

Spectrophotometric properties of surface water dissolved organic matter in an afforested upland peat catchment

Andy Baker,^{1*} Lucy Bolton,² Malcolm Newson³ and Robert G. M. Spencer⁴

¹ School of Geography, Earth and Environmental Sciences, University of Birmingham, Birmingham B15 2TT, UK

² The Environment Agency, Lower Trent Area Offices, Nottingham NG2 5FA, UK

³ School of Geography, Politics and Sociology, University of Newcastle-upon-Tyne, Newcastle NE1 7RU, UK

⁴ Department of Land, Air and Water Resources/Department of Viticulture and Enology, University of California, Davis, One Shields Ave, CA 95616, USA

Abstract:

Many upland catchments in the UK have undergone afforestation; their characteristic waterlogged soils require extensive pre-plantation ground drainage to allow tree establishment. In peatland areas this can result in very highly coloured runoff and enhanced dissolved organic matter (DOM) export in rivers of naturally high concentrations. In 1966, the Coalburn Experimental Catchment, northern England, was established to investigate the impact of afforestation on an upland peat catchment. Here we report the variations in DOM spectrophotometric properties of streamflow in the catchment at canopy closure, especially with respect to potential carbon sources within the artificial drainage ditches. Drainage ditches are characterized by water that has higher absorption coefficients and which is more highly coloured than in the catchment tributaries. Ditched, afforested areas produce more highly-coloured runoff waters that are more fluorescent and absorbent normalized to carbon concentration compared to ditches in open moorland. Ditches that had been experimentally re-excavated have organic matter of different spectrophotometric character, with higher dissolved organic carbon concentration and less aromatic or lower molecular weight material. It is hypothesized that this is due to the exposure of bare peat faces within and adjacent to the ditches that are more susceptible to drying compared to vegetated areas. The large extent of this drainage network acts as both a rapid transport network increasing hydrological connectivity and a pool for the storage of DOM, which is of different spectrophotometric character under low flow conditions, depending on management conditions. Copyright © 2007 John Wiley & Sons, Ltd.

KEY WORDS carbon export; spectrophotometry; afforestation; peat; ditches

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INTRODUCTION

Upland catchments in the UK have characteristic waterlogged soils which, if afforested, require extensive pre-plantation ground drainage to allow tree establishment. This practice is widespread throughout Northern Europe (Robinson, 1998) where, on blanket peat over 45 cm deep, there is an estimated 190 000 ha of forestry (Byrne and Farrel, 1997), much of which is extensively drained. Forestry on peat areas has impacts on hydrology, ecology, surface water quality and carbon cycling. For example, runoff from afforested regions has higher dissolved organic carbon (DOC) concentration and water colour compared to unforested areas (Grieve, 1990; Mitchell and McDonald, 1992). In peatlands, this can result in very highly coloured waters and further enhance dissolved organic matter (DOM) export in rivers which already have naturally high concentrations. Increases in peatland DOM export present water quality concerns, notably with respect to water colour and disinfection by-product formation during treatment of drinking water supplies (Singer, 1999). Broader concerns come with the increasing emphasis on the export of organic carbon from peats

and organo-mineral soils in relation to global climate change (Freeman *et al.*, 2001; Worrall *et al.*, 2005).

In the UK, the highest concentrations of DOC and the most coloured water typically occurs in autumn during high river discharge (Tipping *et al.*, 1997). In peatlands, this is partly due to the transport of relatively fresh organic matter that has been produced due to the seasonal lowering of the water level in the peat during any summer soil moisture deficit (Naden and McDonald, 1989). Afforested peatlands may additionally affect catchment river water colour and DOC concentration by lowering the peat water table through the drainage ditches, through forest interactions with the hydrological cycle and through the production of additional organic carbon from forest sources.

In order to determine the relative importance of these factors, methods are required to differentiate organic carbon from different sources. Conventional DOC and water colour methodologies are good at quantifying organic carbon concentration (Blough *et al.*, 1993; Watts *et al.*, 2001; Worrall *et al.*, 2005), but are poor at identifying organic carbon source. In contrast, spectrophotometric techniques, specifically Ultraviolet–Visible (UV–Vis) absorbance and fluorescence, can quantify organic carbon source in a wide range of freshwater systems (Baker,

*Correspondence to: Andy Baker, School of Geography, Earth and Environmental Sciences, University of Birmingham, Birmingham B15 2TT, UK. E-mail: a.baker.2@bham.ac.uk

2001, 2002b; McKnight *et al.*, 2001; Katsuyama and Nobuhito, 2002; Baker and Inverarity, 2004; Bengraïne and Marhaba, 2004; Cammack *et al.*, 2004), including the use of fluorescence spectrophotometry to investigate runoff pathways in an afforested peatland (Newson *et al.*, 2001).

Having demonstrated the utility of fluorescence spectrophotometry in sourcing organic matter in an afforested upland catchment (Newson *et al.*, 2001), this paper presents work on the same catchment but with the more specific aim of determining the spectrophotometric properties of dissolved organic matter of streams/ditches draining both afforested and open moor. As well as investigating differences in organic matter spectrophotometric properties in tributaries of contrasting land cover, we focus on the characteristics of organic matter found within the drainage ditches. Through the use of micro-catchments, we compare afforested and open moor, and re-excavated and control (in effect, untouched for ~36 years) ditches. The identification of land cover specific spectrophotometric properties would have utility in identifying the potential influence of afforested peatlands on temporal variations in catchment dissolved organic matter.

MATERIALS AND METHODS

Site description

The Coalburn Experimental Catchment (CEC) is located within Kielder Forest, in an upland area of peat and peaty gley/podsol soils that has been largely forested for commercial exploitation. Coalburn is a headwater tributary of the River Irthing, located approximately 40 km to the northeast of Carlisle (Cumbria). The Coalburn Experimental Catchment (Figure 1) is a 1.4 km² upland area with an altitude varying from 330 m (AOD) to 275.3 m at the catchment outfall. The main channel gradient is 25 m km⁻¹. Long term average annual precipitation (1967–1996) is approximately 1350 mm which is distributed relatively evenly throughout the year, and snowfall occurs in most years. Forest interception losses are measured at ~21–27% of the gross rainfall (1994–1998). Mean stream flow at the catchment outfall is 0.046 m³ s⁻¹. The maximum recorded flow value is 6.00 m³ s⁻¹ and zero flow is observed during dry periods (Robinson, 1998).

The geology of the catchment consists of Lower Carboniferous sediments (Upper Border Group, calcareous mudstones, sandstones and shales) covered by locally derived glacial/fluvioglacial boulder clay, of a thickness

