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Processes controlling DOC in pore water during simulated drought cycles in six different UK peats

J. M. Clark · A. Heinemeyer · P. Martin · S. H. Bottrell

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Abstract The effect of episodic drought on dissolved organic carbon (DOC) dynamics in peatlands has been the subject of considerable debate, as decomposition and DOC production is thought to increase under aerobic conditions, yet decreased DOC concentrations have been observed during drought periods. Decreased DOC solubility due to drought-induced acidification driven by sulphur (S) redox reactions has been proposed as a causal mechanism; however evidence is based on a limited number of studies carried out at a few sites. To test this hypothesis on a range of different peats, we carried out controlled drought simulation experiments on peat cores collected from six sites across Great Britain. Our data show a concurrent increase in sulphate (SO_4) and a decrease in DOC across all sites during simulated water table draw-down, although the magnitude of the relationship between SO_4 and DOC differed between sites. Instead, we found a consistent relationship across all sites between DOC decrease and acidification measured by the pore water acid neutralising capacity (ANC). ANC provided a more consistent measure of drought-induced acidification than SO_4 alone because it accounts for differences in base cation and acid anions concentrations between sites. Rewetting resulted in rapid DOC increases without a concurrent increase in soil respiration, suggesting DOC changes were primarily controlled by soil acidity not soil biota. These results highlight the need for an integrated analysis of hydrologically driven chemical and biological processes in peatlands to improve our understanding and

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J. M. Clark (✉)
Soil Research Centre, Department of Geography
and Environmental Science, School of Human
and Environmental Sciences, University of Reading,
Whiteknights, PO Box 233, Reading RG6 6DW, UK
e-mail: j.m.clark@reading.ac.uk

J. M. Clark · S. H. Bottrell
School of Earth and Environment and School
of Geography, University of Leeds, Woodhouse Lane,
Leeds LS2 9JT, UK

J. M. Clark
Grantham Institute for Climate Change Fellow, Civil
and Environmental Engineering, Imperial College
London, South Kensington, London SW7 2AZ, UK

A. Heinemeyer
Stockholm Environment Institute at the Environment
Department and Centre for Terrestrial Carbon Dynamics
(York-Centre), University of York, Heslington, York
YO10 5DD, UK

P. Martin
Department of Biology, University of York, Heslington,
York YO10 5DD, UK

Present Address:
P. Martin
National Oceanography Centre, Southampton, European
Way, Southampton SO14 3ZH, UK

ability to predict the interaction between atmospheric pollution and changing climatic conditions from plot to regional and global scales.

Keywords Dissolved organic carbon · DOC · Sulphate · Drought · Episodic acidification · Peat · Climate change

Introduction

Northern peatlands contain about one third of global soil organic carbon (C) stocks, built up over many thousands of years under water-logged conditions that have limited decomposition (Gorham 1991). Future climate change might result in lower water tables, peat aeration and thus stimulated peat decomposition (Ise et al. 2008) as projections show an increase in the magnitude and frequency of drought events in the northern hemisphere (IPCC 2007). Observations of rising dissolved organic carbon (DOC) concentrations in rivers draining areas dominated by organic rich soils have lead to concerns that these carbon stores are beginning to destabilize (Freeman et al. 2001a). The mechanisms controlling DOC release from peats during droughts have been intensely debated over recent years, given the potential for increased DOC production and release in response to water table draw-down (Clark et al. 2010; Eimers et al. 2008b; Evans et al. 2002, 2006; Freeman et al. 2001a, 2004; Watts et al. 2001; Worrall et al. 2004). However, current dynamic peatland models are still inadequate in reflecting these processes, particularly the dynamic relationship between peatland hydrology and carbon (C) cycling (Heinemeyer et al. 2010). Further experimental work is needed to gain an improved understanding of the underlying decomposition processes that need to be incorporated into these models.

While it is generally accepted that water table draw-down increases peat decomposition and CO_2 efflux, with a concurrent decrease in methane flux (CH_4) (Blodau and Moore 2003; Freeman et al. 1993), the impact on DOC dynamics is less clear. Studies have shown conflicting results, with DOC concentrations increasing (Glatzel et al. 2006), decreasing (Clark et al. 2005; Fenner et al. 2005; Hughes et al. 1998; Pastor et al. 2003; Scott et al. 1998) and showing no change in both soil and stream waters following water table draw-down in peat (Blodau and Moore 2003; Eimers et al. 2008b). In some cases, stream water studies have not been able to report on dynamics during drought events as cessation of flow prevented sample collection (Eimers et al. 2008b; Jager et al. 2009), and therefore DOC dynamics during drought events are not recorded.

Explanations for DOC concentration responses during drought events are varied. Most simply, DOC concentrations might increase during droughts due to 'evapoconcentration' from decreasing water volumes (Waiser 2006). Other studies suggest that DOC concentrations increase as a result of increased biological activity and net DOC production, where more DOC is released during decomposition than is consumed and respired by soil biota (Pastor et al. 2003; Tipping et al. 1999). The DOC produced is either released directly to pore waters during drought events (Glatzel et al. 2006; Strack et al. 2008), or is adsorbed during the drought period and subsequently released as the peat rewets (Clark et al. 2009; Mitchell and McDonald 1992; Scott et al. 1998; Tipping et al. 1999; Watts et al. 2001; Worrall et al. 2003). Conversely, lower DOC concentrations during droughts could be due to decreased biological activity and DOC production (Scott et al. 1998); or because DOC consumption by soil biota exceeds DOC production (Fenner et al. 2005; Pastor et al. 2003; Scott et al. 1998). As DOC fluxes (i.e. mass of DOC transported per unit time per unit area) are controlled by water flow, stream water studies have consistently reported lower DOC fluxes during 'dry' years relative to 'wet' years, irrespective of changes in concentrations (Clark et al. 2007; Dillon and Molot 2005; Eimers et al. 2008b; Schindler et al. 1997; Worrall and Burt 2008).

In our previous work (Clark et al. 2005, 2006), we argued that observed soil water DOC concentrations decreased during drought events because sulphur (S) redox reactions caused an increase in acidity and ionic strength which decreased DOC solubility. This conclusion was based on evidence from one English blanket peat site, where both in-situ pore water monitoring data from the field and laboratory soil core experiments showed consistent results (Clark et al. 2006). A solubility control on DOC by drought-induced acidification could also explain observations of increasing DOC concentrations following drought periods; as both acidity and ionic strength decrease once the water table recovers and SO_4 reduction takes place. Consequently, a store of compounds that are produced during the drought are only soluble at higher pH/lower ionic strength after water tables have recovered to the surface (Clark et al. 2005, 2006; Toberman et al. 2008). In this situation, DOC dynamics during drought events are indirectly hydrologically controlled by changes in soil water chemistry driven by water table fluctuations, rather than directly hydrologically controlled due to changes in water volume or flow.

However, increasing DOC following rewetting has also been attributed to enhanced enzyme activity increasing decomposition and DOC production (Fenner et al. 2005; Hughes et al. 1998; Toberman et al. 2008). Others have suggested that the post-drought recovery in DOC concentrations is due to hydrophobic recovery of peat, where structural changes have delayed complete rewetting of peat and the subsequent release of adsorbed DOC to pore waters (Watts et al. 2001; Worrall et al. 2003). In stream waters, others have argued that the main effect of drought on DOC is to limit its transport through cessation of flow (Eimers et al. 2008b). Therefore at the catchment scale, additional processes to those acting within peat pore waters at the plot/mesocosm scale contribute to overall observed DOC response to drought (Clark et al. 2010; Preston et al. 2011). As DOC in stream waters is controlled by supply from terrestrial sources as well as transport from soil to stream (Thurman 1985), understanding soil processes at the plot scale are important to understand the whole catchment response.

So far, no consensus has emerged on which of these processes controlling the production and release of DOC within pore waters (i.e. plot or mesocosm scale) under drought is ubiquitous with respect to variation in vegetation, peat type, climatic conditions and atmospheric inputs between locations. Studies have tended to focus on a single site or local region, each with a different scale of investigation (e.g. lab, plot or catchment) and/or sampling strategy, making comparisons between studies difficult (Clark et al. 2010). Unified studies across a range of sites at identical scales are required to fully examine the various hypothesised controls on DOC dynamics to ensure data interpretations between sites are based on comparable data. Therefore, we carried out controlled laboratory experiments to test whether evidence of DOC suppression by drought-induced acidification in pore waters (Clark et al. 2005, 2006) could be detected at other sites in Great Britain. We compared responses between peat collected from Moor House (our original study site) with five additional field sites with differing historic acid deposition and/or vegetation cover. We monitored changes in pore water chemistry, water volume and trace gas fluxes during simulated drying and rewetting to determine whether droughts resulted in: (i) decreased DOC concentrations in pore waters; (ii) increased soil water acidification and ionic strength; (iii) increased biological activity and potential consumption of DOC as a substrate for heterotrophic respiration; and (iv) whether decreased water volume affected DOC concentrations.

