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DISCOLOURATION OF WATER BY PEAT FOLLOWING INDUCED DROUGHT AND RAINFALL SIMULATION

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Abstract—This paper examines the discolouration of water by dissolved organic matter under controlled conditions. Winter hill association (raw peat) is subjected to prolonged natural drying to induce a range of moisture deficits. This peat is then subjected to rainfall simulation. Throughflow colour relates to drought duration and near surface water loss and rewetting. Attention is paid to the role of pore spaces in colour generation and removal. The implications for moorland management and the long term pattern of water discolouration are considered.

Key words—colour, decomposition, drought, rewetting, peat, water quality, potable water quality

INTRODUCTION

The uplands are a major source of water for public supply in the U.K. Runoff from these areas is often coloured by dissolved organic matter, such as humic and fulvic acids, derived from organic rich soils within drainage basins. Investigations into the chemical composition of these coloured waters are reviewed by Mitchell (1990a) while the wider implications for public health and upland land management are discussed in Mitchell (1991). Investigations in a variety of upland catchwaters in Northern England and Wales demonstrate that the intensity of runoff colour varies in a consistent manner between catchments (McDonald and Naden, 1987, 1988; Boon *et al.*, 1988). High colour values are found in water draining catchments with significant winter hill peat deposits, particularly where these are interfluve or bench peats (Boon *et al.*, 1988; McDonald *et al.*, 1991). Highest colours are found draining winter hill deposits on south facing slopes and where catchments have been drained or burnt to improve grouse moor. A regression model to predict the spatial distribution of coloured runoff has been developed using characteristics describing catchment topography, pedology and land use (McDonald *et al.*, 1991; Mitchell and McDonald, 1992). These observations suggest that water table depression and soil moisture regimes strongly influence the spatial pattern of runoff colour.

Although upland runoff has always been coloured to some extent, recent evidence suggests that some impoundments are becoming more coloured, particularly following the droughts of 1976 and 1984 (Edwards, 1987; Buckley, 1987; McDonald *et al.*, 1987). In addition water discolouration exhibits a strong seasonal pattern. Water colour is generally low during the dry summer months and increases rapidly to its annual maxima following the onset of high autumn rainfall. Examination of the long term trends in water colour for the Upper Nidd Valley, North Yorkshire, U.K. demonstrates that more than 50% of the variation in runoff colour can be accounted for by soil moisture deficits 3 and 14 months previously (Naden and McDonald, 1989). These observations also suggest that peat moisture status significantly influences water discolouration. This paper aims to determine the relationship between water discolouration and moisture regime in organic rich soils using controlled laboratory experimentation.

METHODOLOGY

Sample collection and storage

Thirteen peat samples were collected from the Scar House area of Upper Nidderdale, North Yorkshire (SE 06 60) and six from the Derwent Valley, Derbyshire (SK 20 90). Three of the Derwent Valley samples were collected from areas of extensive erosion with little or no surface vegetation cover. All samples were taken from areas of winter hill peat, the soil association previously identified as the primary non-point source of water discolouring material in the U.K. uplands (McDonald *et al.*, 1987, 1991). In order to minimize peat disturbance a 20 cm diameter steel ring was driven into the peat to a depth of 30 cm and then dug out with the intact peat core inside. The peat was then covered with thick circular wooden blocks to protect the surface and pushed from the steel ring by hand or using a screw type "hub-puller". The peat core was then firmly wrapped in plastic leaving only the surface exposed to the air. All cores were then stored under glass to exclude any precipitation whilst still being exposed to normal external air temperature and a daily light–dark cycle. Cores were stored in this manner from 1 to 600 days. The more prolonged drying periods were examined in order to assess the influence of severe desiccation on discolouration. Such desiccation has been observed in exposed and burnt peats in several north England catchments, particularly following summer drought (McDonald *et al.*, 1987, 1991). Peats prone to severe desiccation result primarily from exposure following erosion and moorland ditching and from burning. To ensure even drying from the surface only, cores were periodically rewrapped to accommodate peat shrinkage. The deviation in moisture content between the edge and centre of the core after 360 days' storage was 1.7% at 3 cm and 0.15% at 23 cm. Each core was cut down to a standard length of 23 cm prior to rainfall simulation to remove any bottom peat that had suffered compression during storage.