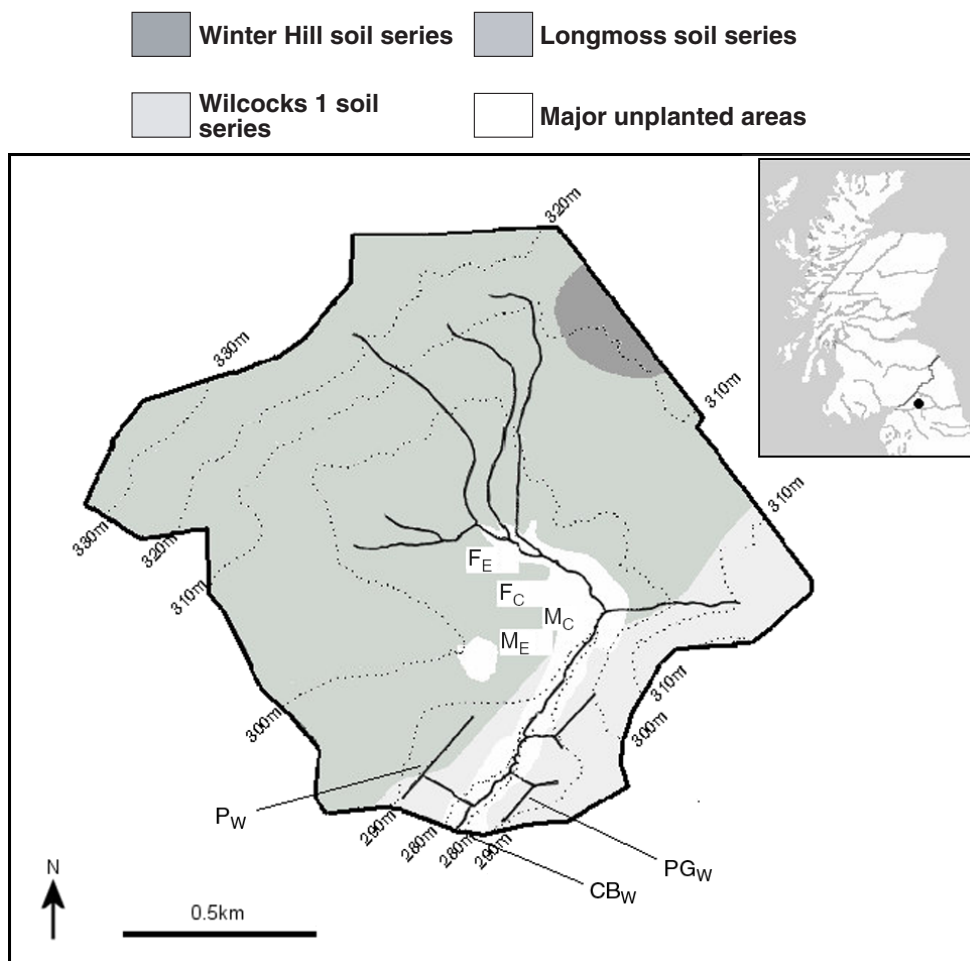


Figure 1. The Coalburn Experimental Catchment, showing location, soil types, topography and main surface water channels. Catchment outfall: national grid reference NY693777; 55°05'39" N 2°28'40" W (adapted from Robinson, 1998). CB_w: main channel; P_w: peat subcatchment surface sample; P_{Gw}: peaty-gley subcatchment surface sample; F_E, F_C, M_E, M_C: forest and moorland experimental and control, respectively

up to 5 m. Above this is a surface layer of blanket peat generally 0.6–3 m deep. Approximately 75% of the catchment is covered by peat bog. The remaining 25% of the area, in the southeast of the catchment, has steeper slopes ($>5^\circ$), and is covered by peaty gley soils (Robinson, 1998).

The catchment has been monitored since 1966 to investigate the hydrological impacts of the local forestry activities, from peat drainage and tree planting to future felling. Prior to forestry, the catchment was used for rough grazing. Vegetation consisted of *Molinia* grassland and peat bog species, such as *Eriophium* spp., *Sphagnum* spp., *Juncus* spp. and *Plantago* spp. The area had rock sulphate applied, was ploughed and drained in 1972 and, following a year for the improvement of soil conditions, Sitka spruce (*Picea sitchensis*) and some Lodgepole pine (*Pinus contorta*) were planted in spring 1973. Approximately 90% of the catchment was planted. Boundary ditches were dug prior to plantation to define the exact area of the catchment. The drainage system, constructed to provide drier and more aerated soils for tree growth, increased the natural drainage density of the catchment by approximately sixty times, to 200 km km^{-2} . The artificial drainage network consists of ditches (plough-furrows) spaced at about 4.5 m, which are intercepted by deeper drains or allowed to run directly into the natural streams. Vegetation growth, litter accumulation and sedimentation have resulted in the infilling of the majority of these ditches that are (in 2004) 0.4–0.5 m deep.

At the end of 1992, 60% of the forest in the catchment had reached canopy closure stage and by the end of 1996, the canopy had closed and trees grown to approximately 10 m tall (Robinson, 1998). The understory currently consists of *Sphagnum* spp. and some *Molinia*, with a spruce needle layer along tree rows (Hind, 1992). Robinson (1998) summarized the implications of the hydrological effects of forestry in the catchment. The effects observed are due to artificial drain network and are manifested in increased water yield after planting and an increase in peak flows. The impact of both of these factors has been reduced due to tree growth and the natural infilling of the drainage system with organic litter and moss growth. However, an increase in low flows has been observed that is thought to be effectively permanent during the period of forestry (Robinson, 1998).

Sample sites

There are two different pedological areas within the CEC, shown in Figure 1. These comprise raw oligofibrous peats (Long Moss and Winter Hill series) to the north and west and cambic stagnohumic gleys (Wilcocks 1 series) to the east (Robinson, 1998). The eastern peaty-gley subcatchment (catchment area ~ 1.6 ha) has a lower mean soil moisture content compared to the western peat subcatchment (catchment area ~ 3.0 ha).

V-notch weirs were installed on drainage ditches on each subcatchment for the monitoring of hydrology. The locations of the sampling points within the catchment are

shown on Figure 1. The abbreviations used in this study to denote samples from each of the points are detailed in Table I. Water sampling was performed from January 2000 to January 2002. During March–August 2001, the site was not accessible due to the Foot and Mouth disease outbreak and subsequent closure of access routes (National Audit Office, 2002). No data were therefore available for this period.

Water samples were collected at approximately weekly intervals from the main channel at a point upstream of the weir (CB_{weir}, Figure 1). Higher resolution sampling of the main channel was performed between 2 January–20 February 2001 and 1 August–21 October 2001 at 8 hour intervals using a Rock and Taylor auto-sampler. Bottles were cleaned by soaking in 10% HCl and thorough rinsing with non-fluorescent distilled water. Due to the nature of the equipment, each bottle had to be reused. Initial checks revealed that if thoroughly cleaned, there was no potential for cross-contamination from previous contents. Sample stability was also addressed as samples were collected at approximately 14 day intervals. Duplicate samples taken at the beginning of each auto-sampler run, one of which was analysed immediately and the other left for 14 days in the auto-sampler, duplicated well and varied by less than instrument analytical errors.

Water samples were also collected at v-notch weirs from ditches draining each subcatchment, located on Figure 1. Both of these ditches are located at the edge of the forested area and intercept flow from ditches draining from closed canopy forest. The sampling points replicate sites sampled by Mounsey (1999) and by Newson *et al.* (2001). A further four ditches were sampled representing micro-catchments of size 300–500 m², all located in the peat subcatchment. These ditches are located on Figure 1. One pair of micro-catchments drain established forest (F_C and F_E) and the other pair drain moorland (M_C and M_E). Two of the ditches were deepened in 1997 to their original depth of 0.9 m as experimental systems, one forest (F_E) and one moorland (M_E) micro-catchment; the others were left as controls. This was originally performed to investigate the effect of remedial drainage treatment on the generation of extreme flows by comparison of re-excavated and partially infilled ditches. Sampling was performed adjacent to v-notch weirs installed on all the ditches.

Table I. Details of the abbreviations of samples sites used in the text

Location/Description	Abbreviation	No. samples
Main channel (manual/autosampler)	CB _{weir}	62/320
Peat subcatchment weir	P _{weir}	31
Peaty-gley subcatchment weir	PG _{weir}	28
Moorland experimental ^a	M _E	19
Moorland control ^a	M _C	7
Forest experimental ^a	F _E	19
Forest control ^a	F _C	19

^a Paired micro-catchment ditches.

