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Long term records of riverine dissolved organic matter

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Abstract. This presents the longest, consistent records of dissolved organic carbon in rivers ever published. This study presents long-term records of organic matter as indicated by water colour that were constructed for three catchments in Northern England for as far back as 1962. Observations show that there have been large increases in DOC concentrations over the period of study with in one case a doubling of the concentration over a period of 29 years. However, in one of the catchments no significant change was observed over a 31-year period. All catchments show common inter-annual control on carbon release in response to droughts, but no step increases in DOC concentrations were observed in response to such perturbations with pre-drought levels being restored within a period 3–4 years. Observed increasing trends do not correlate with changes in river discharge, pH, alkalinity or rainfall, but do coincide with increasing average summer temperatures in the region. The times series of DOC concentration over the period of the record appears stationary, but the distribution of daily values suggests a change in sources of colour over the increasing trend. The evidence supports a view that increases in carbon release are in equilibrium with temperature increases accentuated by land-use factors.

Introduction

Upland peat is an important reserve of carbon within temperate and boreal zones of the globe. Within the UK it is estimated that upland peat bogs are the largest terrestrial pool of carbon nationally (Cannell et al. 1993; Milne and Brown 1997) and a sink of 0.7 Mt C/a (Cannell et al. 1999). However, it is not known whether peatlands will remain a net sink of carbon in response to changes in temperature and rainfall changes.

Concern for the peatland carbon sink has been raised recently by the discovery of enzyme latch mechanisms that may control the oxidation of carbon under anaerobic environments and wetlands such as peat bogs in particular (Freeman et al. 2001a). Oxidative enzymes that are normally repressed in anaerobic conditions become active if the wetland is drained and becomes aerobic. Further, it is suggested that once active, such enzymes are not deactivated, hence the reference to an enzymatic latch. If such latches are operating in peatlands, then oxidation of carbon will continue long after the source of the disturbance has ceased leading to long-term degradation of these carbon stores, changing them from net sinks to net sources.

Upland peat catchments are major water supply catchments in the UK and the loss of carbon from these areas will result in a decrease in water quality with the concomitant release of dissolved organic carbon (DOC), known as water colour. Removing DOC is often the largest recurrent water treatment cost in these catchments and its incomplete removal leads to domestic water supply with:

1. low aesthetic quality;
2. low residual chlorine thus limiting its protection against biological contamination; and
3. potential for the formation of disinfection byproducts.

Long-term records of water colour are rare in the literature. Hope et al. (1994) provide an excellent review of riverine fluxes of carbon across the globe, and Hope et al. (1997) provide an equally good review of export from UK rivers; however, though several studies exist of dissolved carbon flux at specific sites no review exists. Asite and Klavins (1998) examined a 20-year record of monthly water colour and chemical oxygen demand (COD) for 9 sites across Latvia; all these time series showing decreasing levels of anthropogenic pollution and improved land-use practices. For the Upper Nidd catchment, part of the Upper Swale system which shares a watershed with the River Tees, Naden and McDonald (1989) constructed a 9-year record of water colour from variable frequency sampling at raw water intakes. In this period no overall trend was discernable: rather, high colour levels were associated with particular climatic conditions in certain years. For a range of sites in the lower part of Swale system and the larger Humber catchment, of which the Swale system is a part, 3-year time series have been constructed (Tipping et al. 1997; Eatherall et al. 1998). The Environmental Change Network (ECN) has monitored water chemistry in a range of small catchments since 1992 (Sykes and Lane 1996). For six of the catchments in upland Britain (including three sites within the Tees catchment) records of DOC exist for at least six years of weekly monitoring. Miller et al. (2001) analysed these records as means of developing and testing a particular approach to the deconstruction of time series but did not analyse the nature of trends in DOC. However, an increase in DOC levels from the Moor House site in the Upper Tees was observed. Freeman et al. (2001b) gave a brief description of records from a range of lakes and small catchments that showed that DOC concentrations had increased by an average of 5.4% each over the last 12 years. This study brings together the longest records so far described of carbon release from upland peats in the UK. The nature of the record will be examined to assess the reasons for observed trends.

