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Functional properties of DOM in a stream draining blanket peat

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ABSTRACT

The functional properties of dissolved organic matter (DOM) from Rough Sike, a stream draining blanket peat in the northern Pennines, UK, were investigated using a series of 12 standardised assays. Nine stream samples were collected at different discharges during 2003–2006, and DOM concentrates obtained by low temperature rotary evaporation. Suwannee River Fulvic Acid was used as a quality control standard in the assays. Dissolved organic matter in high-discharge samples was more light-absorbing at 280 and 340 nm and adsorbed more strongly to alumina, than DOM characteristic of low streamflow, but was less fluorescent and hydrophilic, and poorer in proton-dissociating groups. No significant differences were found in light absorption at 254 nm, copper- or benzo(a)pyrene binding, or photochemical fading. Combination of the Rough Sike data with previously-published results for other streams and a lake yields totals of 20–23 values per assay, for a range of DOM types. For the combined data, variability in all the assays is significant ($p < 0.001$), as judged by comparison with variations in repeat measurements on the quality control standard. Analysis of the combined data shows that DOM hydrophilicity and adsorption are well-predicted by linear relationships with the extinction coefficient at 340 nm (E_{340}), while good quadratic relationships exist between E_{340} and both buffering capacity and fluorescence.

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1. Introduction

It is increasingly recognised that dissolved organic matter (DOM) is an important environmental component of streamwaters, as it participates in many ecological and geochemical reactions (Perdue and Gjessing, 1990; Kullberg et al., 1993; Hessen and Tranvik, 1998). For example, DOM controls the transport and fate of heavy metals, aluminium, radionuclides and organic pollutants, initiates photoreactions, participates in particle surface and colloid chemistry, and affects ionic balance, including pH. It also plays an important metabolic role in streams, supplying carbon and energy to heterotrophic bacteria (Meyer et al., 1988) and the flux of DOC in streamwaters is an important part of the carbon cycle, particularly in

peatlands (Worrall et al., 2003). Quantitative descriptions of functional properties are needed for ecology, geochemistry, and to understand and predict the toxicity and fate of pollutants. Given these important functions, it is desirable to know the extent to which DOM properties vary between ecosystems, and temporally within individual ecosystems.

The present study concerns the physico-chemical properties of DOM in a stream draining blanket peat of the UK uplands. Interest in the properties of DOM in these systems is of particular current interest, in view of the substantial increases (65–100%) in concentrations and fluxes of DOC seen over recent years and attributed to a variety of causes including climatic warming, acidification reversal and land use change (Worrall et al., 2004; Monteith et al., 2007; Evans

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et al., 2006). Furthermore, catchments of this kind are gathering areas for water supply reservoirs, and knowledge about the properties of DOM, which must be largely removed during water treatment, is therefore of practical importance for human activities.

Peatlands are one of the most important wetland environments in the United Kingdom and form the largest terrestrial carbon pool in the country (Worrall et al., 2003). Peat is the accumulated remains of dead plants, which has formed in waterlogged, anaerobic conditions. The catotelm and acrotelm represent two distinct layers in peat. The catotelm is the lower anaerobic layer and is composed of relatively decomposed compacted organic matter, devoid of peat-forming aerobic microorganisms. The acrotelm is the top layer of the peat and has a live matrix of growing plant material which is rich in peat-forming bacteria and microorganisms. In a detailed hydrological study of blanket peat at Moor House, in the Pennine hills of Northern England, Holden and Burt (2003a) found that the major part of the runoff was due to water that had passed rapidly through the acrotelm. However, Crisp (1966) showed that at least one of the Moor House sub-catchments (Rough Sike) is a significant source of calcium and other metals, derived from weathering of limestone underlying the peat. This suggests that at least some of the runoff water penetrates to the base of the peat before entering the stream, probably via natural pipes or macropores (Holden and Burt, 2003b). Crisp also reported that the Ca concentration declined with discharge, indicating that the relative contribution of the deeper source of water is greatest at low flow; at high flow, water passing through the surface peat is dominant.

Given that the Rough Sike streamwater may be a mixture of water types, possibly with quite different chemical signatures and histories, we investigated whether the physico-chemical functional properties of DOM may exhibit significant variation with discharge. To this end, we collected and analysed DOM samples from Rough Sike at different discharges and times of year, and subjected it to twelve standardised assays of physico-chemical function, introduced by Thacker et al. (2005) and developed by Gondar et al. (2007). These assays

are designed to provide simple indications of the physico-chemical environmental functions of DOM, rather than, for example, its molecular composition. These include its light-absorbing properties (relevant to primary production), interactions with metals and organic contaminants, adsorption to surfaces and hydrophobic–hydrophilic balance. The previous studies have revealed significant differences in some of the functional properties of DOM from different sites, and seasonal variability in lakewater DOM.