Spectrophotometric methods

Samples were filtered with pre-ashed (400 °C) Whatman GF/C glass microfibre filter papers. DOM fluorescence was measured using a Perkin-Elmer luminescence spectrometer LS-50B. Samples were analysed in a 10 mm far UV silica cell, at a constant temperature of 22 ± 2 °C. Sealed water cell blank scans were run every 10–15 samples to test machine stability using the Raman peak of water, at excitation 350 nm and emission 340–420 nm. Raman emission intensity averaged 20.69 ± 2.43 intensity units ($n = 245$) at 390 nm (December 1999–April 2002). Fluorescence emission intensities were standardized to this peak (Baker, 2002b). Fluorescence excitation–emission matrices (EEMs)—three-dimensional contour plots which display fluorescence intensities as a function of a range of both excitation and emission wavelengths—were obtained for all samples. All samples were scanned in the following wavelength regions: excitation 200–500 nm at 5 nm steps and emission 200–600 nm at 0.5 nm steps.

Distinct areas of fluorescence intensity maxima have been attributed by several authors to different components of DOM, derived from different compositional features. Here we report data on three fluorescence peaks. Peaks A and B occur at excitation wavelengths of 320–350 nm and 340–380 nm and emissions 400–450 nm and 440–500 nm, respectively, and have been related to both humic-like and fulvic-like substances (Coble, 1996; Mobed *et al.*, 1996; Baker, 2001; Newson *et al.*, 2001; Baker, 2002a; Stedmon *et al.*, 2003). Peak C is a fluorophore at 270–285 nm excitation and 340–360 nm emission and is attributed to tryptophan-like fluorescence that is associated with biological activity (Baker, 2001; Baker and Inverarity, 2004; Cammack *et al.*, 2004). Excitation wavelength (peak $X_{EX\lambda}$), emission wavelength (peak $X_{EM\lambda}$) were recorded at points of maximum fluorescence intensity (peak X_{Fint}) for peak A, B and C in all analyses. Specific fluorescence intensity, peak XS_{Fint} , was determined as a ratio of peak X_{Fint}/DOC $mg\ l^{-1}$. In a small number of samples, peaks B and C were not identifiable.

At high solute concentrations, chromophores and fluorophores interfere with the normal process of excitation and emission. This results in the suppression of fluorescence intensity (Bashford and Harris, 1987) and is described as inner-filter effects (IFE). IFE may be reduced in a number of ways: by viewing the fluorescence closer to the surface of the cell; by reducing the path length and the potential for absorbance; by dilution or standard additions; by measurement at a long wavelength; by application of a correction factor; and by the use of a triangular analysis cell (Senesi, 1990; McKnight *et al.*, 2001; Ohno, 2002; Chen *et al.*, 2003). A number of correction formulae have been derived to combat IFE (Zimmerman *et al.*, 1999; McKnight *et al.*, 2001; Ohno, 2002). The correction equation derived by Ohno (2002)

(Equation (1)) requires no prior knowledge of DOC concentration and is therefore easily applicable.

$$I = I_0 10^{-b(A_{ex}+A_{em})} \quad (1)$$

where I is the detected fluorescence intensity and I_0 is the fluorescence in the absence of self-absorption. The factor b assumes that both emission and excitation only pass through half a cuvette path length. A_{ex} and A_{em} are the absorbance of the solution at the excitation and emission wavelengths respectively (Ohno, 2002). Because the majority of samples analysed in this study were coloured with high absorbance (see Results section), equation (1) was applied to the fluorescence intensity data to correct for any IFE.

UV–Vis absorbance was measured using a WPA Lightwave UV–Vis Diode-array spectrophotometer (S2000), with a single beam diode array using Rowland Circle optics with a flat field corrected concave grating and pulsed deuterium and pulsed tungsten sources. Absorbance spectra were obtained between 200–700 nm and individual absorption coefficients values were calculated for 254, 272, 340, 365, 410, 465 and 665 nm in units of cm^{-1} . Samples were analysed in a 10 mm far UV silica cell and were blanked against distilled water. Samples were diluted with distilled water of zero absorbance if the measured absorption coefficient exceeded the analytical range ($1.999\ cm^{-1}$).

Absorption coefficient ratios were calculated as follows: a_{254}/a_{365} , a_{465}/a_{665} , a_{254}/a_{410} . These ratios were chosen as they have been proposed to represent molecular weight or aromaticity (Gjessing *et al.*, 1998; Abbt–Braun and Frimmel, 1999; Anderson *et al.*, 2000). Water colour was determined by conversion of a_{410} to Hazen units ($mg\ l^{-1}\ Pt$) following the method of Hongve and Åkesson (1996). Conversion was performed using a dilution series of a stock solution of $500\ mg\ l^{-1}\ Pt$ units (1.245 g of potassium (IV) hexachloroplatinate and 1 g Cobalt (II) chloride hexahydrate in 100 ml HCl, 900 ml water) as detailed in EN-ISO 7887: 1994.

Other analyses

The pH and conductivity of all water samples were measured using a Myron L Company model 6P ultrameter. Filtered samples were analysed for total organic carbon (TOC) using a Shimadzu 5000A TOC analyser. Total carbon was determined by high temperature catalytic oxidation, and inorganic carbon by phosphoric acid digestion. The evolved gases were subsequently dried using a dehumidifier, purified in a halogen scrubber and analysed for CO_2 concentration with a non-dispersive infrared detector (NDIRD). DOC was calculated as the difference between total and inorganic carbon. Samples were analysed in triplicate with the mean taken from the best two (coefficient of variation (CV) <2%).

RESULTS

Non-spectrophotometric analyses

pH, electrical conductivity, DOC and colour were determined for all sample sites; results are summarized in Figure 2. pH and conductivity data observed in this study (Figure 2) were comparable to that seen in previous work, having similar ranges and means, and replicating the broad spatial differentiation of the catchment (Robinson, 1998). Mean conductivity exhibited the patterns seen previously in the catchment (Mounsey, 1999). However, there were no significant differences between main channel, peat subcatchment derived surface waters and peaty-gley subcatchment waters ($P < 0.05$).

Figure 2 shows there was a significantly higher mean pH in the peaty-gley subcatchment (5.84 ± 0.55) compared to the whole catchment (CB_{weir} ; 4.76 ± 0.73) and all the peat subcatchment derived waters (4.15 ± 0.78 ; $P < 0.01$). As expected from previous observations, the peaty-gley subcatchment had the highest surface water pH in the catchment, due to buffering by the inorganic component in the soil (Robinson, 1998). The main channel CB_{weir} site exhibited a significantly higher mean pH in comparison to all peat subcatchment derived waters (4.15 ± 0.78 ; $P < 0.01$), and this suggests that inputs from both subcatchments can be recognized in the water chemistry at the catchment outfall during this study. The observations of pH in the main channel were made during a range of flow conditions (0.00 – $1.28 \text{ m}^3 \text{ s}^{-1}$, mean = $0.039 \text{ m}^3 \text{ s}^{-1}$). pH exhibited a significantly negative relationship with discharge ($P < 0.01$) with the

lowest observed pH values occurring during higher flow conditions. The four monitored ditches in the peat subcatchment had statistically indistinguishable mean pH values ($P < 0.05$).