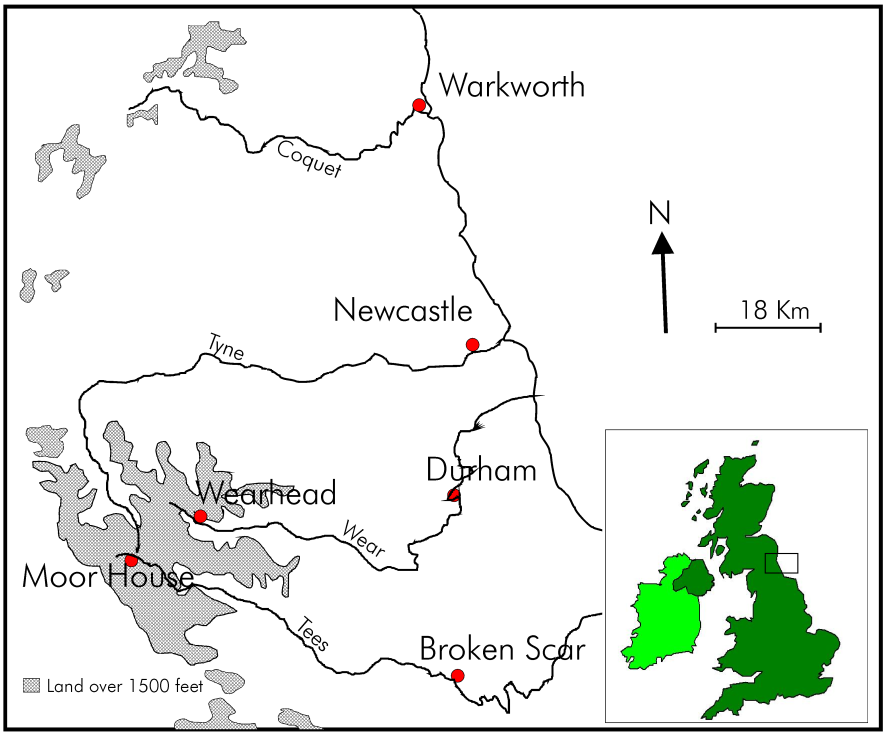

Figure 1. Location of sampling sites and catchments used in this study.

Methodology

Colour records for three sites were constructed for the intake to the treatment works at Broken Scar on the River Tees, Wearhead on the River Wear, and Warkworth on the River Coquet (Figure 1). All three catchments drain areas of upland peat in the Pennine chain of Northern England.

1. Daily records of water colour recorded at Broken Scar were collated for the years 1970 to 2000. To the authors knowledge this is the longest most complete and most detailed record of consistently sampled colour data available for any UK rivers.
2. Records at Wearhead started in 1966, but were initially on an *ad hoc* basis and record keeping was not regular until 1969. For the period 1969–1989 colour is measured weekly, it was recorded monthly for 1992, daily for 1993–1994. For 1991, 1996–1998 only records of annual average and range were available.
3. At Warkworth daily records were available from 1962 until mid 1994. The method of recording was then altered through the remainder of 1994 and throughout 1995, but was returned to the original practise for 1996 to the present.

At all sites water colour is measured spectrographically with an error of ± 5 Hazen units (half the smallest division) (Hongve and Åkesson 1996).

Water colour measurements in the intake waters at Broken Scar were supplemented with pH and turbidity measurements. Monthly average flow records and rainfall totals for the Broken Scar site were obtained from the national surface water archive (T.Martin, Centre for Ecology and Hydrology, Wallingford, UK) and temperature records were taken from the Durham University Observatory. Annual carbon loads were calculated using ″Method 5″ (Walling and Webb 1985), which is the preferred method of the Paris Commission for the calculation of riverine loads (Littlewood 1992).