Rainfall simulation

At the end of its allocated drought period each core was subjected to rainfall simulation. The simulator has a 10 l. reservoir suspended above the core and is kept in gentle constant motion by attachment to an eccentric cam. The reservoir has 40 hypodermic syringes set into its base. Different needle sizes allow various drop sizes to be achieved, which, coupled with the hydrostatic head allows the rainfall rate to be controlled. A needle bore of 0.5 mm and an initial hydrostatic head of 15 cm resulted in a rainfall rate of 4.5 mm h^{-1} falling to 2.8 mm h^{-1} at the end of the 24 h simulation period. Distilled water modified to pH 5.0 ± 0.2 with 0.1 M H_2SO_4 was used. Experiments with disturbed peats and using rainfall with a simulated chemical composition (US EPA, 1978) demonstrate a similar pattern and extent of colour output to rainfall simulation with pH-adjusted distilled water (Mitchell, 1990b; McDonald *et al.*, 1991).

Each peat core is supported on a large funnel which directs the throughflow to a sample bottle. A 15 cm diameter ring is sealed onto the funnel and firmly pushed into the base of the peat core. This ensures that only water passing directly through the peat is collected. Water that does not pass through the ring is diverted through holes in the funnel above the ring to waste.

Moisture content of the peat was determined gravimetrically at 0–3, 3–9, 9–15 and 15–23 cm depth intervals by subsampling 2 cm into the core, before and after simulation. Water colour was measured after 0.45 μm filtration on a Pye-Unicam u.v./vis. spectrophotometer at 400 nm^{-1}. Colour was expressed as a mass (aum^{-1}l) to control for variation in throughflow rate.

Water colour is influenced by pH variation. Acidification of humic waters lowers the colour while raising the pH increases it. However, no pH adjustment was performed prior to colour determination as visible colour is under study, not the organic content of the water. In addition, accurate pH adjustment of small hourly throughflow samples is problematic, while titration analysis indicates that a colour change of <9% occurs across the observed throughflow pH range.

RESULTS

The typical pattern of colour output during rainfall simulation is shown in Fig. 1. All peat samples showed a rapid initial rise in colour, usually peaking after 4–6 h, followed by a gradual decline. Throughflow pH mirrors this pattern, with a rapid increase in acidity to the colour peak, followed by a gradual decline. This is consistent with the removal of colour producing dissolved organic matter, such as fulvic and humic acids, contributing to an "acid flush". Figure 2 illustrates the variation in mean throughflow pH with induced drought period. The positive relationship between acidity and drought duration is believed to be indicative of the accumulation of a "store" of water soluble, colour-producing organic acids. Figure 1 also illustrates the apparent increase in colour with storage time. For each peat core, the total colour output during the 24 h rainfall simulation period (TCO_{24}) was calculated as:

$$TCO_{24} = \Sigma(C_t \times T_t) \qquad (1)$$

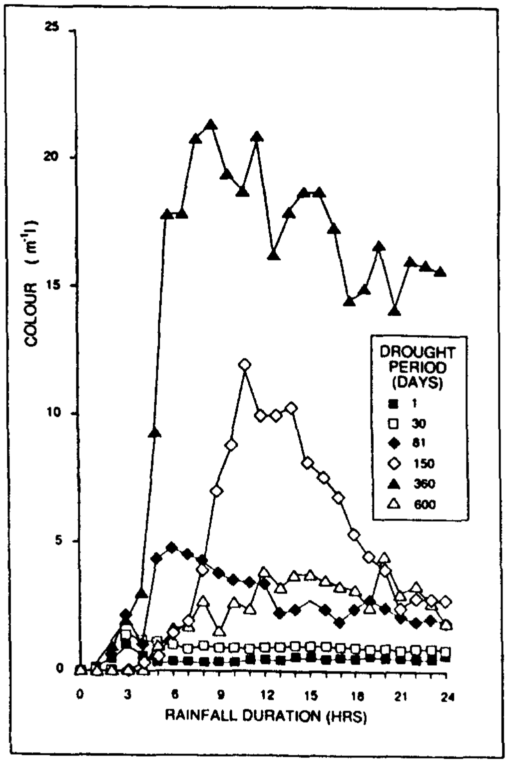

Fig. 1. Throughflow colour from droughted peats during rainfall simulation. (Thirteen intermediate lines omitted for clarity.)