Mean DOC concentration was 32.9% higher in the peat subcatchment and water colour was 48.4% higher in the both peat subcatchment and the whole catchment (CB_{weir}) in comparison to the peaty-gley subcatchment ($P < 0.05$) (Figure 2). The peat subcatchment had a higher mean value of DOC concentration (30.2 mg l^{-1}) compared to the whole catchment, however this was not significant. In samples from all sources, DOC concentration and water colour correlated positively ($P < 0.05$, Spearman's Rho 0.655 – 0.979) and 69.4% of the variations in water colour could be explained by DOC concentration. This confirms that water colouration in the catchment is related to DOC concentration and is primarily derived from peatland DOM.

In the peat subcatchment ditches, mean DOC concentration was the highest in the afforested experimental ditch (F_E), ($40.3 \pm 9.4 \text{ mg l}^{-1}$), significantly higher than the moorland ditches (M_E , M_C) and the peat subcatchment ($P < 0.05$). The moorland control ditch (M_C) had the lowest mean DOC concentration values of the peat subcatchment surface waters (28.5 mg l^{-1}), as shown on Figure 2. The afforested experimental ditch F_E exhibited the highest DOC concentration seen within the catchment (max = 64.0 mg l^{-1}); such elevated levels of DOC concentration have not been previously reported in the Coalburn catchment. Similar values have however been identified in peatland environments using the same analytical

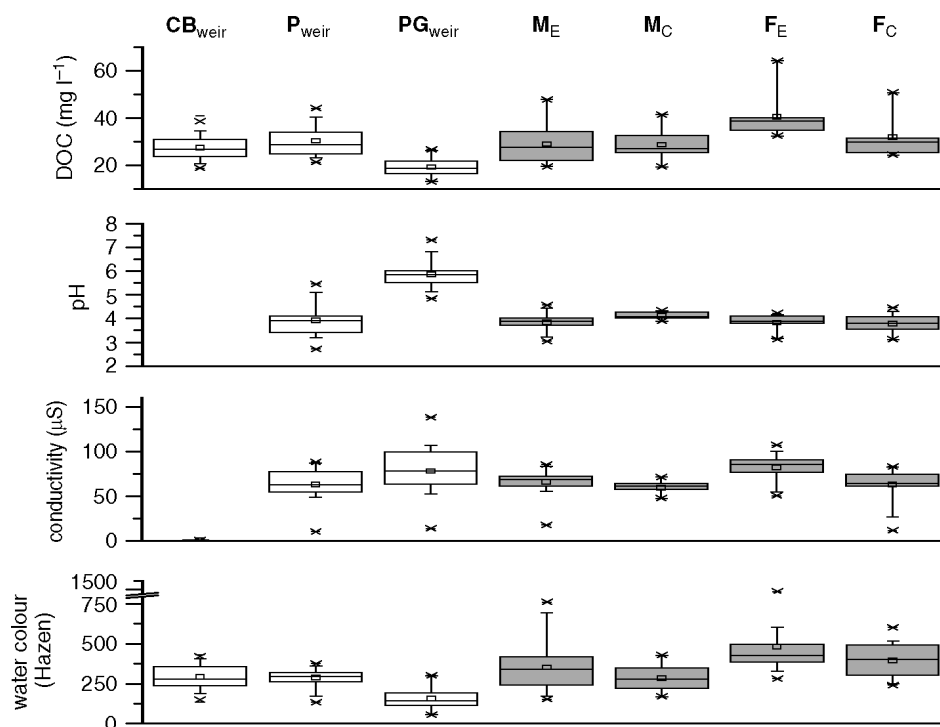


Figure 2. Box plots of DOC concentration (mg l^{-1}), pH; conductivity (μS) and water colour (Hazen) in surface water from the CEC. Key: The square symbol in the box denotes the mean of the column of data. The horizontal lines denote the 25th, 50th and 75th percentile values; error bars denote the 5th and 95th percentile values; two symbols below the 5th percentile error bar denote the 0th and 1st percentile values; the two symbols above the 95th percentile error bar denote the 99th and 100th percentiles

method (Fraser *et al.*, 2001) and higher DOC concentration has been reported in peatlands which have undergone cutting and disturbance (Glatzel *et al.*, 2003; Wallage *et al.*, 2006).

Non-spectrophotometric data suggests that that pH, colour and DOC have some utility in contrasting the peaty-gley and peat subcatchments. It appears that a greater proportion of planted area in the micro-catchment of the ditch enhances DOC concentration in the ditch water, a finding previously observed in other upland environments on a larger scale (Grieve and Marsden, 2001). Water from the four sampled ditches all exhibited higher mean DOC concentrations, compared to the peaty-gley subcatchment ($P < 0.01$) and in the case of the afforested ditches (F_E and F_C) higher than the whole catchment (CB_{weir} ; $P < 0.01$). The variations in water colour values recorded in Figure 2 closely correspond to DOC concentration distribution.

In Table II we calculate the colour/DOC concentration ratio (or C/C ratio; Wallage *et al.*, 2006), an indication of the proportion of coloured DOM in each water source. Whole catchment and waters derived from the peat subcatchment had significantly more coloured DOM compared to peaty-gley subcatchment derived DOM ($P < 0.01$), and ditches from the afforested micro-catchment have the highest colour/DOC ratio. This shows that the peat subcatchment exports runoff with greater colouration compared to the peaty-gley subcatchment and with a higher proportion of coloured, probably more aromatic or higher molecular weight, components in the DOM.

Spectrophotometric properties of dissolved organic matter

Fluorescence intensity and wavelength. Fluorescence intensity and fluorescence intensity ratio data are presented in Figure 3. Mean peak A_{Fint} and peak B_{Fint} were highest in the afforested experimental ditch (378 and 189, respectively), significantly so ($P < 0.05$) in comparison to all other sources except the moorland experimental ditch (344 and 175, respectively). Both experimental ditches exhibited significantly higher mean peak A_{Fint} and peak B_{Fint} compared to control ditches. The highest individual value of peak A_{Fint} was observed in the moorland experimental ditch (506) and highest peak B_{Fint} at the main channel, CB_{weir} (286), the lowest of peak A_{Fint} was seen in peaty-gley subcatchment (151) and peak B_{Fint} in the moorland control ditch (91).

Table II. Summary of water colour/DOC in surface water in the CEC (standard deviations in brackets)

	Mean (standard deviation) colour/DOC
CB_{weir}	10.7 (1.4)
P_{weir}	10.0 (1.2)
PG_{weir}	8.4 (2.5)
M_E	10.8 (3.7)
M_C	9.5 (0.8)
F_E	12.4 (3.7)
F_C	11.5 (2.0)

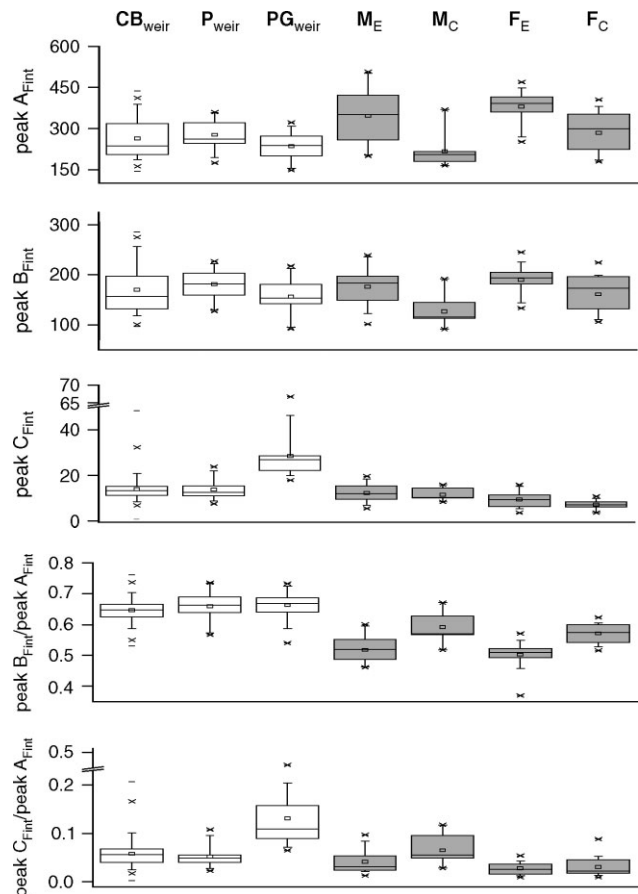


Figure 3. Box plots of peak A_{Fint} ; peak B_{Fint} ; peak C_{Fint} ; peak $B_{Fint}/peak A_{Fint}$; peak $C_{Fint}/peak A_{Fint}$ in surface water from the CEC. For key to box plots see Figure 2