2. Field site and methods

Rough Sike (NGR NY 756 328) is a small stream draining an 83 ha catchment of blanket peat at an altitude of 565 m, in the Moor House National Nature reserve situated in the North Pennines (Crisp and Howson, 1982). The stream is a tributary of Trout Beck, the catchment of which is a freshwater and terrestrial site of the UK Environmental Change Network (ECN), which has maintained detailed chemical and hydrological records since 1993. The underlying geology of the catchment consists of a Lower Carboniferous sequence of limestones, sandstones and shales, masked by clayey glacial till overlain with blanket peat at depths of roughly 1–4 m (Heal and Smith, 1978). The vegetation consists mainly of *Calluna vulgaris* (heather), *Eriophorum* sp. (cotton grass) and *Sphagnum* sp. (moss). The mean annual precipitation of the catchment for the years 1953–2000 was 1953 mm (Worrall et al., 2003). The catchment responds quickly to rainfall events, producing a “flashy” stream hydrograph, so that the majority of the water flux is due to short periods of high discharge (Holden and Burt, 2003a).

Stream water depth was measured at a rectangular weir installed by Crisp (1966) and refurbished by Evans and Warburton (2003). Depths (d , mm) were converted to discharge (Q , $\text{m}^3 \text{s}^{-1}$) using the following equation, derived from unpublished data provided by M.G. Evans; $\log_{10}Q = 1.65 \cdot \log_{10}d - 4.10$ ($n=20$, $r^2=0.99$).

For functional assay measurements, 50-litre water samples were collected from the stream, in 10-litre pre-washed plastic

Table 1 – Assays of DOM functional properties

Assay	Assay result	Abbreviation	Significance	
			QC	Discharge
Optical absorbance 254 nm	Extinction coefficient at 254 nm ($\text{l g}^{-1} \text{cm}^{-1}$)	E_{254}	**	
Optical absorbance 280 nm	Extinction coefficient at 280 nm ($\text{l g}^{-1} \text{cm}^{-1}$)	E_{280}	**	*
Optical absorbance 340 nm	Extinction coefficient at 340 nm ($\text{l g}^{-1} \text{cm}^{-1}$)	E_{340}	**	**
Fluorescence (325/450)	Peak intensity, Ex 325 nm, Em 450 nm, per mg DOC l^{-1}	$F_{\text{DOC}/325/450}$	*	**
Photochemical fading	% Loss in DOM absorbance at 340 nm	$A_{340} \text{ loss\%}$		
Buffering capacity	Acid groups titrated between pH 4 and 8 (meq g^{-1})	Ac_{4-8}	**	**
Copper binding	Conditional stability constant (l C^{-1})	$\log K_C$	**	
Benzo(a)pyrene binding	Partition coefficient ($\text{cm}^3 \text{g}^{-1}$)	$\log K_p$		
Hydrophilicity (DOC)	% of DOC not adsorbed by DAX-8 resin at pH 2	$\text{Hyphil}_{\text{DOC}}\%$	**	*
Hydrophilicity (absorbance)	% of A_{340} not adsorbed by DAX-8 resin at pH 2	$\text{Hyphil}_{A_{340}}\%$		*
Alumina adsorption (DOC)	% of DOC adsorbed at pH 4	$\text{Ads}_{\text{DOC}}\%$	**	**
Alumina adsorption (absorbance)	% of A_{340} adsorbed at pH 4	$\text{Ads}_{A_{340}}\%$	*	**

The column headed QC refers to comparisons of assay Results with the quality control standard. The final column refers to variations of assay results with discharge (see Fig. 2).

* $p < 0.05$, ** $p < 0.01$.