Materials and methods

Field sites

Cores from the top 10 cm of the peat were collected from six sites in May/June 2006. Sites in order of high to low S deposition were: River Etherow (ETH, South Pennines), Afon Gwy (GWY, Mid-Wales), Moor House (MH, North Pennines), Dargall Lane (DL, South-West Scotland), Loch Coire nan Arr (LCNA, North-West Scotland), Allt a'Mharcaidh (AM, Cairngorms). Mean total (marine and acid) S deposition for these sites over the period of 1985–2005 ranged from 10 to 57 kg S/ha/year; with non-marine S (xS) deposition ranging from 7 to 37 kg S/ha/year (Ron Smith, pers. comm.; Table 1). Five of the sites were located within catchments currently monitored by the Acid Waters Monitoring Network (AWMN) (see Patrick et al. 1991) and one site (Moor House) was monitored by the Environmental Change Network (ECN) (see Heal and Smith 1978). All sites were moorland areas used primarily for grazing. Four sites (GWY, MH, AM, ETH) were extensive areas of blanket peat and two sites were basin peat (DL, LCNA) that had developed in glaciated valleys on moraine. The main peatland vegetation species *Calluna vulgaris* and *Sphagnum* spp. were present at three sites (GWY, MH, AM) and absent at the others where *Eriophorum* spp. (ETH, DL) or *Molina* spp. (LCNA) were dominant. ETH is located in the Peak District (east of Manchester), where climate change, peat erosion and high levels of acid deposition following industrial development have been associated with the decline in *Sphagnum* spp. (Tallis 1994). Peats were acidic (pH 3.9–4.9 in H_2O) with moderate to low base saturation (11.1–48.9%)

Table 1 Site locations and description

Site	Sampling location and altitude	Peat	Geology	Climate (1961–1990)		Mean sulphur deposition (1986–2005) (kg/ha/year)	
				Total rainfall (mm/year)	Mean annual temperature (°C)	Total S	Total xS
River Etherow (ETH)	1°49′W 53°30′N [SE121007] (425 m)	Blanket peat	Millstone grit	1,572	6.9	57	37
Afon Gwy (GWY)	3°44′W 52°27′N [SN821866] (525 m)	Blanket peat	Mudstones, shales and grits	2,599	6.6	34	19
Moor House (MH)	2°23′W 54°41′N [NY753333] (555 m)	Blanket peat	Limestone, sandstone and shale	1,917	5.4	31	19
Dargall Lane (DL)	4°26′W 55°4′N [NX447788] (330 m)	Semi-confined peat as part of peat complex	Greywackes, shales, mudstones and granite/gneiss instructions	2,426	6.7	29	16
Loch Coire nan Arr (LCNA)	5°31′W 57°24′N [NG815416] (135 m)	Semi-confined peat as part of peat complex	Torridonian sandstone	3,311	8.2	26	10
Allt a'Mharcaidh (AM)	3°50′W 57°60′N [NH888026] (575 m)	Blanket peat as part of peaty complex	Intrusive biotite-granite	1,331	4.9	10	7

Mean annual rainfall 1961–1990 estimated after (Cooper 2005). Mean annual temperature taken for nearest UK Met Office AWS Station mean and corrected for altitude assuming lapse rate of 0.59°C per 100 m (Bell and Moore 1999). Temperature and rainfall data were provided by UK Meteorological Office through BADC. Total sulphur (S) and non-marine sulphur (xS) deposition estimates (dry and wet) were provided by Ron Smith, CEH Edinburgh for 1986–2005

(Table 2). Further details about the basic peat properties and site descriptions can be found in Clark et al. (2011).

Experimental design

At each site, eight peat cores were collected at random locations within a 30 m radius of a chosen sample point (Table 1). To reduce the amount of live biomass (i.e. roots) within each core, soil samples were collected between tussocks and shrubs rather than directly underneath the plants. Other surface vegetation and litter were removed. Each intact core was extracted by carefully cutting a PVC tube (10 cm diameter, 11 cm length) into the peat using a serrated edge knife, taking care to leave a 0.5–1 cm gap between the surface of the peat and the top of the tube. Once excavated, cores were planced into straight-sided Nalgene poly-carbonate bottles (11 cm in diameter, 12 cm in length) and chilled during transport.

On return to the laboratory, a 10 cm Eijkelkamp Rhizon soil water sampler (SMS) was inserted into each core. Pore water is extracted by applying suction from a syringe attached to the Rhizon SMS (see Clark et al. 2006). Cores were then slowly rewetted with deionized water until the surface peat was covered with 0.5–1 cm water. Deionized water was used in preference to a synthetic soil water solution to ensure no additional solutes were added. Variation in precipitation and soil water chemistries between sites also precluded the use of a single standard synthetic

Table 2 Peat chemical and physical properties: soil pH (ratio 1:10 wet soil to solution), C:N ratio, base saturation and bulk density

Site	pH		Base saturation (%)	C:N ratio	Bulk density (g/cm^3)
	H_2O	0.1 M $CaCl_2$			
ETH	3.93	3.07	14.6	29.2	0.159
GWY	4.34	3.29	32.9	32.9	0.069
MH	4.30	3.15	34.7	36.2	0.088
DL	4.31	3.64	11.1	20.6	0.102
LCNA	4.85	3.87	23.9	25.2	0.078
AM	4.60	3.38	48.9	46.5	0.075

Mean value shown ($N = 5$). After Clark et al. (2011)

solution. All cores were then placed in an incubator for 6 months at 10°C to allow soil water to stabilize, background SO_4 and NO_3 concentrations to reduce naturally to negligible concentrations, and any labile carbon produced as an artefact from decaying fresh roots to be consumed prior to the start of the experiment, as rates of carbon turnover are elevated in disturbed peat cores (Blodau and Moore 2003). Lids were placed loosely on the bottles to reduce evaporation whilst maintaining air exchange.

The experimental simulation was split into three stages: (1) initial pre-treatment (all cores saturated), (2) 12 weeks of simulated drought by water table draw-down (four cores each unsaturated and saturated for each site) and (3) 20 week rewetting period (all cores saturated) (Fig. 1). Water table draw-down was simulated by pouring off excess drainage water from soil cores during the first 4 weeks of the 12-week drought (i.e. weeks 0–4), and then by extracting an additional 20 mL every 2 weeks (weeks 4–12) using a syringe and the Rhizon SMS samplers. Cores were rewetted following soil water sample extraction in week 12 and monitored for a further 20 weeks until soil water concentrations stabilized.

For chemical analysis, 20 mL of soil water was collected every 4 weeks using Rhizon SMS samplers, starting with a pre-treatment sample taken just prior to Stage 2 (week 0). Core weights were recorded prior to sample collection. Water loss due to evaporation and sample extraction was replaced with deionised water after sampling in the saturated cores to maintain constant water levels throughout the experiment when saturated conditions were required.

At the end of the experiment, all peat cores were dried in an oven at 70°C for 48 h to determine their final water content and oven dry mass.