DOM from the peaty-gley catchment had the highest mean peak $B_{Fint}/peak A_{Fint}$ (0.63 ± 0.04). This mean value was similar to that of the peat catchment; all river sites were significantly higher than the experimental ditches ($P < 0.05$). Mean peak $B_{Fint}/peak A_{Fint}$ was significantly higher in both control ditches compared to experimental ditches, which of all the samples exhibited the lowest value in the catchment (0.50). Peak C_{Fint} and peak $C_{Fint}/peak A_{Fint}$ were highest in the peaty-gley subcatchment (mean = 28 and mean = 0.13, respectively). DOM from this source also exhibited the maximum values of peak C_{Fint} (67) and peak $C_{Fint}/peak A_{Fint}$ (0.42) (Figure 3). This distribution resulted in significantly higher mean values in peaty-gley subcatchment DOM compared to other sources (Figure 3). Throughout the catchment peak B_{Fint} and peak A_{Fint} strongly correlated (Spearman's rho 0.964, $P < 0.01$) and both of these values had a negative correlation with peak C_{Fint} ($P < 0.01$). This relationship replicates the increased peak B_{Fint} and peak A_{Fint} in peat subcatchment DOM compared to increased peak C_{Fint} in the peaty-gley subcatchment.

Fluorescence results demonstrate several parameters which might have the potential to source DOM. Peak $A_{EM\lambda}$ and $B_{EM\lambda}$ only discriminate the peaty-gley catchment, whereas fluorescence intensities, and intensity ratios, of peaks A, B and C discriminate between micro-catchments and between ditch and catchment samples.

Peak B_{Fint} /peak A_{Fint} is of particular interest, as it is a recognized measure of humification based upon the observed increase in the number of highly substituted aromatic nuclei aromaticity and conjugated unsaturated systems (Senesi *et al.*, 1991) in DOM with increasing wavelength. Other indices using this assumption have been applied to DOM spectrophotometric analyses (for example Kalbitz *et al.*, 1999; Zsolnay *et al.*, 1999, McKnight *et al.*, 2001). In the current study, peaty-gley derived DOM might be expected to have lower values of peak B_{Fint} /peak A_{Fint} , which would be interpreted as less aromatic or humified DOM compared to peat waters, reflected in its colour/DOC ratio. However, no differences between peat and peaty-gley catchments were observed: in the overall relationship of spatial data in the catchment there is a weak positive correlation of pH and peak B_{Fint} /peak A_{Fint} , suggesting that this spectrophotometric property of DOM also varies in response to the pH of the water as previously observed by Patel-Sorrentino *et al.*, (2002).

Peak C_{Fint} and peak C_{Fint} /peak A_{Fint} were higher in peaty-gley subcatchment waters in comparison to peat subcatchment. This may derive from a significantly greater proportion of protein-like DOM in the former resulting in greater fluorescence from tryptophan-like components. The source of this material is unclear, although it has been recognized in river, lake, marine and waste waters as being related to biological activity (Mayer *et al.*, 1999; Baker, 2002a, b; Cammack *et al.*, 2004). The intrinsic spectrophotometric properties of the DOM, however, may control peak C_{Fint} distribution. Energy transfer can occur when the emission energy from peak C (340–360 nm) is reabsorbed by peak A, or other non-fluorescent chromophores. The relatively high specific absorbance and DOC concentration of peat subcatchment waters suggests that this may occur preferentially in this DOM compared to peaty-gley subcatchment DOM, resulting in suppressed peak C_{Fint} in the former. Despite all samples being IFE corrected, the highest levels of peak C_{Fint} were seen in waters with the lowest DOC concentration and specific absorbance.

Fluorescence intensity/DOC ratio. To investigate fluorescence intensity normalized to DOC concentration peak AS_{Fint} (peak A_{Fint} /DOC mg l^{-1}) was calculated. This revealed, as shown on Figure 4, that peaty-gley subcatchment DOM was significantly more fluorescent per mg l^{-1} OC (13.2 ± 2.2) than both the whole catchment (10.3 ± 1.9) and the peat subcatchment (10.6 ± 1.8 , $P < 0.05$). Moorland and forest control ditches exhibited the lowest mean values of peak AS_{Fint} (8.5 ± 1.1 and 8.5 ± 1.7) compared to other peat derived DOM as shown in Figure 5, significantly so in comparison to the whole catchment, peat subcatchment and the moorland experimental ditch (mean = 11.4 ± 2.5 , $P < 0.05$).

The overall relationship of peak A_{Fint} with DOC concentration is shown in Figure 5 and indicates a strong positive correlation (Spearman's $\rho = 0.721$; $P < 0.01$). Peak B_{Fint} exhibited a similar positive correlation with DOC concentration (Spearman's $\rho = 0.639$; $P < 0.01$).

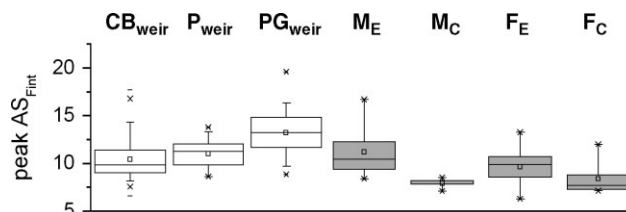


Figure 4. Box plots of peak AS_{Fint} in surface water from the CEC. For key to box plots see Figure 2

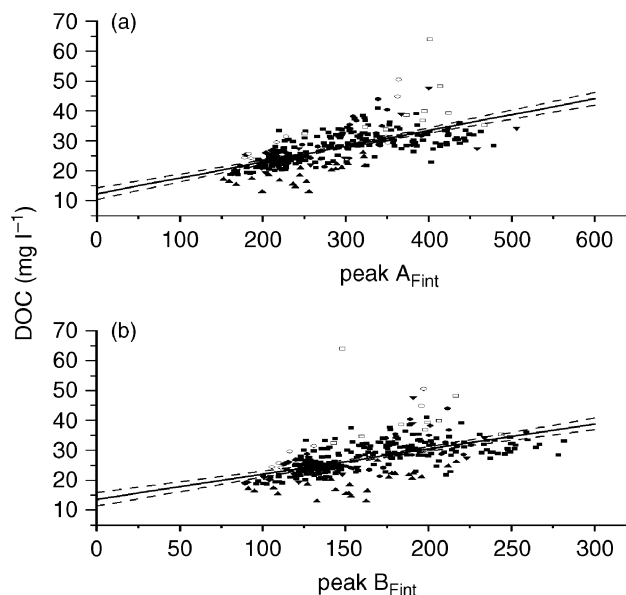


Figure 5. The relationship of peak A_{Fint} and peak B_{Fint} to DOC concentration in surface water from the CEC. (■) CB_{weir} (●) P_{weir} (▲) PG_{weir} (▼) M_E (◆) M_C (□) F_E (○) F_C (—) linear regression (---) 95% confidence level; equations refers to combined data from all sources. (a) $DOC = 12.312 + A_{Fint} \times 0.053$, $r^2 = 0.432$, $P < 0.001$, $\rho = 0.721$. (b) $DOC = 13.611 + B_{Fint} \times 0.084$, $r^2 = 0.306$, $P < 0.001$, $\rho = 0.639$