polyethylene bottles. The method used to isolate the DOM is described in detail by Thacker et al. (2005) and involved concentrating the filtered (GF/F Millipore, nominal pore size $0.7\ \mu\text{m}$) sample to approximately $500\ \text{cm}^3$ (c. 100-fold) using a high capacity, low pressure, low temperature ($20\ ^\circ\text{C}$), rotary evaporator (Buchi Rotavapor R-220). The concentrate was then passed through a $100\ \text{cm}^3$ column of Amberlite IR-120 (in the sodium form), which removed 97% of the alkaline earth cations (Thacker et al., 2005), and filtered through Whatman GF/F and Millipore $0.22\ \mu\text{m}$ filters. The raw water samples and concentrates were analysed for DOC (TOC-VCN/CPN analyzer, Shimadzu, Kyoto, Japan), pH (Radiometer GK2401C combination glass electrode), conductivity (Jenway 4510 m), and major cations (ICP-OES, Perkin Elmer Optima 4300 DV). Raw water samples were also analysed for alkalinity (Gran titration) and major anions (Dionex DX100). Twelve standardised assays, previously tested and described in detail by Thacker et al. (2005) and partly modified by Gondar et al. (2007), are summarised in Table 1. The assays involved replicated measurements on DOM solutions with standardised pH and background electrolyte composition. Concentrations of added salts (NaCl or NaNO_3 , phosphate buffer in some cases) were chosen to ensure that differences in inorganic components among samples had negligible effect on the solution composition in the assay. Blank solutions lacking DOM were prepared from deionised water, with the same pH and electrolyte concentrations. A quality control standard, reference Suwannee River fulvic acid (SRFA) purchased from the International Humic Substances Society, was analysed simultaneously with the each field sample to permit evaluation of assay reproducibility. A stock solution was prepared by adding $0.0445\ \text{g}$ of solid SRFA to $200\ \text{cm}^3$ of ultra-pure water. Assay solutions of SRFA were prepared to achieve the same conditions of pH and background electrolyte as for the field samples.

3. Results

3.1. Streamwater properties

Information on the sampling dates, basic inorganic chemistry and discharge values ($\text{m}^3\ \text{s}^{-1}$) for the streamwaters is given in Table 2. The dissolved organic carbon concentration,

Table 2—Chemical data for filtered raw streamwater samples

Sampling date	Discharge $\text{m}^3\ \text{s}^{-1}$	pH	Cond ^a $\mu\text{S}\ \text{cm}^{-1}$	Ca $\text{mg}\ \text{l}^{-1}$	DOC $\text{mg}\ \text{l}^{-1}$
27/08/03	0.0003	7.7	118.1	17.1	8.3
02/06/04	0.0077	7.2	69.2	8.4	12.9
26/01/05	0.0093	6.9	57.7	4.4	5.2
16/03/05	0.1612	6.0	19.7	0.7	5.9
11/02/06	0.1612	5.7	25.5	1.7	13.3
21/05/06	0.6140	5.2	35.8	1.7	19.0
05/07/06	0.0069	7.3	86.2	11.0	11.0
11/10/06	0.0346	6.1	32.3	3.5	24.2
15/11/06	0.0601	5.8	32.8	2.9	16.5

^a Cond = conductivity.

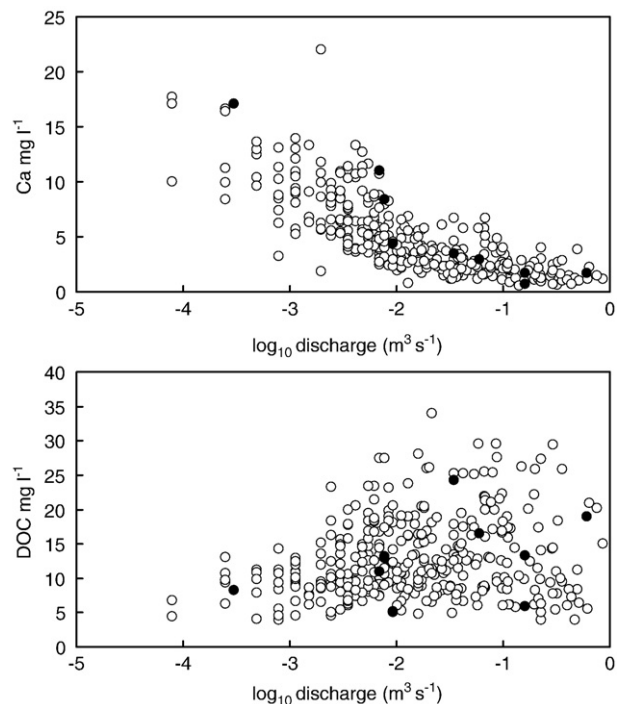


Fig. 1—Dependence of calcium and DOC concentrations on stream discharge for the period 1998–2005. Data from EGN fortnightly monitoring are shown as open circles, values for the samples studied in the present work as closed circles.