where C_t is water colour, T_t is throughflow in litres and t is time in hours. Two observations were omitted. Both of these had high standard residuals (>2.0) whereas all other observations were typically at or

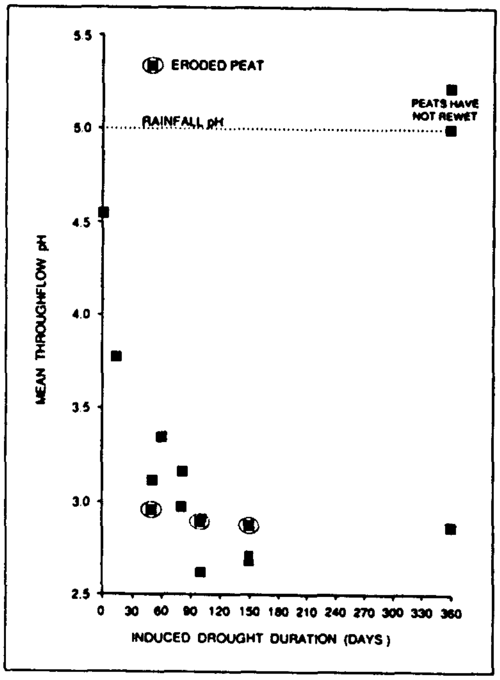

Fig. 2. Variation in mean throughflow pH with induced drought period.

Table 1. Pearson correlation coefficient between total colour output in 24 h and moisture content

Depth interval (cm)	R	N	Probability
0–3	0.916	18	<0.001
3–9	0.733	18	<0.001
9–15	0.588	18	<0.01
15–23	0.459	18	<0.01

below 1. The anomalies were in cases which had dried to a point where they shed water and did not begin to rewet within the 24 h period relevant to this examination (Fig. 4 shows the increased delay in colour response as drought severity increases thus taking the time of peak response beyond 24 h). After omitting these two observations, regression analysis of colour on drought period gives the relationship:

$$TCO_{24} = 0.576S + 1.3 \tag{2}$$

where S is drought period in days. This relationship is highly significant ($r = 0.713$, $N = 19$, $P < 0.001$) and demonstrates that the store of water soluble colour in the peat cores increases as a function of drought duration.

The Pearson correlation coefficients between TCO_{24} and moisture content at each depth interval were determined and are presented in Table 1.

Near surface drying has the strongest single influence on the production of a soluble colour store. Peat moisture content determinations at each depth interval indicate the role of the surface and near surface peat in acting as a "protective crust", preventing anything more than light dewatering below 3 cm. At the surface (0–3 cm) all peats sampled had lost at least 25% moisture after 50 days drying. However, at 3–9 and 9–15 cm 25% moisture loss is attained only after 360 and 600 days drought, respectively. Below 15 cm peat moisture content remains above 80% even after 600 days drought. The protective crust, while preventing drying beneath it, is itself subject to great aerobic decomposition and oxidation processes. This results in enhanced organic matter breakdown and increased availability of water soluble colour-forming organics.

Products of organic matter breakdown are only translated into colour on contact with water. For each peat sample the per cent moisture before and after rainfall simulation was determined at each depth interval. The difference between these observations determines the degree to which the peat has rewet. The Pearson correlation coefficients between TCO_{24} and per cent rewetting at each depth interval (δM) were determined (Table 2).

Table 2. Pearson correlation coefficient between total colour output in 24 h (TCO_{24}) and rewetting (σM) at the specified depth intervals

Depth interval (cm)	R	N	Probability
0–3	0.957	18	<0.001
3–9	0.772	18	<0.001
9–15	0.340	18	<0.01
15–23	0.410	18	<0.01

These results indicate that rewetting of the surface peat layers is strongly related to and may be responsible for the greatest proportion of discolouration. At depth there is little drying due to the structure of the peat and the protective surface crust, resulting in only a small increase in the store of soluble decomposition products. Therefore, rewetting in these lower peat layers cannot account for water discolouration. The near surface peat has been subject to more extensive drying producing a larger colour store. When this peat rewets the soluble organic store is mobilized and removed as coloured water.