This demonstrates that there is a strong concentration component to fluorescence intensity. However, the presence of a positive intercept on the DOC concentration axis of the linear regression line indicates that there is a non-fluorescent component of the DOM ranging from approximately $5\text{--}15 \text{ mg l}^{-1}$ between each sample group. In the data set as a whole there was a negative correlation between peak C_{Fint} and DOC concentration (95% confidence level), as shown in Figure 6. This showed the small contribution of peak C_{Fint} derived fluorophores to the total DOC concentration in comparison to peak A_{Fint} and peak B_{Fint} .

The DOC concentration gradient in the catchment is highlighted in Figure 6; peaty-gley derived water has a low DOC concentration and high peak C_{Fint} . Relatively large errors and relatively low r^2 values were incurred in the linear regression of peak A_{Fint} and peak B_{Fint} and DOC concentration suggesting that if this technique were employed as a method to determine DOC concentration, inaccuracies would occur. This is also suggested by the percentage variation in fluorescence intensity that is explained by DOC concentration (Table III). Additionally, the DOC concentration relationship with fluorescence intensity in waters from each sample source

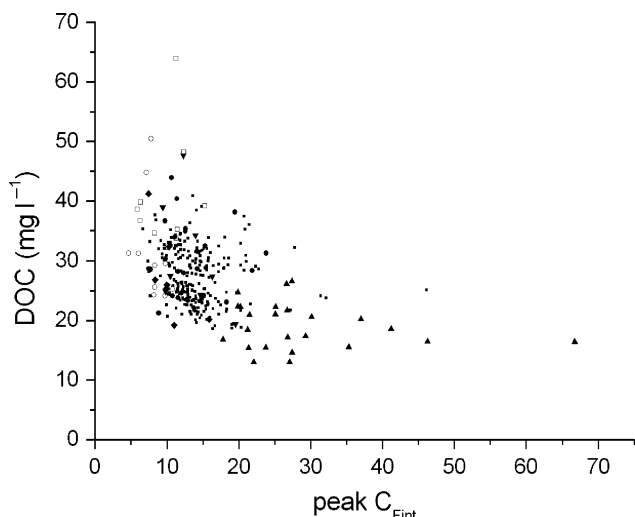


Figure 6. The relationship of peak C_{Fint} to DOC concentration in surface water from the CEC (■) CB_{weir} (●) P_{weir} (▲) PG_{weir} (▼) M_E (◆) M_C (□) F_E (○) F_C

resulted in different linear regression equations. This suggests that a calibration of fluorescence intensity to DOC concentration such as that in Figure 5 may not be applicable to DOM from different sources within one catchment.

UV-Vis absorbance. DOM from the CEC exhibited typical absorbance spectra, comparable to that recognized in DOM analyses from many sources (Korshin *et al.*, 1997). As all measured individual wavelengths correlated positively in the data set as a whole and in each individual data set (95% confidence level), a single wavelength, $a_{340} \text{ cm}^{-1}$, is presented in Figure 7. This represents the distributions within and between data from each sample source.

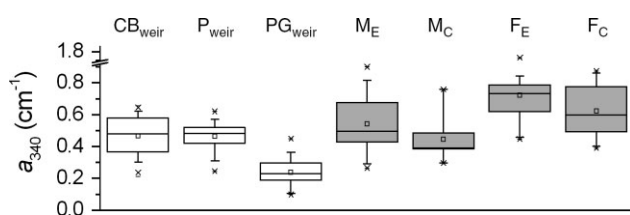


Figure 7. Box plots of a_{340} in surface water from the CEC. For key to box plots see Figure 2

The peaty-gley subcatchment exhibited the lowest absorption coefficient values for $a_{340} \text{ cm}^{-1}$ ($a_{340} = 0.082 \text{ cm}^{-1}$) and the lowest mean values ($0.232 \pm 0.086 \text{ cm}^{-1}$), as shown in Figure 7. Mean absorption coefficients from the whole catchment were indistinguishable from the peat subcatchment at wavelengths longer than 300 nm. However, at a_{254} and $a_{272} \text{ cm}^{-1}$ the peat subcatchment was significantly higher than whole catchment ($P < 0.05$). The whole catchment exhibited a wider range of values. Maximum absorption coefficient values at $a_{340} \text{ cm}^{-1}$ were observed in the afforested experimental ditch ($a_{340} = 1.588 \text{ cm}^{-1}$). The forest micro-catchment had significantly higher mean absorption coefficients compared to other peat subcatchment derived DOM ($P < 0.05$).

Absorption coefficients at all wavelengths correlated strongly and positively with DOC concentration in all sample sets and the data set as a whole, as shown in Figure 8. This indicates that there was a strong component of concentration in the absorption coefficient signal. Within each sample group the correlation was strongly positive with Spearman's rho > 0.73 ($P < 0.01$). The linear regression relationships between DOC concentration and absorption coefficients are summarized in Table IV. These relationships indicate that absorbance is explained by variations in DOC concentration to a greater extent than fluorescence intensity in the data set as a whole (Table III). This, however, varies between each group. For example, in data from the moorland control ditch, DOC concentration explained variations in peak A and peak B to a greater extent than at all absorbance wavelengths. Additionally, the relationship of absorption coefficients and DOC concentration varied between the wavelengths observed in DOM from the same sample source. For example, the whole catchment exhibits the greatest relationship of absorption coefficients to DOC concentration at 340 nm; however this occurs at 272 nm in DOM from the peat subcatchment. The maximum variation in absorption coefficients explained by DOC concentration in DOM ranged from 54% in the moorland experimental ditch to 95% in DOM from the afforested experimental ditch (Table IV).

In addition to the DOC concentration of the solution, the aromaticity and the content of hydrophobic material of the DOM can influence the absorbance of DOM

Table III. The results of linear regression of fluorescence intensity against DOC concentration in surface water from the CEC, showing the percentage variation explained by DOC concentration and the equation of the linear regression

	Peak A _{Fint}		Peak B _{Fint}	
	% Variation	DOC =	% Variation	DOC =
CB_{weir}	49.3	$15.427 + A_{Fint} \times 0.045$	44.7	$15.324 + B_{Fint} \times 0.045$
P_{weir}	32.3	$5.928 + A_{Fint} \times 0.077$	29.4	$6.816 + B_{Fint} \times 0.077$
PG_{weir}	50.6	$5.551 + A_{Fint} \times 0.054$	45.8	$7.110 + B_{Fint} \times 0.054$
F_C	58.0	$9.487 + A_{Fint} \times 0.084$	53.6	$7.608 + B_{Fint} \times 0.084$
F_E	25.8	$23.335 + A_{Fint} \times 0.038$	25.2	$22.501 + B_{Fint} \times 0.038$
M_C	90.9	$8.208 + A_{Fint} \times 0.082$	80.5	$-2.289 + B_{Fint} \times 0.082$
M_E	43.5	$11.371 + A_{Fint} \times 0.055$	39.5	$8.366 + B_{Fint} \times 0.055$