denoted by [DOC], varied between samples, with an average [DOC] of $12.9\ \text{mg}\ \text{l}^{-1}$ (standard deviation, $\text{SD}=6.2$). Discharge values ranged from 0.0003 to $0.614\ \text{m}^3\ \text{s}^{-1}$ for the occasions on which the present water samples were collected. At high flow, the streamwater is acidic ($\text{pH}<6$) and of low conductivity, with a low concentration of Ca, whereas at low flow it has relatively high pH (>7), conductivity, and [Ca], attributable to weathering of the limestone-rich clay at the base of the peat column. A fuller picture is shown by Fig. 1, in which routine EGN monitoring data for Ca and DOC are plotted, together with values from the present work. The comparison shows that our samples provide a reasonably good coverage of the different streamwater conditions. It is also evident that the [DOC]–discharge relationship is complex, largely because, for a given discharge, higher DOC concentrations are observed in summer–autumn than in winter–spring. The paucity of samples at very low discharge ($<10^{-3}\ \text{m}^3\ \text{s}^{-1}$) means that the first sample of Table 2 represents a rare stream condition.

3.2. Isolation and assay of DOM

The isolation method gave an average DOC yield of 97.6% (ranging from 93% to 107%). No cloudiness was generated during the rotary evaporation step, indicating both that the streamwater samples were low in colloidal particles and that oversaturation and precipitation of calcium carbonate (Gondar et al., 2007) did not occur. Therefore, it can be concluded that full recoveries of DOM were obtained, with minimal losses.

For most of the assays, the SRFA (quality control) results showed good reproducibility, with relative standard deviations (RSD) of less than 5%. However, the fluorescence assay gave an RSD of 10.9%, while RSDs of 17.9% and 11.6% were respectively obtained for the assays of hydrophilicity, as monitored by optical absorption or [DOC]. Ranges of QC values are indicated by the shaded areas in Fig. 2. The results from the quality control standard were used to assess variability in the functional properties of the DOM samples (Table 1). For seven of the assays the variation among the Rough Sike DOM samples was significantly greater ($p < 0.01$) than can be explained by analytical error, i.e. by comparison with results for the SRFA standard, while for a further two assays, fluorescence and adsorption monitored by optical absorption, the variation was significant at $p < 0.05$. No statistically significant variations were found for the assays of photo-

chemical fading, benzo[a]pyrene binding or hydrophilicity monitored by optical absorbance.

3.3. Dependence of assay results on discharge

Fig. 2 shows the dependence of the assay results on stream discharge. In a number of cases the functional assay result shows a clear dependence on discharge and the results were fitted with a simple “broken-stick” model that takes account of the near-constancy of the results at high discharge. The model was parameterised by assuming that results for discharge equal to or greater than $0.06 \text{ m}^3 \text{ s}^{-1}$ (log value = -1.22) were equal, and with a linear dependence on log discharge for lower discharges. Thus, two parameters, the high-discharge value and the slope, were found by least-squares minimisation. Of the 12 assays, eight gave statistically significant results at