Stepwise regression of TCO_{24} moisture content before and after rainfall simulation, and moisture change for each depth interval was able to account for 92.43% of the variation in TCO_{24}. However, the change in moisture content of the near surface peat (0–3 cm interval) was able to account for 91.58% of the variation alone (Fig. 3).

$$TCO_{24} = 7.85\delta M_{0-3} + 5.16 \tag{3}$$

where δM_{0-3} is the change in moisture content of the 0–3 cm interval on rewetting. The next most significant varable, δM_{3-9} adds less than 1% to the total explained colour variance.

DISCUSSION

The natural discolouration of water results from the action of two basic processes. These are firstly, the accumulation of water soluble organic decomposition products, and secondly, their subsequent removal by

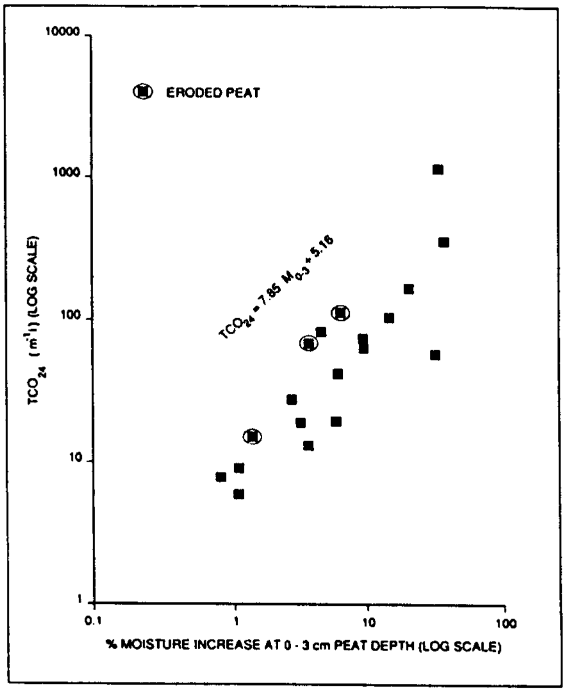

Fig. 3. Relationship between total colour output (TCO_{24}) and surface rewetting following rainfall simulation ($r^2 = 0.91$, $P < 0.001$).

Table 3. Theoretical peat pore size-frequency distribution

Pores/cm^3	Pore diameter (μ)	Pore volume (m^3)	Pore internal surface area (m^2)
10^2	300	7×10^{-9}	2.8×10^{-4}
10^4	30	7×10^{-10}	2.8×10^{-4}
10^6	3	7×10^{-11}	2.8×10^{-4}
10^8	0.3	7×10^{-12}	2.8×10^{-4}
10^{10}	0.03	7×10^{-13}	2.8×10^{-4}

water. These may be considered as processes of colour production and removal.

Colour production

Colour production results from the accumulation of water soluble organic decomposition products. These products are produced by the action of oxidation and soil micro-organisms on the internal walls of soil pore spaces. The importance of soil micro-organisms in discolouration has been demonstrated by McDonald *et al.* (1991) where a significant decrease in soil respiration and extractable colour was observed following micro-organism control in disturbed peats treated with antibiotic solutions. In winter hill association peat the aerobic decomposition rate is approximately three times the anaerobic rate (Mitchell, 1991). Thus the quantity of decomposition products is largely dependent on the total pore space surface area of peat exposed to air.

Table 3 gives the hypothetical distribution of pore frequencies as a function of pore diameter (after Loxham and Burghardt, 1986). The rapid moisture loss experienced by saturated peats in the initial stages of drying is a result of dewatering from the large diameter pores with low suction pressure. Dewatering of these pore spaces results in the exposure of peat to aerobic bacteria and oxidation processes, the subsequent breakdown of organic matter, and thus production of a colour store. Organic matter breakdown continues if further pore space surface areas are exposed. This requires either the physical disturbance of the peat structure or further drying to dewater pores with progressively higher suction pressures. Physical disturbance is most commonly a result of changes in soil moisture status, and is likely to result in the removal of those water soluble organics already produced. Thus it is continued peat drying that is likely to be the most significant factor in the growth of the colour store.