A calibration experiment was performed to estimate the link between colour levels expressed in Hazen units and DOC concentrations. At Moor House, in the upper Tees catchment (Figure 1) weekly monitoring of DOC and absorbance at 436 nm has been performed since 1993 as part of the Environment Change Network (ECN – Sykes and Lane (1996)). To compare results from this study with ECN colour measurements on the 20th June 2000, all major tributaries of the Rivers Tees and Tyne were sampled from Moor House to the tidal limit of each river. The date was chosen as it followed 5 days of dry weather and so base flow conditions could be said to exist for both rivers over their entire length. Both rivers were chosen because their headwater sources are adjacent to each other at the Moor House site. The rivers were sampled along their lengths to enable a range of DOC concentrations to be sampled. In all 39 sites were sampled. Each sample was filtered through a 0.45 μm filter before being analysed for colour (Hazen units), and absorbance at 400 and 436 nm. These results could then be compared to the ECN samples to provide a calibration against DOC concentration. It should be noted that calibration between DOC measurements and absorbance measures of DOC can vary with season (Kaiser et al. 2001; Watts et al. 2001). However, the ECN monitoring of absorbance and DOC continues across the whole year, in this way a calibration between DOC and absorbance could be generated that was broadly applicable across all seasons. A second calibration was then generated for the period of the calibration experiment between absorbance, colour and DOC measurements. The comparison between these two calibration experiments means that a single, broadly applicable calibration between colour (in Hazen units) and DOC (in mg C/l) can be made.

Results

Flux of dissolved organic matter

The calibration experiment gave the following relationship between recorded colour and DOC:

$$DOC - 110Abs_{400} + 0.75 \qquad r^2 = 0.80 \tag{1}$$

$$DOC = 0.051\,Colour + 1.09 \quad r^2 = 0.82$$

where DOC = the dissolved organic carbon content in mg C/l; Abs400 = absorbance at 400 nm; and colour = water in colour in Hazen units. Eatherall et al. (1998) used a relationship of DOC = 0.1265 Colour, i.e. for that study an increase of one Hazen unit is more than twice the increase in DOC found in this study.

Colour levels at Broken Scar range as high as 400 Hazen (22 mg C/l), while at Wearhead the maximum is just over 200 Hazen (11–12 mg C/l) and Warkworth the maximum is 300. The annual load values at Broken Scar range from 0.75 Kt/a to 6.3 Kt/a, with the areal export ranging from 9.33 Kg/ha/a to 77.48 Kg/ha/a. These values must be considered an underestimate of the carbon load of the Tees at Broken Scar because the average flow figures tend to assume a normal distribution of the colour loads and this has been shown above not to be the case.

A comparison of the measured dissovled carbon loads with those measured on other UK rivers show that these values are comparable with other peat-dominated catchments (Hope et al. 1994). In general, the riverine carbon flux is thought to be 1 to 2 orders of magnitude less than annual exchange between vegetation, atmosphere and ocean (Dixon and Turner 1991). Nationally, the annual loss of organic carbon in rivers is about 0.01% of the total soil organic carbon (Hope et al. 1997) and less than 1% of Britain's estimated national fossil fuel emissions of carbon (based on 1993 values – Her Majesty Stationery Office, 1994). However, Clymo (1983) and Gorham (1991) have estimated that the net accumulation rate of carbon in peat in the UK is of the order of 0.4 – 0.7 t/ha/a: export rates for the Tees are of this order of magnitude. Equally, given that the values at Broken Scar are diluted by low carbon water from sub-catchments with little or no peat, it might be expected that export coefficients for peat catchments might well be higher, with the dissolved organic flux representing a significant proportion of the net accumulation.

It should also be noted that the fluxes are those for dissolved organic carbon fluxes and do not include particulate organic carbon (POC). For the Humber catchment (the Tees shares a watershed with the Humber system) the annual flux of POC shows a good linear relationship to the annual flux of DOC ((annual flux of POC) = 0.593 (annual flux of DOC) – 0.1185, $r^2 = 0.99$, n = 12 – Tipping et al. (1997)). Given this relationship total carbon fluxes could be as high as 9.9 Kt/a, equivalent to 121 Kg/ha/a. Eatherall et al. (2000) estimated that sewage fluxes to the River Swale represented up to 11% of the total carbon flux; this proportion might be expected to increase downstream as larger centres of population are encountered. All the sites in this study are upstream of the major centres of population in their respective catchments and so should not be significantly affected by sewage sources of carbon. Annual loads could not be calculated for Wearhead or Warkworth because of the lack of flow records for these sites.