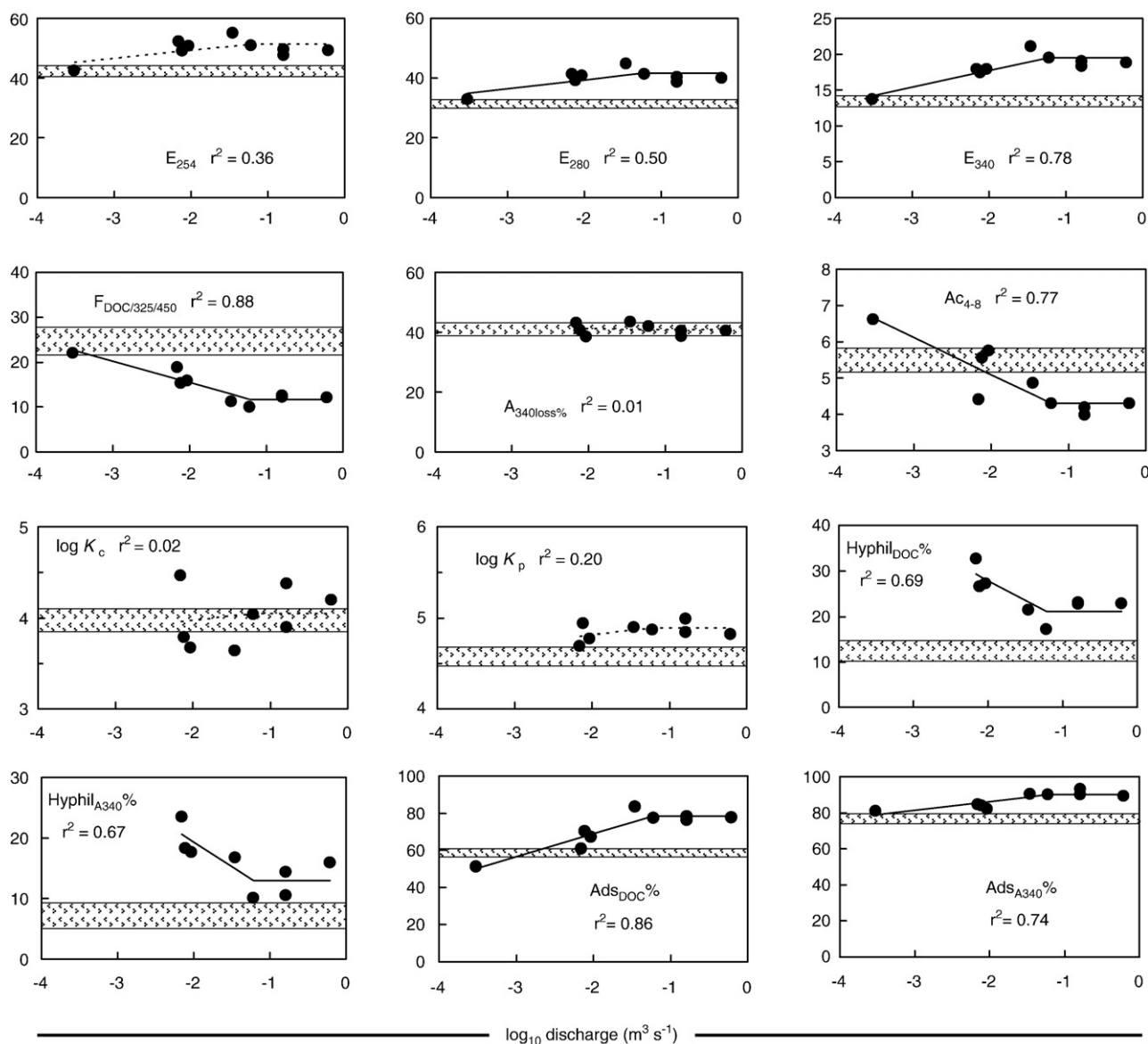


Fig. 2 – Functional assay results for DOM samples from Rough Sike (symbols) plotted against discharge. Full lines show model fits for cases where the functional property varied significantly with discharge ($p < 0.05$). Units for the y-axes are given in Table 1. The shaded areas represent the ranges of results for the quality control standards.

$p < 0.05$, (five at $p < 0.01$). In the case of hydrophilicity measured by optical absorbance, the QC variation is not significant and so we do not attach significance to its variation with discharge; however when hydrophilicity is expressed in terms of DOC there is a significant relationship. Therefore the results show that DOM at high discharge is more light-absorbing at 280 and 340 nm and adsorbs more strongly to alumina, whereas it is less fluorescent and hydrophilic, and poorer in proton-dissociating groups. Discharge dependence is not evident in the other assays.

3.4. Comparison with results for other systems

In previous work (Thacker et al., 2005; Gondar et al., 2007) the functional assay approach was applied to other surface waters. These included two streams draining more mineral soils, and a

eutrophic lake, with DOM derived from both catchment runoff (allochthonous) and phytoplankton decomposition (autochthonous). The results of some of the assays were found to be correlated. We have now added the Rough Sike assay results to the previous ones, in order to explore further these correlations. With the addition of the present data, the total number of DOM samples analysed is 23, although for two assays, only 22 results, and for another three only 20 results, have been obtained. We select E_{340} as a “master assay” against which to plot other results (Fig. 3), because it can be determined with high precision, and because it varies more among samples than E_{254} and E_{280} , having a coefficient of variation of 44% across all samples, compared with 28% and 33% for E_{254} and E_{280} respectively. For clarification, it is worth noting that E_{254} is equivalent to SUVA (Specific Ultra-Violet Absorbance), an established indicator of the chemical composition and reactivity of DOM (Weishaar et al., 2003); only the units