Table IV. The results of linear regression of absorbance against DOC concentration in surface water from the Coalburn Experimental Catchment showing the percentage variation explained by DOC concentration and the equation of the linear regression

	% Variation	DOC =	% Variation	DOC =
		a_{254}		a_{272}
CB _{weir}	41.23	$14.24 + a_{254} \times 10.13$	44.94	$12.29 + a_{272} \times 13.70$
P _{weir}	70.05	$18.17 + a_{254} \times 6.69$	72.85	$13.75 + a_{272} \times 12.02$
PG _{weir}	69.01	$13.76 + a_{254} \times 6.66$	67.19	$12.93 + a_{272} \times 9.68$
F _C	84.95	$8.94 + a_{254} \times 13.97$	87.21	$6.09 + a_{272} \times 18.84$
F _E	76.63	$-3.78 + a_{254} \times 26.87$	81.16	$-2.32 + a_{272} \times 28.68$
M _C	61.49	$13.07 + a_{254} \times 13.09$	69.13	$13.71 + a_{272} \times 14.69$
M _E	54.53	$6.20 + a_{254} \times 16.43$	52.47	$5.98 + a_{272} \times 19.16$
		a_{340}		a_{365}
CB _{weir}	60.75	$10.81 + a_{340} \times 36.31$	56.40	$11.62 + a_{365} \times 51.09$
P _{weir}	70.22	$6.11 + a_{340} \times 49.36$	65.99	$3.29 + a_{365} \times 84.36$
PG _{weir}	59.29	$10.46 + a_{340} \times 35.25$	57.64	$11.40 + a_{365} \times 47.44$
F _C	91.22	$11.75 + a_{340} \times 33.63$	92.79	$10.41 + a_{365} \times 55.67$
F _E	88.94	$-1.46 + a_{340} \times 66.09$	82.77	$-3.50 + a_{365} \times 110.22$
M _C	53.24	$18.08 + a_{340} \times 29.15$	57.56	$20.15 + a_{365} \times 38.48$
M _E	29.10	$6.34 + a_{340} \times 44.01$	30.81	$7.60 + a_{365} \times 63.36$
		a_{410}		a_{465}
CB _{weir}	37.76	$10.18 + a_{410} \times 113.02$	2.28	$10.70 + a_{465} \times 230.26$
P _{weir}	67.65	$-4.63 + a_{410} \times 224.99$	11.52	$14.14 + a_{465} \times 218.18$
PG _{weir}	46.74	$11.687 + a_{410} \times 87.56$	0.01	$12.99 + a_{465} \times 157.30$
F _C	95.07	$14.850 + a_{410} \times 86.67$	89.79	$19.18 + a_{465} \times 125.77$
F _E	69.26	$-0.395 + a_{410} \times 206.80$	26.26	$-11.59 + a_{465} \times 694.86$
M _C	34.06	$25.52 + a_{410} \times 54.96$	11.59	$26.55 + a_{465} \times 100.44$
M _E	20.03	$8.834 + a_{410} \times 121.79$	3.08	$6.47 + a_{465} \times 308.29$

(Dilling and Kaiser, 2002). The varying relationship presented in Table IV may show a spatial variation in DOM composition.

The proportion of chromophores in the DOM that, on absorbance, results in the emission of energy, is represented by peak A_{Fint}/a_{340} and is shown in Figure 9. For this parameter, the peaty-gley subcatchment DOM had a significantly higher mean (189 ± 208) than the peat subcatchment derived DOM, including the whole catchment ($P < 0.05$). Within the peat subcatchment derived DOM peak A_{Fint}/a_{340} , no significant differences in mean values were observed (Figure 10).

Ratios of absorption coefficient values at different wavelengths correlate with certain properties of DOM such as molecular weight and aromaticity (Gjessing *et al.*, 1998). The ratios shown in Figure 10 have been calculated to identify spatial differences within the catchment and to establish compositional differentiations, in conjunction with fluorescence properties. The three absorption coefficient ratios did not correlate with DOC concentration, suggesting that the variations observed are related more to compositional differences in DOM. a_{465}/a_{665} varied little between surface water DOM and no significant differences were observed in the mean values of whole catchment, peat subcatchment and experimental ditches ($P < 0.05$). The moorland (mean 14.0 ± 7.0) and afforested control ditches (mean 10.1 ± 4.6) exhibited significantly higher values than all other sources and peaty-gley subcatchment showed a significantly lower mean value (mean 5.3 ± 3.6) compared to all other sources ($P < 0.05$). a_{254}/a_{365} and a_{254}/a_{410} measure

ratios of short and long wavelengths and exhibit the same spatial patterns.

As shown in Figure 10, the means of both a_{254}/a_{365} and a_{254}/a_{410} were significantly higher in peat and peaty-gley subcatchments compared to the whole catchment and all other peat subcatchment derived DOM. The peat subcatchment also had significantly higher means when compared to the peaty-gley subcatchment ($P < 0.05$). This is largely accounted for by a number of high values in the peat subcatchment, which was the highest observed (maximum $a_{254}/a_{410} = 22.7$ and maximum $a_{254}/a_{365} = 10.8$). If these extreme figures, sampled under dry and low flow conditions are removed, the peaty-gley subcatchment has significantly higher mean values of a_{254}/a_{410} (mean 9.1 ± 1.5) and a_{254}/a_{365} (mean 4.9 ± 1.0) compared to peat subcatchment DOM (a_{254}/a_{410} mean 7.5 ± 1.4 ; a_{254}/a_{365} mean 3.2 ± 0.6) (95% confidence level).

DISCUSSION

Spectrophotometric properties at a subcatchment scale demonstrate that DOM from the peaty-gley subcatchment has smaller molecular size and less aromatic DOM when compared to peat subcatchment DOM, consistent with previous studies. This was observed in a lower specific absorbance, higher peak $A_{\text{EM}\lambda}$ and peak $B_{\text{EM}\lambda}$, and higher peak A_{Fint}/a_{340} . This differentiation may relate to the stabilization of aromatic and/or higher molecular weight DOM in the inorganic components of the peaty-gley subcatchment soil in comparison to peat subcatchment