Soil water analysis

Soil water was filtered on extraction by the PTFE membrane in the Rhizon SMS samplers to <1 μm (Clark 2005). Water samples were analysed for pH; conductivity; SO_4, chloride (Cl) and nitrate (NO_3) by ion chromatography (Dionex); calcium (Ca), magnesium (Mg), sodium (Na) and potassium (K) by atomic absorption spectrophotometry (Hitachi); DOC by combustion infra-red analyser (Thermalox TOC-

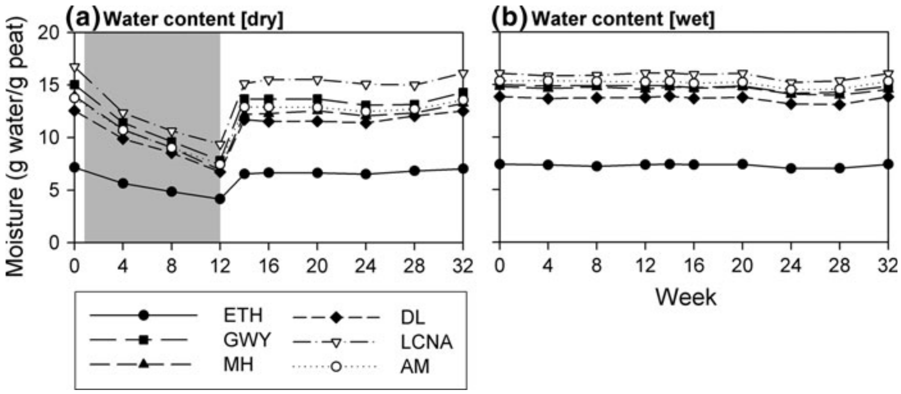


Fig. 1 Changes in water content over 32 week experimental period in **a** dry and **b** wet (i.e. control) treatments. Water context expressed as mass (g) of water per mass (g) of dried peat. Mean value shown ($N = 4$)

TN); and colour with scanning UV–VIS–NIR spectrophotometer (Shimadzu).

Gas analysis

Real-time trace gas flux measurements were taken before soil water sampling in weeks 0, 4, 8, 12, 16 and 32. A closed gas flow system was established using a Li-Cor 8100 carbon dioxide (CO_2) infra-red gas analyser (IRGA) connected to a flux chamber (8100-102; Li-Cor Biosciences, USA). The chamber (diameter of 10 cm and a volume of 955 mL) was placed over each core for 10 min. CO_2 flux data presented in this paper were calculated as the linear increase in humidity corrected CO_2 concentrations (ppm) at a 1 s recording frequency during the first 2 min of chamber closure.

Further calculations

Changes in DOC characteristics were inferred from SUVA (specific ultra-violet absorbance) and E_{340} (extinction coefficient at 340 nm) values calculated from the absorbance and measured DOC concentration data. SUVA was calculated as the absorbance at 254 nm in units/m divided by the concentrations of DOC in mg/L. Analysis has shown a good relationship between SUVA and coloured aromatic humic acids (Weishaar et al. 2003). E_{340} was calculated as the absorbance at 340 nm in units/cm divided by the concentration of DOC in g/L; and has been shown to have a negative relationship with the hydrophilic fraction of DOC and positive relationship with the aluminium (Al) adsorption capacity (Thacker et al. 2008). 'Evapoconcentration' effects, that may cause a change in concentration due to a change in water volume, were examined by (1) taking the ratio of a solute (e.g. DOC) to Cl, assuming Cl is a conservative tracer (Waiser 2006) and by (2) calculating the total amount of a solute per mass of dry peat.

Acid neutralising capacity (ANC) is a conservative measure of acidity of pore waters, as unlike pH and alkalinity measurements, it is unaffected by CO_2 degassing, aluminium reactions (Al) or organic species (Neal et al. 1999) and has been widely used a key chemical indicator of acidification status in Critical Load assessments (CLAG 1994). The ANC was determined here as the difference between the sum of strong base cations (SBC; calcium (Ca), potassium (K), magnesium (Mg), sodium (Na)) and the sum of strong acid anions (SAA; chloride (Cl), NO_3, SO_4) (Hemond 1990):

$$\begin{aligned}\mathrm{ANC} = {} & \left(\left[\mathrm{Ca}^{2+}\right] + \left[\mathrm{Mg}^{2+}\right] + \left[\mathrm{Na}^{+}\right] + \left[\mathrm{K}^{+}\right]\right) \\ & - \left(\left[\mathrm{Cl}^{-}\right] + \left[\mathrm{NO_3}^{-}\right] + \left[\mathrm{SO_4}\right]\right) \qquad (1)\end{aligned}$$

where concentrations of each ion was in μeq/L.

Ionic strength was estimated as:

$$\mathrm{IS} = 0.5 \sum_{i=1}^{n} C_i z_i^2 \qquad (2)$$

where IS is in mol/L; C_i is the concentration of a substance in mol/L and z is the valence of the substance (Sparks 2003). Ionic strength is typically calculated from all solutes in solution. However, in this case only base cation, acid anion and H^+ data were available. Other studies on similar organic rich waters have included ammonia (NH_4), aluminium (Al^{3+}) and bicarbonate (HCO_3^-) in their calculations (Hruska et al. 2009). As soil waters were acidic, HCO_3^- concentrations will be negligible and inorganic carbon present as dissolved CO_2. As blanket peat soils are typically low in N and Al, it is unclear whether these values were negligible. Al was present in semi-confined peats following analysis for exchangeable acidity (Clark et al. 2011), due to inputs of Al via throughflow from upslope sources (Mulder et al. 1991) and NH_4 may also be present in sites impacted by N deposition. Therefore, values of IS calculated here are likely to have underestimated actual values.

Mass balance calculations were made to estimate the balance between (1) DOC consumption/production and subsequent respiration as CO_2 and (2) changes in DOC due to chemical solubility. The rate of change in DOC between sample weeks was estimated (i.e. week 0–4, 4–8, 8–12 etc.). Total DOC amounts were corrected at each time point for removal of DOC by sample collection for analysis. For consistency, the average CO_2 flux was estimated between the sampling periods (i.e. week 0–4, 4–8, 8–12 etc.). All changes were expressed in terms of unit mass of carbon (as either DOC or CO_2) per unit mass of dry peat.

Further stochiometric calculations were carried out to determine possible changes in CO_2 flux due to SO_4 and NO_3 reduction during peat rewetting. Since acidic conditions prevail in these soils, the reaction for SO_4 reduction used was that for conditions of pH 4.5 and below:

$$SO_4^{2-} + 2CH_2O + 2H^+ \Rightarrow H_2S + 2CO_2 + 2H_2O \quad \text{(Reaction 1)}$$

where CH_2O is organic matter and H_2S is hydrogen sulphide. For NO_3 reduction, two possible reactions could occur depending on the presence of oxygen within the system. As the actual redox status was unknown, calculations were made using both equations. Under oxic conditions, the reaction is likely to be:

$$2NO_3^- + 2CH_2O + 2H_2O + 2H^+ \Rightarrow N_2O + 2CO_2 + 5H_2O \quad \text{(Reaction 2)}$$

where N_2O is nitrous oxide. Under anoxic conditions, dissimilatory NO_3 reduction produces nitrogen gas (N_2):

$$4NO_3^- + 5CH_2O + 4H^+ \Rightarrow 2N_2 + 5CO_2 + 7H_2O \quad \text{(Reaction 3)}$$

From these reactions, the production of CO_2-C per unit mass SO_4-S reduction can be calculated by multiplying the mass of SO_4-S reduced by 0.749; for NO_3-N reduction, the unit mass production of CO_2-C can be calculated by multiplying the mass of NO_3-N reduced by 0.858 under oxic conditions and 1.07 under anoxic conditions.

Statistical analysis

The experiment design used here reflects a two-way ANOVA with repeated measures, where both peat site and dry–wet/wet–wet cycle are treatment factors and response variables (e.g. DOC) were measured at many points over time from the same replicate. However, data analysis was problematic as the variations between sites and over time in many response variables produced data sets with unequal variance that resulted in model fits with unequal error distributions. Transformations through log or power transformations did not improve this because of the nature of data distribution and in some cases was not possible due to negative values (e.g. ANC).

Instead, the data were analysed using standard two-way ANOVA for two critical points during the experiment where the change in response variable between the start and either week 12 (end of the dry period) or week 32 (end of experiment after rewetting) was calculated to remove the temporal pseudo-replication (Crawley 2007). Homogeneity of variance was tested using the Fligner–Killen test (Crawley 2007) and reported so analysis based on untransformed data where variances were unequal can be interpreted with caution. Post-hoc tests were only carried out when the equality of variance assumption was satisfied. Otherwise, graphical representation of standard error (i.e. standard deviation divided by the square root of the number of samples) in tables and figures were provided to allow comparisons. The Scheirer–Ray–Hare test, essentially a non-parametric version of two-way ANOVA were analysis is carried out on ranked data (Dytham 2011), was also preformed where variances were unequal. The 95% confidence interval of the mean was reported using the exact confidence interval from the Student's T distribution.