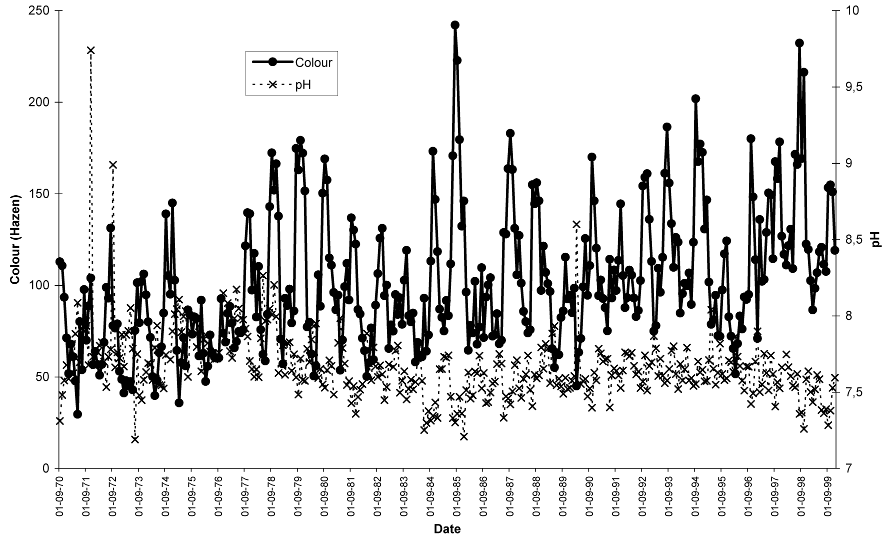

Figure 2. Monthly average water colour concentrations at Broken Scar.

Trends in organic colour

The overall trend in the Broken Scar record is clearly upward over the period of the record (Figure 2). A simple least-squares fit to this line explains 16% of the variation in the data. Alternative trend fitting techniques were used: a polynomial fit explained only 16% of the variation and an exponential fit explained 12% of the variation. The trend of this line shows that there is a average year-on-year increase of 1.75 Hazen – an increase of approximately 0.1 mg C/l every year. There is an increase of 51 Hazen units (2.6 mg C/l) over the entire period of the record – an effective doubling in the colour concentrations at Broken Scar therefore during this time. The record shows seasonal stationarity, i.e. the annual cycle in the DOC concentrations is not proportional to the annual average. If the series were non-stationary the amplitude of the cycle would be expected to decrease or increase with the trend in the DOC concentrations.

There is no statistically significant trend in the Wearhead data (Figure 3). At Warkworth there is a significant increase in the colour over the course of record amounting to 29 Hazen (1.5 mg C/l) annual average concentration over a period of 39 years – an increase of 61%. Comparing the annual average records for the three series shows a clear common phase relationship suggesting common controls between the three catchments. The peaks in the three records match each other suggesting that inter-annual controls are similar save for the factor which is causing linear trend in the Broken Scar and Warkworth records but not at Wearhead.

Several causes of this trend can be easily discounted since at Broken Scar records of river flow and water chemistry have been maintained at the same sampling frequency and over the same time period as the colour records. There is no