Due to compression by overlying peat, sub-surface peat is deficient in larger pore spaces. However, surface peats have a relative abundance of these larger pore spaces due to root growth, movement of soil fauna and absence of overburden. This produces a skewed pore frequency–diameter distribution. Given this skewed distribution, with large pores dominant in the surface peat, and small pores dominant below, drying results in a rapid moisture loss at the surface, with a relatively small exposure of internal pore surface areas. At depth, dewatering could produce an increase in exposed internal surface areas over a range of up to four orders of magnitude (Table 4). Thus at depth, a uniform volume of peat may have up to 1×10^4 times the total internal surface area of near surface peat.

A prolonged drought will thus draw out water from pores with smaller volumes, higher suction pressures, and a much greater total internal surface area. This will result in a considerable increase in organic matter breakdown and produce a larger colour store. In the near surface peats the rate of colour accumulation increases when the drought period exceeds 120 days. This may be the point at which a particular pore size first becomes dewatered allowing decomposition processes to add to the colour store.

Colour removal

Decomposition products are removed by the movement of water. Some of these products are water soluble, and will cause discolouration. The extent of discolouration is determined by the degree to which water can access pore spaces, rewetting the peat, and removing the colour store. Under rainfall simulation the degree of discoloration of peat core throughflow was directly proportional to the extent of near surface peat rewetting. The near surface peats experience the greatest drying and so have the largest colour store to be released on rewetting.

Severely dried peats ($\geq$35% moisture loss) are particularly resistant to rewetting. This is due to macro-pore collapse following drying, and to high suction-pressures found in micro pores. In addition, drying causes humic macromolecules to shrink, binding the lower weight molecular fractions responsible for colour (Hayes, 1987). On initial wetting these peats will shed water, preventing the removal of organic matter. However, continued wetting will eventually lead to the access by water to all pore spaces, dependent upon pore size and pore structure the eventual saturation and the removal of the colour store. For changes of up to 50% in moisture content in peat, permeability can range over five orders of

Table. 4. Theoretical peat pore surface area–diameter distribution

Pore diameter (μ)	Internal surface area (m^2)	Pore volume (m^3)	Number pores per 300 μ pore	Relative surface area (m^2)
300	2.8×10^{-7}	7×10^{-12}	1	1
30	2.8×10^{-9}	7×10^{-15}	1×10^3	10
3	2.8×10^{-11}	7×10^{-18}	1×10^6	1×10^2
0.3	2.8×10^{-13}	7×10^{-21}	1×10^9	1×10^3
0.03	2.8×10^{-15}	7×10^{-24}	1×10^{12}	1×10^4

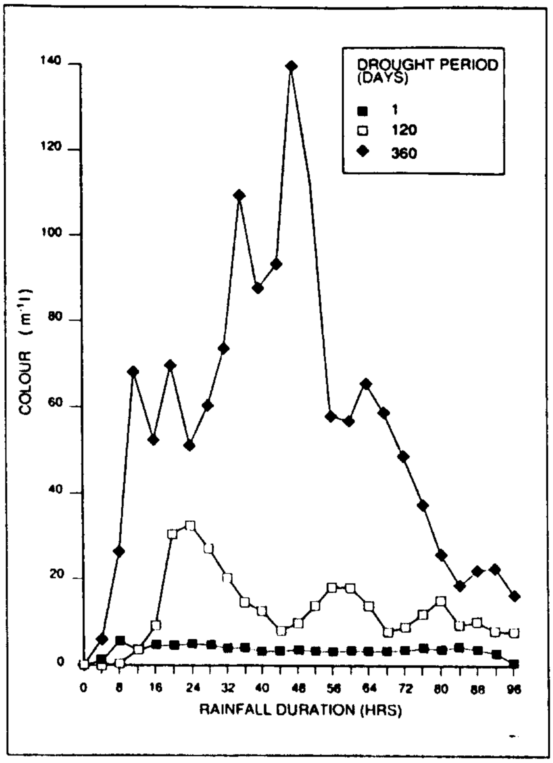

Fig. 4. Throughflow colour from droughted peats during prolonged rainfall simulation.

magnitude (Loxham and Burghardt, 1986). During rainfall simulation it took several days continual rainfall until peak colour output was reached (Fig. 4). The peat samples subject to the most prolonged drought take the longest to attain peak colour output, and release the most colour.