Results

DOC response to simulated water table drawdown

Both pore water DOC concentrations and the total amount of DOC per core declined during the simulated dry period and increased during the wet period in all peat cores exposed to the 'dry' treatment (Fig. 2a, c). Results from both the parametric (score data) and non-parametric (rank) two-way ANOVA showed a significant difference between dry and wet treatments between 0 to 12 weeks ($p < 0.001$) but not between weeks 0 and 32 ($p = 0.05$–0.10) . Concentrations and amount of DOC released varied significantly between sites ($p < 0.001$). Overall change in DOC concentrations in the dry treatment from week 0 to 12 ranged from −36 to −87% with mean absolute concentrations in the dry cores ranging from 6.1 to 39.3 mg/L compared to 39.6 to 276.0 mg/L in the wet cores. Although the dry treatment period lasted from week 0 to 12, the greatest decline in DOC concentrations occurred during weeks 4–8.

The ratio of DOC:Cl also decreased during the simulated dry period for all peats except AM (Fig. 2e), where the ratio of DOC:Cl increased. If Cl is assumed to be a conservative tracer, 'evapo-concentration' would not change the DOC:Cl ratio. Decrease in the DOC:Cl show that DOC

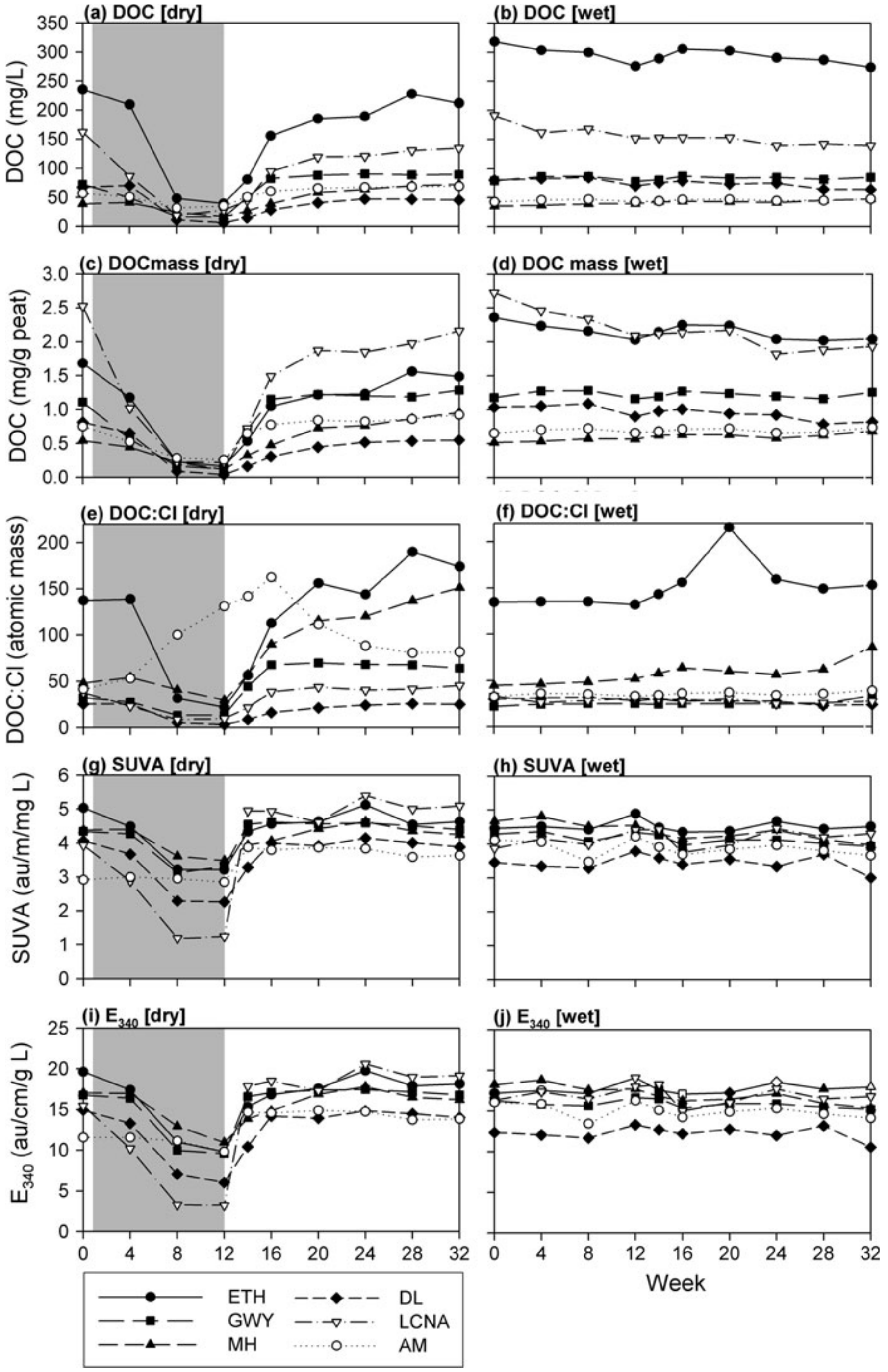


Fig. 2 Change in DOC amount and quality over the 32 week experimental period under the dry–wet and wet treatments: **a**, **b** DOC concentrations; **c**, **d** amount of DOC per unit mass dry peat; **e**, **f** molar ratio of DOC:Cl; **g**, **h** SUVA; **i**, **j** E_{340}. Mean values shown ($N = 4$)

concentrations declined in both absolute and relative terms during the dry period.

All sites (except AM) showed a consistent decline in SUVA during the dry period indicating a change in DOC quality associated with a decline in the coloured humic acid fraction (Fig. 2g, h). Like DOC concentration and amount, both SUVA and E_{340} showed the greatest rate of decline between weeks 4 and 8, hence changes in DOC quality occurred at the same time as changes in DOC quantity. Following rewetting in week 12, DOC concentration and amount increased rapidly (Fig. 2a, c). SUVA and E_{340} in all peats between week 12 and 14 responded immediately to rewetting, showing that the DOC quality recovered faster than absolute concentration or amount.

In contrast, both concentrations and amount of DOC in the wet treatment cores showed either a steady decrease (LCNA, DL, ETH) or small increase (MH, AM, GWY) over time (Fig. 2). No significant pattern in SUVA or E_{340} was seen in the wet treatments, with values remaining constant or showing a slight decline as well (Fig. 2h, j).

Overall, observations support widespread evidence that a shift from saturated (i.e. 'wet') to unsaturated (i.e. 'dry') conditions resulted in a net decline in DOC, particularly the coloured hydrophobic humic fractions measured by SUVA and E_{340}, and rewetting resulted in a rapid increase in both DOC and the proportion of humic material. These changes in DOC concentration and quality appeared to be independent of changes in the volume of water as both the amount of DOC in solution per g of peat and the ratio of DOC:Cl decreased.

Relationship between soil water acidification and DOC

Drying resulted in increased SO_4 concentrations in all peats, which decreased when peats were rewetted, due to the oxidation and subsequent reduction of S (Fig. 3a) (Bottrell et al. 2004). The magnitude of peak SO_4 concentrations varied considerably between peats (102–2,130 μeq/L), with greatest concentrations in peats that have received the greatest atmospheric S deposition (Table 1). Mean SO_4 concentrations remained at <20.8 μeq/L (1 mg/L; Fig. 3b) in the wet treatment core throughout the experiment.