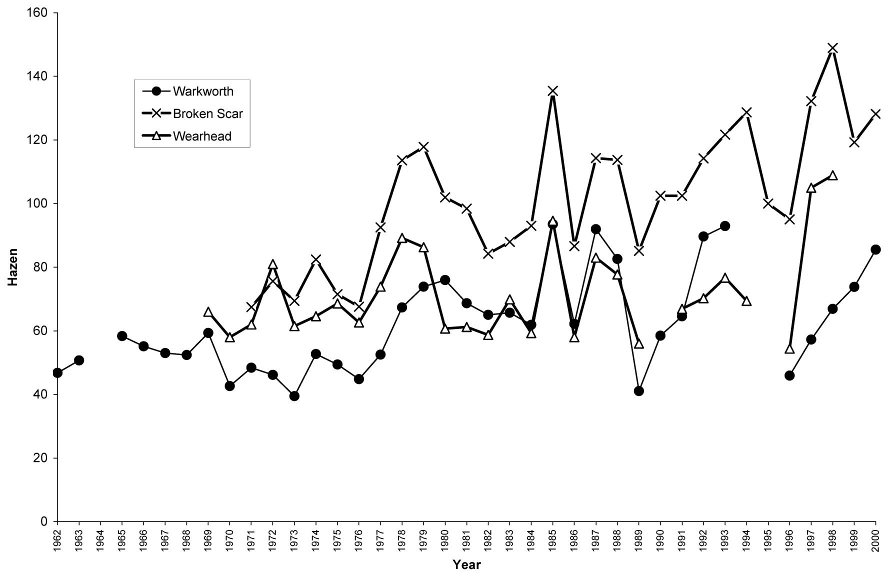

Figure 3. Annual average colour concentrations at Broken Scar, Wearhead and Warkworth.

significant trend, neither increase nor decrease, in discharge, monthly average rainfall, turbidity or alkalinity at Broken Scar over the period of the record. A significant decreasing trend is observed in the pH record (Figure 2); however, the annual cycles of colour release and pH are not in phase. The pH cycle follows the cycle in river discharge, i.e. winter maxima and summer minima as opposed to maximum in the early autumn for the colour levels. This suggests that different mechanisms may be driving catchment responses in colour and pH.

When monthly average temperatures are considered the relationship between colour and temperature is not clear, however, the important period is the period for production of mobile carbon which is in the summer months (June–August). The comparison between the colour records and the average summer temperature over the period of observations shows that a period of especially heightened colour follows the 1976 drought, but does not coincide with it (Figure 4) similar high-colour episodes follow the drought of 1984 and 1995. The greater the drawdown of water tables in upland peat, the greater is the capacity for oxidation of organic matter and the greater the reserves of mobile organic carbon built up over the summer period, and thus the greater the carbon flux during the autumn and winter period. The long summer drought of 1976 provided ample opportunity for the production of mobile organic carbon for release over the subsequent winter. However, this might be expected only to explain high levels of organic colour in winter subsequent to the drought, in fact approximately 3 years of high values are observed in each of the three observed sequences. Organic-rich peat is hydrophobic if dried extensively and will not re-wet easily, at least in the short term. In this case it appears that the long, deep drought of 1976 caused substantial drawdown in the peat water tables that

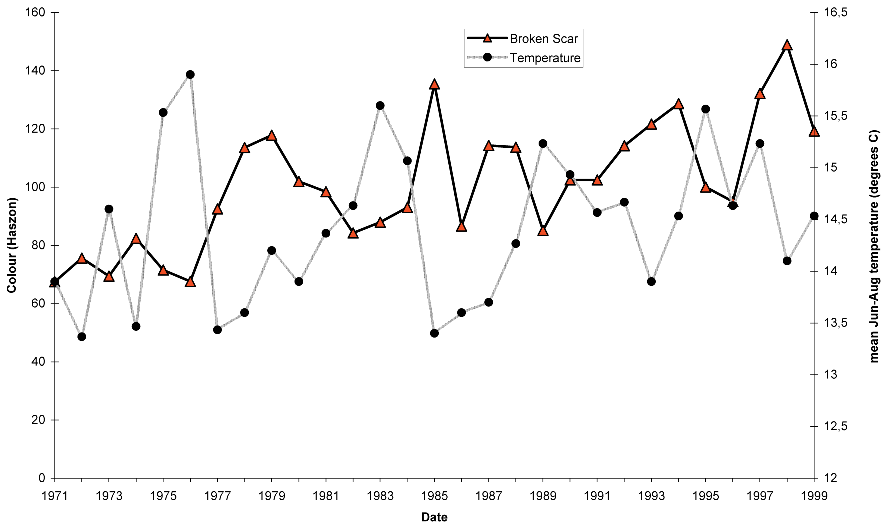

Figure 4. Annual average colour concentration at Broken Scar in comparison to average summer temperature for the region.