Implications for the long term trend in colour

The seasonal cycle of water discolouration is attributed to the accumulation of organic decomposition products during the dry summer months and their subsequent removal following periods of prolonged rainfall. This gives rise to the "autumn flush" phenomena. Particularly high colour levels were observed following the droughts of 1976 and 1984. Following these droughts, highest colours were observed not in the autumn of the drought year, although levels were high, but in the autumn flush of the following year. This lag time can be interpreted in the light of peat rewetting. The time taken for peat catchments to rewet following drought is likely to be prolonged as real rainfall is discrete and rates are very much lower than those used in the rainfall simulation to flush the colour store from the peat samples. A significant proportion of the summer colour store will not be accessed by the autumn flush of that year. This part of the store will be removed the following autumn when the peat fully rewets, and will be added to that summer's store, producing an exceptionally intense colour flush.

If the long term climatic trend remains relatively constant then the seasonal pattern of water discolouration is also likely to remain constant. However, the most favoured climate scenario for the U.K. following global warming is a shift in the timing of precipitation from spring and summer to autumn (Wigley and Jones, 1987). A scenario of drier summers and wetter autumns is likely to result in later, more intense colour flushes. If summers are in addition not only drier but warmer too, then peat micro-organism activity may be promoted, increasing total decomposition and the colour store.

Implications for moorland management

Any action that causes severe drying at the peat surface ($\geqslant 35\%$ water loss) will greatly increase the store of decomposition products that can discolour water. The pattern of colour release from the eroded Derwent Valley cores was consistent with their drying and rewetting (Fig. 3). These cores are thus not dissimilar to the other peats examined. Thus peat erosion is not thought to increase colour *per se*, but results in increased colour due to enhanced surface drying. Eroded peats dry more readily due to a lower albedo, and an absence of plant roots transporting water to the surface. Catchment studies in the Derwent Valley, Derbyshire indicate that a high proportion of the annual colour load does originate in areas with significant peat erosion (McDonald and Naden, 1988). However, the relative colour fluxes from eroded and uneroded moorland was not determined during the autumn flush period.

Similarly moorland drainage ditches expose large surfaces of bare peat contributing to severe drying and colour release on rewetting. Intense drying of bare peat also results in vertical cracking, greatly increasing the total area on which drying processes act. Moorland burning will also act to increase the colour store by lowering infiltration capacities and enhancing drying of sub-surface peat. These actions may dry near surface peat to a far greater extent than any natural drought, producing water of extreme colour when complete rewetting eventually takes place. The colour of standing water in one heavily ditched sub-catchment of the Upper Nidd Valley was observed to be in excess of 1000 aum^{-1} (*c.* 14,000 Hazen), up to three orders of magnitude greater than waters in adjacent unditched catchments. This water has such a significant impact on mean catchwater colour following catchment flushing that water from the entire catchment is excluded from water supply.

Eroded, burnt and mechanically exposed peats have a darker surface and lower albedo than moorland vegetation. These peats experience greater absorption of solar radiation which acts to elevate surface temperatures and further promotes decomposition. Intensive sampling of a small moorland catchment (<2 km^2) demonstrates that during the autumn flush period a major proportion of the total colour load in runoff originated from such highly localized areas within the catchment (McDonald *et al.*, 1987)

Severe peat drying, whether as a result of erosion, ditching, burning or simply through prolonged natural drought, greatly increases the accumulation of decomposition products. The capacity of these peats to rewet quickly is much reduced prolonging the available time for decomposition, so that when saturation is achieved runoff will carry a very high load of water discolouring organic solutes.

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