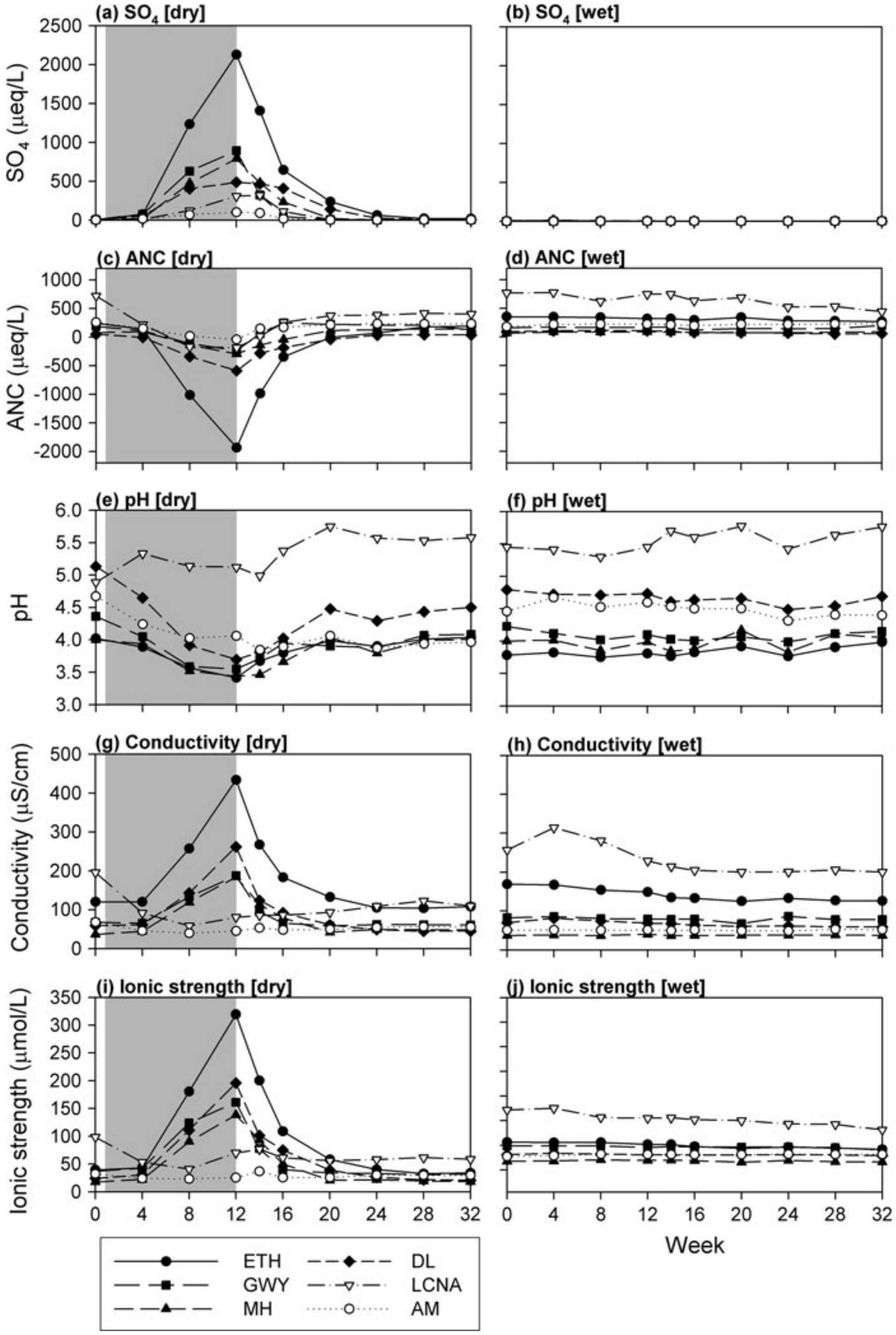
Interestingly, the response of both conductivity and estimated ionic strength to drying and rewetting differed between those sites that had received the greatest levels of pollutant non-marine S deposition (DL, MH, GWY, ETH) and the least acid-impacted sites in north Scotland (AM, LCNA). Conductivity and ionic strength increased in the most acid-impacted peats, but decreased in the least acid-impacted peats during the dry treatment (Fig. 3g, i). The difference in responses between the peats can be attributed to differences in SBC concentrations, as drying resulted in a decline of −63 to −64% in the least impacted peats and increase in SBC concentration of 102–390% in the most acid impacted peats. However, the increase in the amount of SBC (μeq/g peat) in the most acid-impacted peats was proportionally smaller than increases in concentrations.

Drying and rewetting also resulted in the decrease and subsequent increase in ANC in all samples (Fig. 3c). The pH also showed a concurrent increase and decrease in peats from all sites except LCNA, where pH continued to rise (Fig. 3e). However, it should be noted that the pH meter seldom stabilised in LCNA solutions, so pH readings were taken after a fixed time period (1 min) and results should be viewed with caution. The decline in SBC at the least impacted sites contributed to the overall decline in ANC during dry periods where SAA increases were small. By contrast, at the more acid-impacted sites increased SBC partly offset increased SAA concentrations. Increased SAA was principally driven by increased SO_4 due to the oxidation of reduced S, although significant increases in NO_3 and were seen in ETH and DL peats (436 and 1,018 μeq NO_3/L, respectively). The Cl concentrations showed a slow and steady decrease in both wet and dry treatments over the experiment, most likely due to continued removal of water during sample collection. As with other chemical variables, pH, conductivity and ionic strength remained reasonably constant or showed a slow decline over time in the wet treatment (Fig. 2e, g, i).

Inverse relationship between SO_4 and DOC seen in MH peats were repeated in five other peats studied here (Figs. 2, 3). However, the magnitude of the SO_4 increase (102–2,130 μeq SO_4/L) and DOC decrease (−36 to −87%) varied between peats, such that no single relationship between SO_4 concentration and the percentage change in DOC concentrations (ΔDOC%) emerged (Fig. 4). Furthermore, as noted above, two of the least acid impacted peats showed a decrease in conductivity with increasing SO_4 concentrations, and one peat (LCNA) showed no pH response in spite of a change in ANC (Fig. 5).

However, ANC, like DOC, showed a consistent response between peats. Clear relationship between the change in ANC and change in DOC in terms of both percentage ($r = 0.7$) and absolute change ($r = 0.94$) were seen between sites (Fig. 5), with less variability between sites than the relationship between SO_4 and change in DOC (Fig. 4). A linear

Fig. 3 Change in soil water chemistry over the 32 week experimental period under the dry–wet and wet treatments, respectively: **a**, **b** SO_4; **c**, **d** ANC; **e**, **f** pH; **g**, **h** conductivity; **i**, **j** ionic strength. Mean values shown ($N = 4$)



relationship was observed between ANC and change in DOC concentrations in mg/L (Fig. 5c). The relationship between ANC and DOC observed between sites was more consistent when relative changes in ANC and DOC were considered rather than the absolute concentration (Fig. 5).

Changes in soil respiration: biological production and consumption

Observations showed CO_2 fluxes in dry treatments were significantly greater than wet treatments in all peats ($p < 0.001$), with the lowest overall fluxes seen