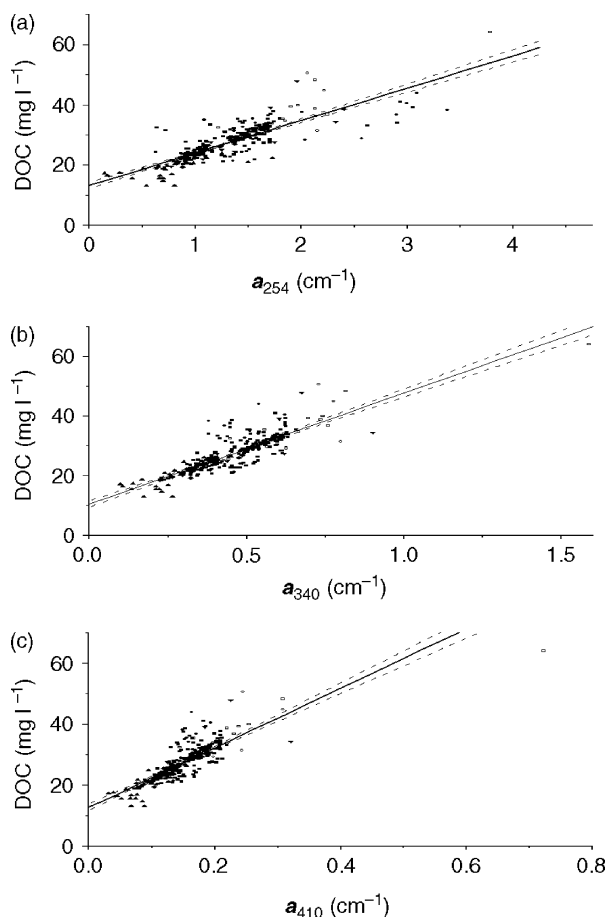


Figure 8. The relationship of a_{254} , a_{340} and a_{410} to DOC concentration in surface water from the CEC. (■) CB_{weir} (●) P_{weir} (▲) PG_{weir} (▼) M_E (◆) M_C (□) F_E (○) F_C (—) linear regression (---) 95% confidence level equations refers to combined data from all sources. (a) $DOC = 13.22 + a_{254} \times 10.80$, $r^2 = 0.691$, $P < 0.001$. (b) $DOC = 10.43 + a_{340} \times 37.46$, $r^2 = 0.739$, $P < 0.001$. (c) $DOC = 12.85 + a_{410} \times 98.41$, $r^2 = 0.696$, $P < 0.001$

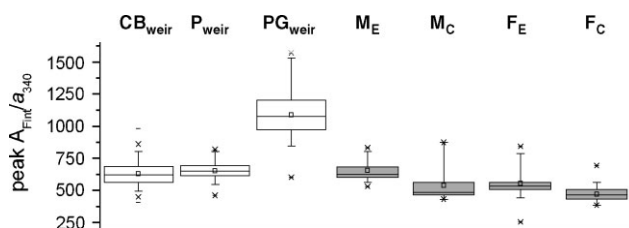


Figure 9. Box plots of peak A_{Fint}/a_{340} in surface water DOM from the CEC. For key to box plots see Figure 2

(Zhou *et al.*, 2001; Maurice *et al.*, 2002), resulting in an effective fractionation of the surface water DOM.

At the micro-catchment scale, the highest colour/DOC ratio and a_{340} normalized to DOC was observed in the forested rather than open moor micro-catchments. Forestry does not therefore cause significantly more DOC to be present in the drainage ditches, but the organic matter that is produced is more coloured and aromatic and has a higher molecular weight. The reason for this is unclear but could be due to the significant input of forest material, such as spruce needles, to the ditches. Coniferous litter degrades by the action of micro-organisms, and

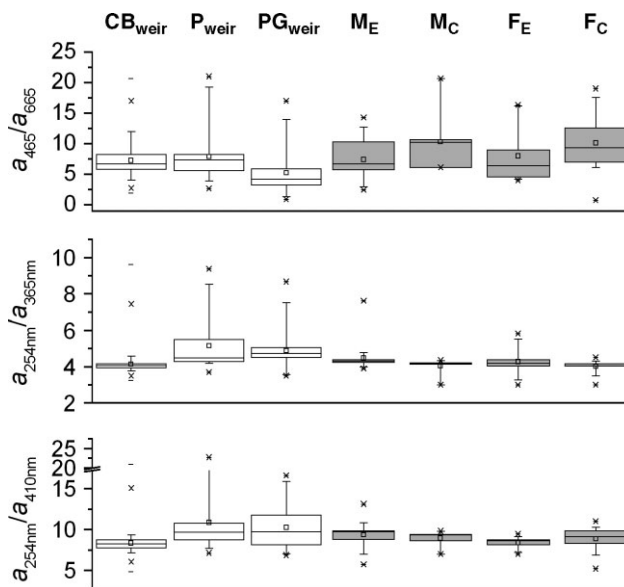


Figure 10. Box plots of a_{465}/a_{665} , a_{254}/a_{365} and a_{254}/a_{410} in surface water DOM from the CEC. For key to box plots see Figure 2

the removal of labile components results in the accumulation of recalcitrant material. Coniferous needles comprise primary components such as lignin and cellulose and secondary components such as terpenoids, monoterpenes and phenolics. The latter two components have been recognized to be water soluble and to decrease in concentration from fresh green litter upon decomposition (Kainulainen and Holopainen, 2002). Further spectrophotometric characterization of coniferous litter is required.

With ditch clearing, DOC concentrations increase, and the organic matter has higher fluorescence AS_{Fint} , higher fluorescence A_{Fint}/a_{340} and lower peak $B_{Fint}/\text{peak } A_{Fint}$ ratio, all indicative of a relative increase in less aromatic/low molecular weight organic matter. This suggests that the input from soil waters to the ditches may be modified or retarded in the infilled ditches. Experimentally-cleared ditches exhibit high values of DOC concentration related variables in relation to both control ditches and to P_{weir} and CB_{weir} . It is hypothesized that this is due to the exposure of bare peat and removal of vegetation. Bare peat faces within and adjacent to the ditches are more susceptible to freezing and drying compared to vegetated areas, providing a source of relatively fresh organic material that can be flushed into the ditches during wetting up of the peat. This process was also observed at a German fen (Kalbitz, 2001) and at a catchment scale in peat rich catchments (Evans *et al.*, 2005). The removal of vegetation during ditch clearing resulted in a greater proportion of precipitation reaching the ditch and surrounding area, compared to control ditches, thus allowing the DOM produced within the surface peat layers to be exported. The large extent of this drainage network acts as both a rapid transport network increasing hydrological connectivity and a pool for the storage of DOM under low flow conditions.

Our investigation has shown that a wide range of spectrometric properties are required in order to determine

the spatial patterns and sources of dissolved organic matter. Fluorescence intensity and wavelength alone are not good in this regard, as these spectrophotometric properties reflect a combination of the correlations between intensity and DOC and their correlation with discharge, possible inner-filter effects remaining despite correction, and pH–fluorescence intensity effects. Apart from that between the peaty-gley catchment and all other sample sites, there is not enough variation in source organic matter fluorescence intensity or wavelength to be able to differentiate organic matter. However, fluorescence in combination with absorbance and DOC concentration do provide useful information on organic matter aromaticity and molecular weight. Gradients are seen in spectrophotometric properties, such as the colour/DOC and peak A_{Fint}/a_{340} , that do not relate to concentration, indicating a spatial and source-related variation in DOM composition. In particular, our results show that re-excavated ditches will contain a source of high DOC concentration but relatively uncoloured waters, which we propose to be dominated by fresh organic material, in contrast to unexcavated ditches which contain a lower concentration of DOC but of material that is more coloured and dominated by recalcitrant organic matter.

CONCLUSIONS

We show that a combination of DOC, colour, absorbance and fluorescence measurements can provide information on both the concentration and properties of DOM in an afforested peat catchment. In particular, the ratios of peak A_{Fint} to DOC or a_{340} and colour/DOC provide information on organic matter aromaticity or molecular weight. From this limited study, it is apparent that both the location and the management conditions of the ditch influences both the amount of DOM exported from the micro-catchment as well as its quality. Further study is required to explore the variability of spectrophotometric properties of DOM in forestry ditches, using a greater variety of ditch physical conditions. Ongoing monitoring of runoff colour in the four re-excavated ditches as they fill with debris and moss growth will reveal the importance of the total area of bare peat and any changes in DOM characteristics through time. Ongoing monitoring of all major Coalburn runoff pathways will continue for three other reasons: to coincide with an extreme drought and subsequent re-wetting (not yet observed); to maintain a continuous record through a period of climate change; and to create baseline data for comparisons with the felled catchment after timber harvesting, anticipated between 2010 and 2020.

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