allowed extensive reserves of mobile carbon to be generated; the hydrophobic nature of the peat meant that this reserve could not accessed nor completely drained over the subsequent year. Rather the effect of the 1976 drought is seen in relatively increased levels of colour over at least the subsequent 3 years. Relative drought years can also be the explanation for other peaks in the three colour records, in particular the high average colour loads in 1985, through the early 1990's, and post-1995. Two alternative explanations, for this delayed effect to drought have been proposed, firstly, Holden (2000) has suggested that during severe water table drawdown as in drought new flowpaths are created that are not easily destroyed after the drought. These new flowpaths bypass the reserves of mobile DOC created during the drought. Secondly, Freeman et al. (2001a) has suggested that an enzymic latch is opened during drought period and this not readily switched off post-drought. This mechanism would mean that DOC production would remain high in the post-drought period, potentially for several years.

The average summer temperature over the period of the colour record (Figure 4) shows that there has been a rising trend in summer temperatures – approximately 0.6 °C in 29 years since 1970. Increasing summer temperatures would tend to lead to increased drawdown of water tables, this means an increased depth of peat is oxidised and so produces more mobile carbon. An additional effect comes from increased temperatures leading both to increased microbial activity and to increased evaporation, probably a major cause of falling water tables in summer in peat. Hence, increasing trends observed at Broken Scar and Warkworth can therefore be explained by increasing temperatures, but for the fact that the Wearhead catchment, which has experienced the same temperature increases, there is no increasing trend. At Warkworth values return to pre-drought levels: compare, for example, 1976 with

1980, and 1984 with 1989. This means that rises in temperature can only be a partial explanation for any observed long-term trend in organic colour.

One indication of the nature of the trend observed at Broken Scar can be seen if the data for the distribution of daily values are examined. The distribution of the daily values shows a distinct bimodality and, when this is compared over the period of the observation at Broken Scar, several trends in colour can be observed (Fig. 6). The bimodality could be explained as representing the event-based nature of the colour export from the peat headwaters. Worrall et al. show that levels of colour export from peat rise rapidly during runoff events and thus the higher mode of this distribution might represent the colour levels experienced at times of peak export.

There is trend in the magnitude of the higher mode of colour (Line B – Figure 5) with not all years showing a bimodal distribution of colour, for example, in years like 1983 there is little bimodality whereas in 1989 there is a strong bimodality. Over the course of the study there is cross-over between the two modes of colour distribution: earlier in the series the lower mode is dominant but the higher mode becomes dominant towards the end of the series. Over the course of the period of observation there appears little change in the spread of the distribution, i.e. the series reflect stationarity already observed in the data (Figure 3). These observations suggest that there has been a consistent increase in the colour levels as a whole, but that part of the changes represent a shift in importance between two sources of colour. This change may be explained in a number of ways. Firstly, changes in the relative importance of the observed modes (Figure 5) could be due to changes in the relative importance of the various flowpaths that govern the movement of DOC from peat uplands over the course of the record at Broken Scar. Secondly, the observed changes may be due to changes in the importance of sources within the catchment. Alternatively, the change in the relative importance of the modes could represent changes in the colour loads carried on the baseflow as opposed to being carried in runoff.

Discussion

What causes the long-term trends observed in DOC? There is an decrease in pH of the River Tees over the observed period and the solubility of organic compounds is strongly influenced by pH (Thurman 1985). Acidification of catchments might be expected to lead to increased levels of DOC and this has been observed in both natural circumstances (Hall et al. 1987) and in manipulation experiments (Broberg 1990). However, Grieve (1990a & 1990b) showed that DOC levels increased in three Scottish catchments that had been limed, whereas Kullberg and Petersen (1987) observed no changes in DOC upon liming. However, there is no necessary link between pH and DOC changes and the two have very different annual cycles. Therefore, although it can be known that pH is decreasing in the River Tees, this not necessarily related to increases in DOC.