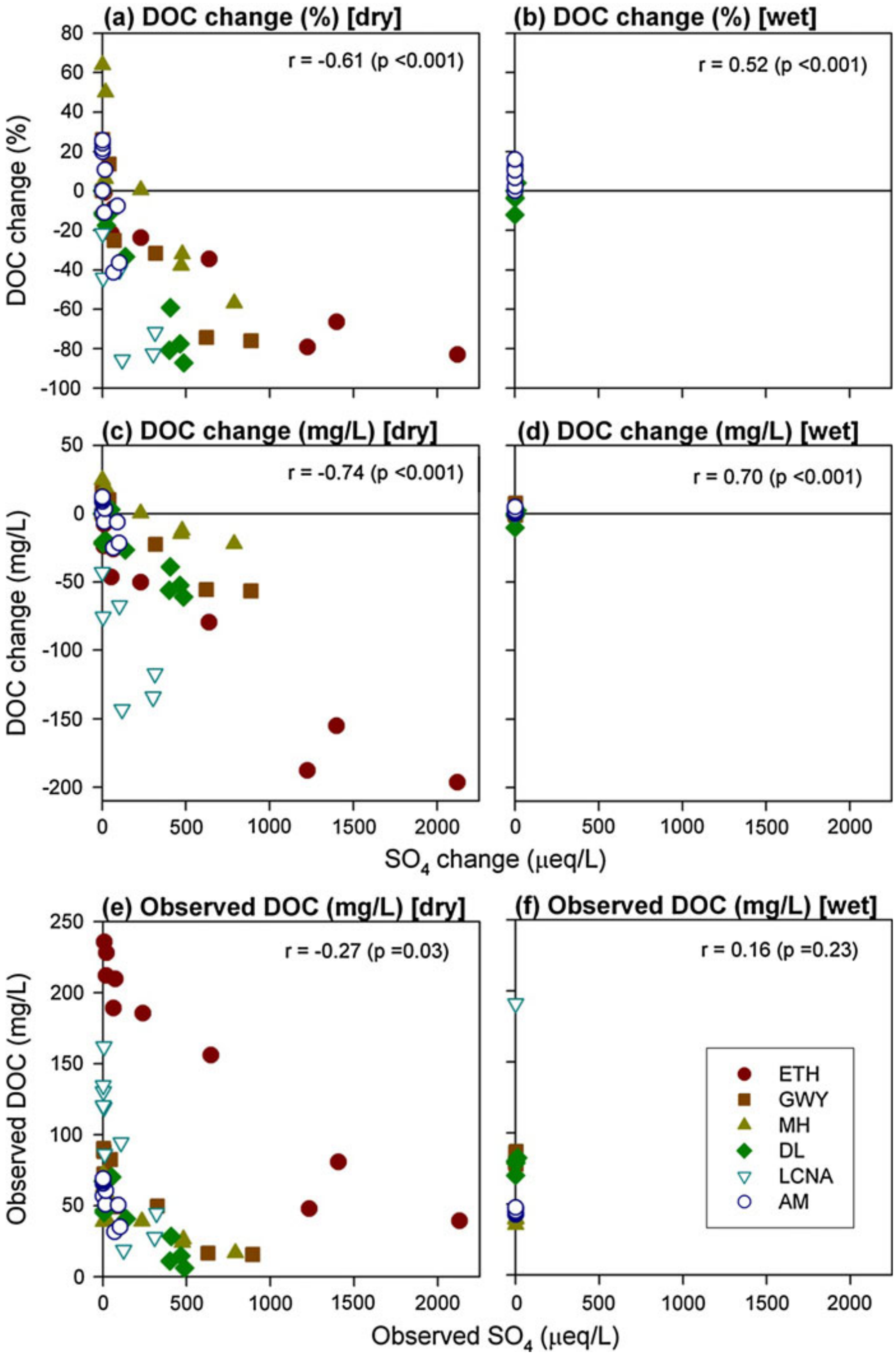
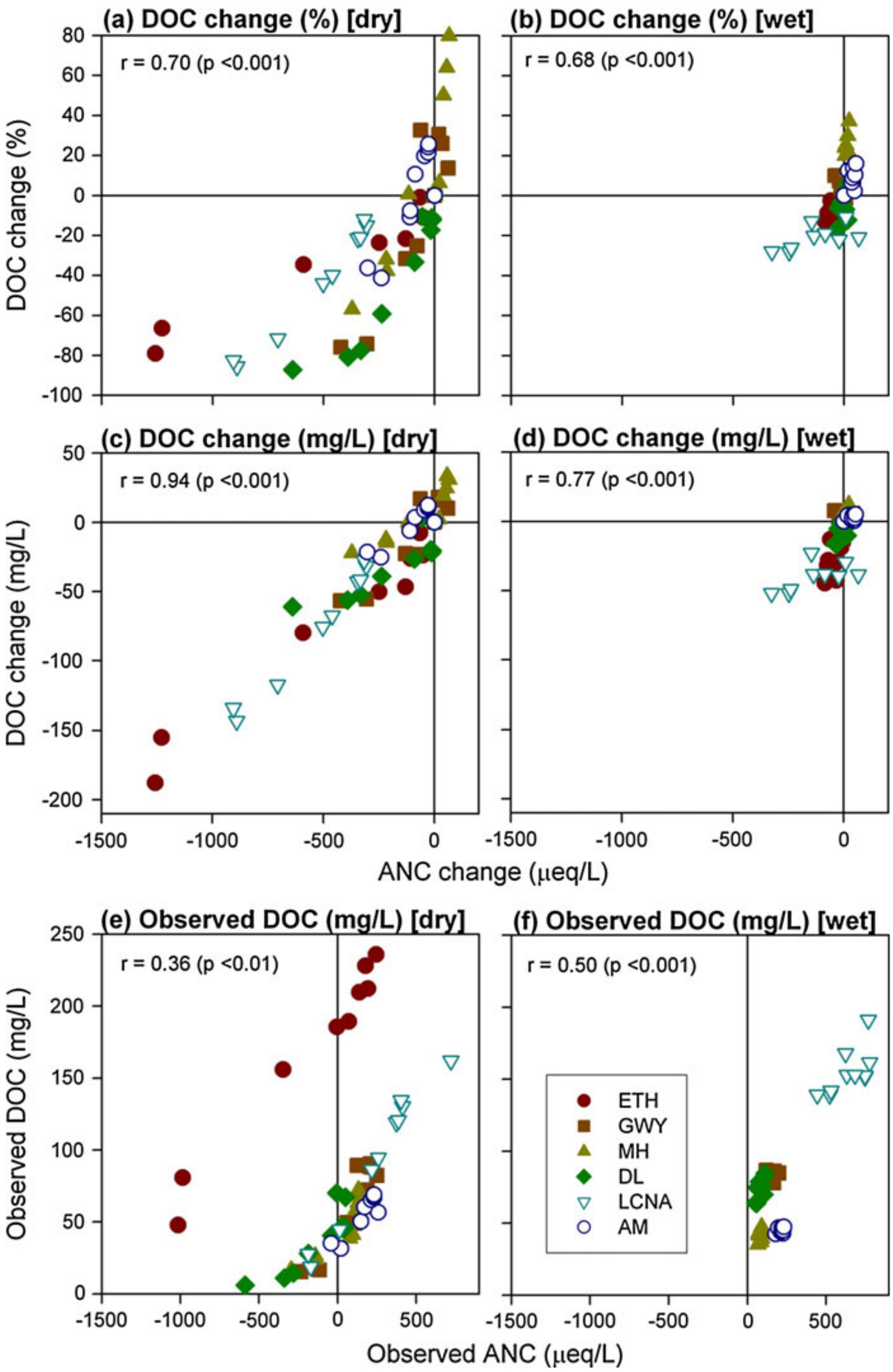


Fig. 4 Relative change in DOC (expressed as both **a**, **b** percentage and **c**, **d** concentration) with respect to change in SO_4 concentrations, compared to the relationship between **e**, **f** observed values. Change relative to initial DOC concentration in week 0. Mean value shown ($N = 4$) for each treatment and soil type for each of the ten sampling points in time. Pearson's correlation coefficient (r) and the significance value are shown

in ETH peats and greatest in LCNA (e.g. Fig. 6a). Comparison between the rate of change in DOC concentrations and CO_2 fluxes were made to determine whether the increase in CO_2 flux in response to drying could be explained by decreased DOC concentrations due to consumption and respiration. Only LCNA in weeks 0–4 showed a significantly greater change in DOC than elevated CO_2 flux ($p = 0.03$), whereas GWY in week 8–12 showed a significantly lower change in DOC than elevated CO_2

Fig. 5 Relationship between change in ANC and relative change in DOC concentrations (expressed as both **a**, **b** percentage and **c**, **d** change in concentration), compared to the relationship between the **e**, **f** absolute values. Change relative to initial concentration in week 0. Mean value shown ($N = 4$) for each treatment and soil type for each of the ten sampling points in time. Pearson's correlation coefficient (r) and the significance value are shown



flux ($p = 0.01$). For all remaining times during the dry period, rate of change in DOC concentration and CO_2 flux were similar.

During the rewetting phase (week 12–14), the increases in DOC concentrations were generally greater than the CO_2 fluxes (Table 3). CO_2 fluxes declined during rewetting relative to elevated fluxes during the dry period, although were greater than under steady-state wet conditions. Stoichiometric calculations suggest that some of the CO_2 fluxes during rewetting could be explained by CO_2 released from SO_4 and NO_3 reduction, which would also

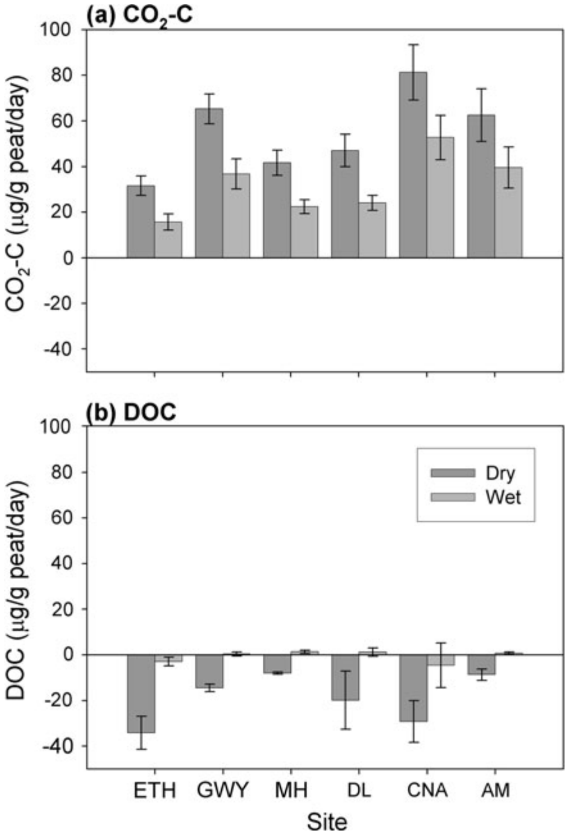


Fig. 6 Net C production of **a** CO_2-C and **b** DOC between week 4 and 8 under both dry and wet experimental treatments. Mean value and standard error shown ($N = 4$). Two-way ANOVA for **a** CO_2-C showed a significant difference between sites and dry/wet treatment ($p < 0.001$) but no significant interaction between these factors ($p = 0.95$). Two-way ANOVA for **b** DOC showed a weakly significant different between sites ($p = 0.01$) and significant difference between dry/wet treatment ($p < 0.001$) but no signification interaction between these factors ($p = 0.12$). As variances for DOC were not homogeneous ($p < 0.01$), the Scheirer–Ray–Hare test was also used for these data, producing similar findings: both site and treatment were significant ($p < 0.001$), with no significant interaction ($p = 0.57$)

consume DOC, however these fluxes were small in comparison to the total measured fluxes (Table 3).