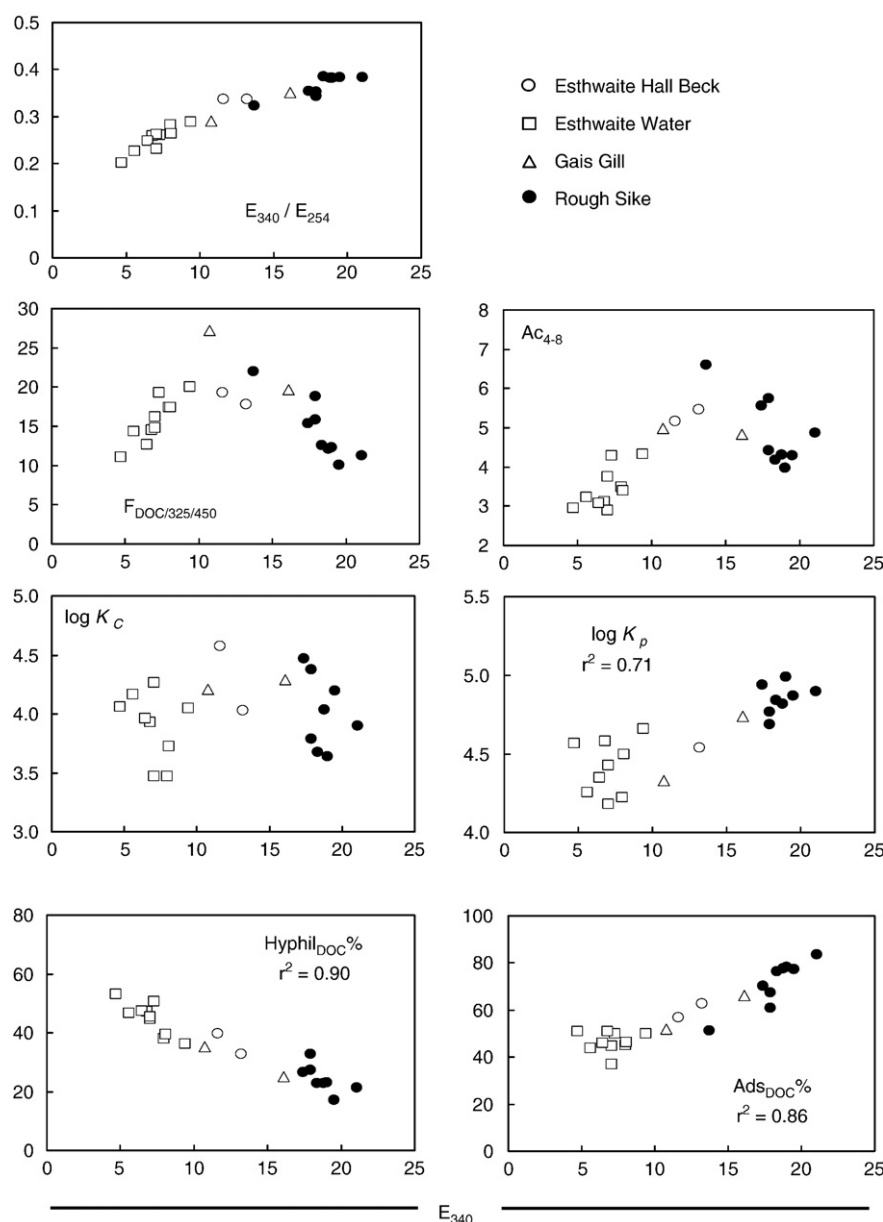


Fig. 3 – Assay results plotted against E_{340} . Units for the y-axes are given in Table 1.

differ, so that E_{254} ($l\text{ gC}^{-1}\text{ cm}^{-1}$) = $10 \times \text{SUVA}$ ($l\text{ mgC}^{-1}\text{ m}^{-1}$). Although E_{254} , E_{280} and E_{340} are well-correlated, the relationships are not completely direct. Thus, the increase of E_{340}/E_{254} with E_{340} (Fig. 3) shows that the DOM with higher overall absorbance is relatively more absorbing at the longer wavelength; in other words the DOM spectrum varies in shape. It can be seen from Fig. 3 that the DOM samples from Rough Sike are the most light-absorbing of all the samples studied.

As found in the previous work, several of the assays are directly and strongly correlated with E_{340} . Results for hydrophilicity and adsorption to alumina, expressed in terms of DOC, are plotted in Fig. 3. A high correlation ($r^2=0.85$) was also found for all the data with $\text{Hyphil}_{A340}\%$, but a lower one with $\text{Ads}_{A340}\%$ ($r^2=0.48$). The results show that the Rough Sike DOM samples are the least hydrophilic and most strongly adsorbing of all samples studied. It is also established that benzo(a)pyrene binding to DOM from Rough Sike is stronger than found for DOM from other sites. This extension of the range of values by the inclusion of Rough Sike data means that $\log K_p$ is significantly correlated with E_{340} when all the samples are considered.