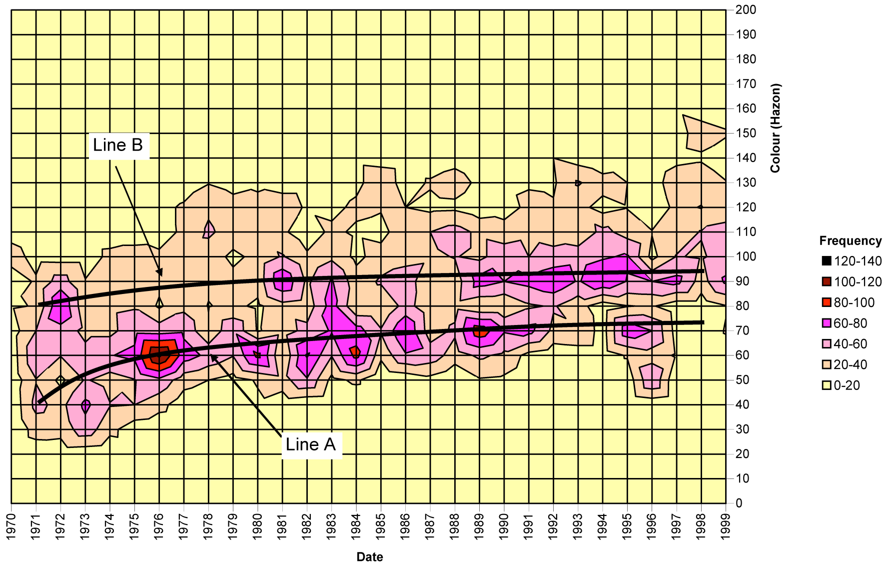

Figure 5. Annual distribution of daily water colour concentrations art Broken Scar over the period of the record. Lines A and B are indicative and were fitted by eye.

Climate change is being driven by changes in the global carbon cycle; soils represent a major sink of carbon and a large proportion of the of the total carbon store (Tans et al. 1990; Dixon and Turner 1991). Increased atmospheric CO_2 would mean increased carbon accumulation in the soil carbon reservoir (Smith and Shugart 1993). This could in turn increase the amount of carbon released to rivers, as a strong relationship exists between soil carbon content in a catchment and DOC released (Aitkenhead et al. 1999). Climate change would, however, have a range of other effects, in particular changes to temperature, rainfall quantities and rainfall distribution. Tipping et al. (1999) showed that increases in temperature *per se* would not lead to increased release of DOC but rather it is the combination of warming and drying cycles that leads to increases in DOC release. Changes in warming and drying represent a combined effect: firstly the increased temperature stimulates microbial degradation, secondly, increased drying allows increased access for oxygen into the soil. This extends the natural annual cycle that leads to flushing of DOC from peat uplands in the late summer/early autumn period. However, no such change upon increased drying was observed for forest soils (Borken et al. 1999), but in this case the effects of climate change may be buffered by the presence of mineral soil horizons. Clair et al. (1999) suggested, on the basis of modelling results for Canadian watersheds, that with a doubling of atmospheric carbon the release of DOC would increase by approximately 14%. The Tees catchment has shown an increase of 100% over the period of the record, i.e. far larger than would be expected on that basis.

The trend observed in the Broken Scar and Warkworth records do not correlate with simple measures of either rainfall or river discharge. There is an increasing trend in the average summer temperatures over the period which could lead to increased supply of mobile carbon. However, there could be unobserved features of the climate that could give rise to the increasing trend. For example, it could be related to changes in the rainfall distribution, such as rainfall intensity, rather than rainfall totals as used here. Burt et al. (1998) have suggested that winter-summer differences in rainfall are increasing and this may accentuate the effect of temperature change noted above. Given the limited data available to this study it is impossible to say. However, any climate change, be it increased carbon deposition or changes in temperature and rainfall, would be expected to occur in both catchments studied here and only one catchment shows a continuous upward trend.