Discussion

Data from these experiments are consistent with our previous work at Moor House, where DOC concentrations in peat pore waters were shown to decrease during drought events and increase following rewetting (Clark et al. 2006). Similar observations have been reported elsewhere (Blodau and Moore 2003; Fenner et al. 2005; Hughes et al. 1998; Pastor et al. 2003). Other additional work reporting increased DOC concentrations in response to water table drawdown were only able to measure peat leachates or soil water during the rewetting phase (Mitchell and McDonald 1992; Tipping et al. 1999). It is unclear in these cases whether DOC concentrations increased or decreased during the actual dry period as no data were available from this time period. Likewise, no changes in DOC concentrations in streams have been shown when flow ceases (Eimers et al. 2008b), making it impossible to infer soil processes during these periods without stream water or additional pore water data.

Change in the water volume in stream and peat pore waters have also been suggested to affect DOC concentrations during drought periods (Eimers et al. 2008a; Waiser 2006). For instance, in the mineral horizon of an organo-mineral soil exposed to drought, increased DOC concentrations were attributed to decreased water volume (Sowerby et al. 2010). However, decreased water volume during drought periods and increased water volume following peat rewetting would have the opposite concentration/dilution effect to the actual observed decrease/increase in DOC concentrations seen in soil (Clark et al. 2006; Hughes et al. 1998) and stream waters (Scott et al. 1998; Watts et al. 2001). Instead of influencing DOC concentrations, the impact of 'evapoconcentration' appeared to be more apparent in terms of increasing base cation concentrations in the most acid-impacted soils, affecting the overall balance between acid anions and neutralising base cations (i.e. ANC) and hence the degree of acidification which in turn influences DOC solubility. However, H^+ ions and Al can also displace cations from peat exchange sites, so increased base cation concentrations could be due to acidification induced cation exchange.

In this study and our previous work, clear relationships between SO_4, acidity and DOC were only seen when changes in both variables were considered, rather than the absolute values. As many factors influence DOC dynamics, particularly in the field, variations due to seasonal changes in temperature needed to be removed before the effect of drought-induced acidification were seen (Clark et al. 2005). Integration of more processes with scale of

Table 3 Average rates of change in the measured CO_2-C flux and net DOC production compared to the calculated CO_2-C flux from SO_4 and NO_3 reduction during the rewetting period (week 12–16) in dry treatment cores

Site	Carbon release rates (μg C/g peat/day)					
	Measured			Calculated		
	Total CO_2-C	CO_2-C above baseline	DOC	CO_2-C from BSR	CO_2-C from BNR_1	CO_2-C from BNR_2
Dry treatment						
ETH	35.3 ± 21.0	4.9 ± 8.0	30.4 ± 19.0	1.9 ± 2.7	0.8 ± 0.6	1.0 ± 0.7
GWY	55.7 ± 21.0	16.3 ± 14.7	36.4 ± 23.2	2.6 ± 1.5	0.0	0.0
MH	36.1 ± 14.6	14.8 ± 17.1	12.6 ± 5.2	1.1 ± 0.7	0.0	0.0
DL	28.3 ± 12.0	5.7 ± 12.6	9.0 ± 14.3	0.0	2.8 ± 1.6	3.5 ± 2.0
LCNA	54.5 ± 13.1	7.7 ± 18.8	43.6 ± 39.5	0.6 ± 1.3	0.0	0.0
AM	48.2 ± 21.3	11.6 ± 29.1	18.1 ± 6.9	0.3 ± 0.5	0.0	0.0
Wet treatment						
ETH	17.0 ± 17.9	−0.2 ± 4.5	7.7 ± 3.0	0.0	0.0	0.0
GWY	31.7 ± 17.4	0.6 ± 9.5	4.0 ± 2.2	0.0	0.0	0.0
MH	17.0 ± 5.9	−6.6 ± 4.6	2.4 ± 1.3	0.0	0.0	0.0
DL	18.9 ± 3.6	−4.5 ± 12.9	3.8 ± 4.2	0.0	0.0	0.0
LCNA	59.1 ± 39.3	−3.7 ± 5.3	1.1 ± 6.2	0.0	0.0	0.0
AM	32.6 ± 17.9	−3.1 ± 5.7	2.0 ± 2.1	0.0	0.0	0.0

BSR is biological SO_4 reduction (Reaction 1); BNR_1 is biological NO_3 reduction (Reaction 2) and BNR_2 is biological NO_3 reduction (Reaction 3). Mean value shown with the exact 95% confidence internal ($N = 4$)

measurement can make it difficult to disentangle the signal from processes operating in the soil (or laboratory experiment scale) to those operating at a catchment scale (Preston et al. 2011), unless care is taken with the analysis to factor out the larger scale catchment or site specific drivers (Clark et al. 2010). In peatland streams where DOC concentrations vary little with stream flow, seasonal changes in temperature are the main source of variation (Clark et al. 2007; Schiff et al. 1998). However, in catchments with organo-mineral soils and mixed soil types, changes in stream flow are the principle driver of variations in DOC concentrations (Clark et al. 2007; Hope et al. 1994); therefore, like temperature, the effect of stream flow needs to be removed before the effect of other factors, like drought-induced acidification, on DOC dynamics can be seen. For instance, in the analysis presented by Eimers et al. (2008b), no consistent relationship was found between absolute SO_4 and DOC concentrations in stream waters. Rather than contrary to our findings, these observations are consistent with our earlier work, which also showed no clear overall relationship between SO_4 and observed DOC concentrations when the effect of temperature was not removed from the data (Clark 2005; Clark et al. 2006).

Comparison between different peats showed that the relationship between drought-induced acidification and DOC mobility was more consistent when changes were measured in terms ANC rather than SO_4. The ANC provided a more robust measure of acidification change, as SO_4, NO_3 and the base cation responses are all accounted for. Observations from minerotrophic fens have shown that increased SO_4 concentrations in response to drying are not always associated with increased acidity (Knorr et al. 2009). An inverse relationship between the change in ANC and change in DOC during episodic droughts is consistent with seasonal inverse relationships between ANC and DOC seen in field observations in pore waters at both MH and GWY (Chapman et al. 2008) and also in long-term nitrogen addition experiments (Evans et al. 2008). It is possible that change or no change in ANC may also explain DOC dynamics in organic horizons of organo-mineral soils, where no relationship between SO_4, pH and DOC has been found (Sowerby et al. 2010). Further work is required to determine whether this is likely.

Rapid and reversible changes in DOC quality measured in terms of changes in SUVA and E_{340} associated with drought-induced acidification in these experiments and other field observations (Scott et al. 1998) are also consistent with acidification driving changes in DOC. Both SUVA and E_{340} are associated with the larger coloured humic fractions, which carry greater charge and are more sensitive to changes in acidity in terms of their solubility. Acid addition experiments in humic rich lakes have observed changes in coloured humic DOC following long-term acidification linked to either Al-mediated coagulation and flocculation or chemical oxidation to CO_2 (Donahue et al. 1998); and laboratory batch experiments have shown similar decreases in SUVA associated with declining DOC following increases in acidity and solute strength (Clark et al. 2011).