For two of the assays, fluorescence and buffering capacity, the addition of the Rough Sike results establishes a maximum in the relationship with E_{340} (Fig. 3). In both cases the assay result rises with lower values of E_{340} , dominated by the lake water DOM samples, but then falls at higher values, due mainly to the Rough Sike DOM samples. The same pattern may also apply to the copper binding results, although the relationship is much less convincing. We explored the possibility that $\log K_C$ might correlate with fluorescence or buffering capacity, finding a significant but weak correlation with the latter ($r^2=0.19$, $p<0.05$). No significant variation in the results of the photochemical fading assay was seen for Rough Sike, as already mentioned, but considering all 20 DOM samples for which assay results are available, a modest positive correlation with E_{340} is obtained ($r^2=0.22$, $p<0.05$).

Statistical analysis of the entire data set, i.e. 20, 22 or 23 results for each assay, shows that for all 12 assays the variability in the DOM functional property is significantly greater ($p<0.001$) than the variability in the results for the quality control standard.

4. Discussion

4.1. Results for Rough Sike

Variability in the assay results for the Rough Sike samples can be judged in two ways, by comparison with the QC standard, and in terms of stream discharge. The summarised results in Table 1 show that all the functional properties of Rough Sike DOM vary more than those of the QC standard, except for photochemical fading, benzo(a)pyrene binding and hydrophilicity measured by optical absorbance. Benzo(a)pyrene binding was also found not to vary significantly in previous work on DOM from four different surface waters (Thacker et al., 2005) and from a eutrophic lake sampled at different times (Gondar et al., 2007). Photochemical fading did not vary in the surface waters study, but it did in the lake study. In neither of the earlier studies was there significant variation in Cu binding, whereas there was in the present work.

Systematic discharge-dependent variability in the functional properties of DOM from Rough Sike was demonstrated for 8 of the 12 assayed properties (Table 1, Fig. 2). However, because hydrophilicity monitored by optical absorbance ($\text{Hyphil}_{A340}\%$) did not vary significantly in comparison to those for the quality control standard (see above), the discharge dependence cannot be counted in this case. Overall, the results show that high-discharge DOM (i.e. for discharges $>0.06\text{ m}^3\text{ s}^{-1}$ as used in the broken-stick model; Fig. 2) is more light-absorbing at 280 and 340 nm and adsorbs more strongly to alumina than the low-discharge material, whereas it is less fluorescent and hydrophilic, and poorer in proton-dissociating groups. No significant variability with discharge could be demonstrated with respect to light absorption at 254 nm, photochemical fading, the binding of copper, or the binding of benzo(a)pyrene.

The variation of functional properties with discharge suggests that there are at least two sources of DOM to the streamwater. At high discharge, the DOM is mainly supplied by the near-surface zone of the peat, the acrotelm, since that is where the great majority of the runoff comes from (Holden and Burt, 2003a). At low discharge, the high Ca content of the streamwater (Fig. 1) indicates that it has contacted the calcium carbonate that underlies the peat, suggesting that at least some of the DOM could come from deeper in the peat, the catotelm, which might explain its different properties. Possibly some of the low-discharge DOM is formed from deeper peat solids, or it may be DOM from the surface that has been modified or fractionated during passage through the peat and/or the underlying mineral material.

4.2. The complete data set

Addition of the data reported here for Rough Sike to previously reported data (Thacker et al., 2005; Gondar et al., 2007) generates a data set that covers a fairly wide range of DOM types, with samples from two streams draining mineral soils, allochthonous and autochthonous lakewater material, and the peatland stream samples described here. The DOC concentrations of the raw samples vary considerably, from 2.6 to 24.2 mg l^{-1} .

In terms of optical absorbance, the highest value of E_{254} (equivalent to SUVA) is $55\text{ l g}^{-1}\text{ cm}^{-1}$, comparable to the highest values reported by Weishaar et al. (2003). The highest E_{280} value in our data, $45\text{ l g}^{-1}\text{ cm}^{-1}$, is only about half the highest values reported by Bertilsson and Tranvik (2000) for Swedish lake waters, but those waters were high in iron which is likely to have increased the optical absorbance. Our lowest E_{340} of $4.7\text{ l g}^{-1}\text{ cm}^{-1}$ is about six times the lowest value reported for salt lakes of long residence time in Alberta (Curtis and Adams, 1995), in which photodegradation and fractionation result in high concentrations of low-absorbance DOC. The data set therefore cannot be regarded as fully representative of all DOM, but it covers a substantial range of DOM types. As noted in Section 3.4, functional variability has been found to be significant at the 0.1% level for all the assays.