Most studies of the effect of land use upon the release of DOC have focused on forested catchments (e.g. Swank (1986)). The pattern for carbon is similar to that of other nutrients, i.e. high values associated with any disturbance followed by a decline as new trees take up nutrients and a slow increase to a ″saturated″ situation as forest stands mature. In the case of afforestation, Grieve (1990b) found little difference in DOC concentrations released between an afforested catchment and a moorland catchment except at peak runoff. For upland peat, there are no observations available for catchments undergoing distinct land use changes other than afforestation. Freeman et al. (2001a) have suggested that land use changes could have a dramatic effect on the release of carbon from peatlands on the basis of an ″enzymatic latch″ mechanism. Anaerobic degradation in peat bogs is restricted by repression of certain enzymes. When the peat experiences drying out the repression is reduced and does not re-occur upon re-wetting. In upland peat drying out could be related to severe droughts or to land-use management such as drainage. For the catchments studied here drought effects parallel each other between the catchments, but the trends do not. It might then be possible that one of the catchments have undergone sufficient disturbance to trigger the enzymatic latch mechanism whereas the other has not. Indeed, the severest of the effect of the severest of droughts during the period of the study (summer of 1976). The advantage of the enzymatic latch mechanism is that would it predict increases in the production of mobile carbon across such disturbances, just as observed. However, in response to distinct drought years an irreversible step change in the DOC record would be expected but this is not observed. Are there other disturbances which could causes these trends? The most likely candidate is drainage of the North Pennine peatland. The permanent lowering of water tables caused by peat drainage would cause an increase in the depth of oxidation and could lead to the derepression of oxidative enzymes predicted by an enzymatic latch mechanisms and hence to increased carbon release. However, drainage of the peat and the permanent lowering of the water table in peat bogs would in itself be expected to increase oxidation of the peat, this coupled with the increased runoff could be sufficient to cause an upward trend without needing to invoke the latch hypothesis. The lack of drainage in the Wearhead catchment would provide a difference between the three catchments that can explain the lack of consistent trend in the Wearhead catchment.

Differences in land use could also be coupled with changes in climate to cause the effects observed. Evidence from the frequency distribution of colour in the Tees has suggested that there may be a change in importance of flowpaths in the upland peat (Figure 5). Indeed effects of land use and summer temperature may well be accentuated by enzymatic mechanisms, and Freeman et al. (2001b) have shown that phenyl oxidase activity increased with increase temperature incubation of peat. However, drainage and increasing summer temperatures are themselves sufficient to explain the trends and differences between the catchments observed. Furthermore, no step changes are observed in these long-term records as would be expected if enzmatic latch mechanism were operating.

Conclusions

This study has demonstrated consistent, stationary upward trends over at least a 39-year period in the levels of water colour from two upland peat catchments. The trend shows up to a doubling of colour concentrations over the period of the record with the annual load of dissolved organic carbon ranging from 0.75 Kt/a (9.33 Kg/ha/a) to 6.3 Kt/a (77.5 Kg/ha/a) with total organic load perhaps as high as 9.9 Kt/a (121 Kg/ha/a). However, no upward trend was observed in a third catchment. All records show a consistent response to inter-annual controls in all respects save for the one that causes an upward trend. In comparison to other records maintained for one of the study catchments, the upward trend in water colour cannot be explained by reference to rainfall, river flow, turbidity, alkalinity or pH. There is an upward trend in summer temperatures over the period of observation that could cause the increases observed in organic colour. Differences between the trends observed for different catchments can be explained by differences in land use principally differences in peat drainage. It has been hypothesized that land use changes and summer droughts could trigger an enzymatic latch phenomenon to lead to continuing carbon release from peat bogs; however, the change in land use and summer temperature are alone sufficient in themselves to cause the trends and differences observed. Enzymatic latch mechanisms would predict step changes in response to, for example, summer droughts; no such step changes are observed in any of the catchments and in one catchment average DOC concentrations return to pre-drought levels within 3 years.

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