given dissimilarities between UK peatlands and larger boreal and sub-arctic peatlands in Russia, North America and Fennoscandia, it would be unwise to extrapolate from the UK to a global prediction of DOC flux. However, changes in DOC export from these regions of a similar magnitude to those observed in the UK would represent a major transfer of organic C from terrestrial stores to more active dissolved forms, and ultimately to the atmosphere as CO_2.

6. Conclusions

There is now overwhelming evidence that DOC concentrations have increased during the last two decades at the AWMN sites, and other UK upland surface waters. There is evidence of similar changes at other monitoring sites across Europe and North America. These observations suggest a systematic response to one or more external drivers across a large spatial scale. At the AWMN sites, concentrations have now almost doubled, and it seems likely that changes of this magnitude will have significant long-term impacts on lake and stream biota. At a larger scale, these increases may also impact on drinking water treatment, coastal marine ecosystem functioning, and UK upland carbon balances. However, data remain equivocal regarding causal mechanisms. Although some potential drivers, such as land-use change, can probably be excluded at a UK scale, it is difficult to determine the relative importance of deposition-related and climate-related factors. The tentative conclusion of this assessment is that both appear significant; it seems probable that recovery from acidification has contributed to DOC trends in those regions where sulphur deposition has decreased, but comparable trends at essentially unimpacted sites in the northwest can only apparently be explained by climatic factors.

Ultimately, although monitoring programmes such as the AWMN have been essential to the identification of long-term trends in DOC, at present there is a limit to the extent that driving mechanisms can be inferred on the basis of monitoring data alone. There is a clear need for additional research in order to test the hypotheses that have been put forward to explain observed increases, including further study of DOM generation processes within terrestrial systems; manipulation experiments incorporating a range of potential climatic and chemical drivers; and studies of DOM transfer between soils and drainage waters. Improved palaeo reconstruction techniques are also needed to establish baseline conditions, and the trajectory of past changes in DOC concentration relative to known historic variations in climate and deposition. Ultimately, process-based models are required in order to predict future response of terrestrial carbon stores to changes in climatic and/or deposition drivers, and to simulate the chemical and biological impacts of these changes on aquatic ecosystems.

Acknowledgements

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