Some properties, notably the extinction coefficients, hydrophilicity and adsorption, have been found to vary significantly with time in both a eutrophic lake (Gondar et al., 2007) and in the peatland stream studied here. The variations can be related to DOM sources, either autochthonous or allochthonous production in the case of the lake, or

the acrotelm or catotelm of the peat. These assay results are well-correlated with extinction coefficient at 340 nm, as shown by the plots in Fig. 3. Thus, E_{340} is a good predictor of hydrophilicity and adsorption. Considering the entire data set, E_{340} is also a reasonable predictor of benzo(a)pyrene binding ($r^2=0.71$), although this relationship is not significant when the lake or Rough Sike samples are considered as separate data sets. Our results for surface water DOM now agree qualitatively with those of Chin et al. (1997) for pyrene binding to a range of isolated humic substances. The significant but weak correlation of photochemical fading ($A_{340}\%$) with E_{340} is unlikely to be useful for prediction.

The results for buffering capacity (Ac_{4-8}) and fluorescence ($F_{DOC/325/450}$) are interesting in that they both give a maximum when plotted against E_{340} (Fig. 3). In each case a quadratic can be fitted to the data ($r^2=0.67$ and 0.70 respectively) that might be used to predict these properties from E_{340} . However, further confirmatory data should be collected before such predictions could be considered reliable, especially in view of results from other systems. In particular, the higher fluorescence shown by the low-discharge DOM from Rough Sike, which is presumably older and/or more processed than the high-discharge material, contrasts with the conclusion of Cumberland and Baker (2007) that fresher DOM gives greater fluorescence intensity. There is also a suggestion of a maximum in the plot of $\log K_C$ (copper binding assay) versus E_{340} but the quadratic fit is not significant ($r^2=0.07$). The only significant correlation of $\log K_C$ with another assay result is the weak increase with Ac_{4-8} , which could arise because the greater number of proton-binding sites increases the binding strength. However, the relationship is of little predictive value.

4.3. Environmental implications

Considering the full set of assay data from all four surface waters, we have found that surface water DOM displays statistically significant variability, in all of the functional properties examined, on the basis of comparisons with results for the quality control standard. Dissolved organic matter varies in its absorption and emission of light, susceptibility to photodecomposition, interactions with metals and hydrophobic compounds, adsorption to surfaces, and general hydrophilic–hydrophobic character. Ideally, efforts to understand and predict the behaviour and influence of DOM in natural aquatic systems should take this variability into account, rather than assuming constant DOM properties.

For example, a model that involved the prediction of DOM interactions with organic pollutants in surface waters could be run with the range of $\log K_p$ values found for our samples to generate an average prediction together with an uncertainty interval. Similarly, the prediction of chemical speciation involving proton and metal binding by DOM could draw on the ranges of properties indicated by the assay results for buffering capacity and copper binding. More directly, the variability in DOM extinction coefficients could be used when evaluating light absorption by freshwaters of differing DOC concentration, and thence photosynthetically available radiation.

Another way to use the results arises when both [DOC] and optical data are available for field samples, and when a functional property correlates with the extinction coefficient(s). For

example, prediction of the tendency of DOM to adsorb to oxide surfaces, or to bind organic pollutants would be more precise if both types of input data were used in their calculation, rather than simply using the average property based only on [DOC].

However, it should also be recognised that, as noted by Gondar et al. (2007), environmental models that incorporate DOM functional properties into descriptions of interacting processes, will probably involve approximations to do with factors other than DOM, either because of lack of input data, or incomplete process characterisation. For example, a catchment-scale contaminant transport model, in which binding to DOM is taken into account, might make simplifying assumptions about soil physical and chemical properties, or it might average temporal variability in rainfall amounts and composition. Uncertainties arising from such approximations could then substantially outweigh uncertainty arising from DOM functional variability, so that taking the latter into account would be of little benefit. But information on ranges of DOM properties would still be useful by permitting quantitative assessment of the consequences of simplification.

Ultimately, we would wish to combine knowledge about the functional properties of DOM with understanding of its formation in soil, sediment and water decomposition processes. In this context, the results in Fig. 3 which show that the ranges of assay values for Rough Sike (filled circles) are comparable to those for the eutrophic lake (open squares), are interesting. Whereas the lakewater DOM is derived from the decomposition of contrasting terrestrial vegetation (allochthonous) and phytoplankton (autochthonous), the Rough Sike DOM must come solely from peatland vegetation. The results therefore imply that variability in DOM functional properties does not arise simply from differences in source material, but also from differences in decomposition conditions and post-formation fractionation.

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