As noted above, some studies have suggested that decreased DOC concentrations in response to water table draw-down could be because consumption and respiration of DOC during heterotrophic respiration is greater than the net rate of DOC production (Fenner et al. 2005; Pastor et al. 2003; Scott et al. 1998). If correct, increased CO_2 fluxes should be greater than decreased DOC. Mass balance calculations suggest this mechanism is plausible. However, without isotopically labelling the DOC pool, it is difficult to determine the source of DOC respired, making it difficult to quantify relative changes in DOC due to consumption and/or solubility. Studies have shown DOC released from peats to be resistant to degradation (Kalbitz et al. 2003). However, the quality of organic matter between sites is likely to differ due to differences in surface vegetation, particularly the presence or absence of *Sphagnum* spp. (Table 1); and studies have shown marked difference in the biodegradability between DOC leachates from *Sphagnum* spp. and *Eriophorum* spp. (Wickland et al. 2007).

Rapid increases in DOC concentrations following water table recovery have also been attributed to increased biological activity and net DOC production (Scott et al. 1998), especially in relation to increased activity of phenol-oxidase which is thought to play a key role in removing the inhibitors of the enzymes responsible for peat decomposition (Freeman et al. 2001b; Toberman et al. 2008). In unsaturated soils, rewetting has been associated with increased mineralisation and CO_2 fluxes, possibly due to microbial priming by hydration and lysis of dead microbial cells as a substrate for respiration (Borken and Matzner 2009). However, rapid increases in DOC observed in peat pore waters here following rewetting were not accompanied by increased CO_2 production rates, suggesting this is not a biologically mediated process (Blodau and Moore 2003). Whilst some of the CO_2 released during rewetting could be attributed to organic carbon consumption during SO_4 and NO_3 reduction (Goldhammer and Blodau 2008), these fluxes were a small proportion of total values. Therefore, increased biological production of DOC during rewetting seems unlikely to fully account for the observed increases in DOC concentrations. However, it is worth noting that surface vegetation was absent during the experimental manipulations, therefore DOC production by 'priming' where heterotrophic decomposition is stimulated by inputs of labile plant exudates was excluded (Freeman et al. 2004).

Overall, these data suggest that conflicting results between studies conducted at a similar scale are not solely due to the methodological approach, but could reflect inherent differences in biogeochemical processes operating at each location due to different site characteristics. Therefore, further understanding of various processes operating between specific locations is needed to reconcile reported differences in observations between studies. There is a limit to how far these difference can be reconciled by focusing on process responses at one location, such as comparing blanket peatlands to minerotrophic fens (e.g. Clark et al. 2005; Eimers et al. 2008b; Preston et al. 2011), although these comparisons help to identify key research questions.

While it is clear that decreased stream flows during drought periods will undoubtedly limit the net transport of DOC from soils to surface waters (Eimers et al. 2008b), changes in biogeochemical cycling that occur within peat pore waters due to hydrologically driven changes in soil water chemistry will also affect the short and long-term exchange of carbon from peatlands with both the atmosphere and freshwater systems. As declining acid deposition will decrease the available S and N pool, the severity of drought-induced acidification driven by increased SAA concentrations is likely to decline over time (Tipping et al. 2003). However, our data suggest that where S and N deposition are low, drought-induced acidification can still occur in response to decreased

SBC concentrations. Given the link between acid deposition and changes in *Sphagnum* distribution (Berendse et al. 2001), and the difference in the bioavailability of DOC leachates from different peatland vegetation substrates (Wickland et al. 2007), the interactions between acid deposition and vegetation change could result in substantial variations in the overall DOC responses to drought events between locations due to differences in DOC bioavailability and solubility.

Conclusions

Our re-examination of the relationship between drought-induced acidification and DOC dynamics during simulated droughts events in six peats broadly supported our earlier findings from one peat site—Moor House (Clark 2005; Clark et al. 2006). Peat pore waters consistently showed a decrease in DOC following water table draw-down and an increase in DOC after rewetting. There was no evidence that changes in water volume had a direct influence on altering DOC concentrations, although 'evapoconcentration' of base cations in the most acid impacted peats occurred.

Inverse relationships between increased SO_4 and decreased DOC concentrations were found in all peat cores, although these varied in magnitude between sites. Instead, the relationships between ANC and DOC were more consistent between the different peats. In the most acid impacted peats, ANC decreased because of oxidation of large amounts of S to SO_4 (combined with N to NO_3 in two peats). By contrast, in the least acid impacted peats, ANC decreased because of the decline in base cations. As the ANC takes into consideration differences in both acidifying anions and neutralising base cations between sites, this parameter is therefore a more effective measure of drought-induced acidification between different locations.

Previous analysis of soil water chemistry and soil respiration suggest that decreased DOC could be attributed to both drought-induced acidification of pore water and microbial consumption and respiration. While biotic and abiotic controls could regulate DOC during periods of water table draw-down, the absence of a pulse in soil respiration following rewetting in our study suggest that abiotic chemical controls were the principle cause of rapid increases in DOC and DOC quality following rewetting.

While reduced stream flow ultimately limits DOC transport from soil to surface waters during drought periods (Eimers et al. 2008b), our study highlights the important balance between changes in soil water chemistry and net DOC production/consumption within peat soils that supply DOC to stream waters. Correctly understanding abiotic factors, like chemical and physical processes alongside biotic DOC production and consumption is necessary to enable their inclusion within dynamic peatland C models.

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References

Bell VA, Moore RJ (1999) An elevation-dependent snowmelt model for upland Britain. Hydrol Process 13(12–13): 1887–1903

Berendse F, Van Breemen N, Rydin H, Buttler A, Heijmans M, Hoosbeek MR, Lee JA, Mitchell E, Saarinen T, Vasander H, Wallen B (2001) Raised atmospheric CO_2 levels and increased N deposition cause shifts in plant species composition and production in *Sphagnum* bogs. Glob Change Biol 7(5):591–598

Blodau C, Moore TR (2003) Experimental response of peatland carbon dynamics to a water table fluctuation. Aquat Sci 65(1):47–62

Borken W, Matzner E (2009) Reappraisal of drying and wetting effects on C and N mineralization and fluxes in soils. Glob Change Biol 15(4):808–824

Bottrell S, Coulson J, Spence M, Roworth P, Novak M, Forbes L (2004) Impacts of pollutant loading, climate variability and site management on the surface water quality of a lowland raised bog, Thorne Moors, E. England, UK. Appl Geochem 19(3):413–422

Chapman PJ, Clark JM, Reynolds B, Adamson JK (2008) The influence of organic acids in relation to acid deposition in controlling the acidity of soil and stream waters on a seasonal basis. Environ Pollut 151(1):110–120

CLAG (1994) Critical Loads Advisory Group. Summary report to the Department of Environment, Institute of Terrestrial Ecology, Edinburgh

Clark JM (2005) Environmental controls on the production and export of dissolved organic carbon from an upland peat catchment. PhD Thesis, University of Leeds, UK

Clark JM, Chapman PJ, Adamson JK, Lane SN (2005) Influence of drought-induced acidification on the mobility of dissolved organic carbon in peat soils. Glob Change Biol 11(5):791–809

Clark JM, Chapman PJ, Heathwaite AL, Adamson JK (2006) Suppression of dissolved organic carbon by sulfate induced acidification during simulated droughts. Environ Sci Technol 40(6):1776–1783

Clark JM, Lane SN, Chapman PJ, Adamson JK (2007) Export of dissolved organic carbon from an upland peatland during storm events: implications for flux estimates. J Hydrol 346:438–447

Clark JM, Ashley D, Wagner M, Chapman PJ, Lane SN, Evans CD, Heathwaite AL (2009) Increased temperature sensitivity of net DOC production from ombrotrophic peat due to water table draw-down. Glob Change Biol 15(4): 794–807

Clark JM, Bottrell SH, Evans CD, Monteith DT, Bartlett R, Rose R, Newton RJ, Chapman PJ (2010) The importance of the relationship between scale and process in understanding long-term DOC dynamics. Sci Total Environ 408(13):2768–2775

Clark JM, van der Heijden GMF, Palmer SM, Chapman PJ, Bottrell SH (2011) Variation in the sensitivity of DOC release between different organic soils following H_2SO_4 and sea-salt additions. Eur J Soil Sci 62(2):267–284

Cooper DM (2005) Evidence of sulphur and nitrogen deposition signals at the United Kingdom Waters Monitoring Network sites. Environ Pollut 137(1):41–54

Crawley MJ (2007) The R book. Wiley, Chichester

Dillon PJ, Molot LA (2005) Long-term trends in catchment export and lake retention of dissolved organic carbon, dissolved organic nitrogen, total iron, and total phosphorus: the Dorset, Ontario, study, 1978–1998. J Geophys Res Biogeosci 110(G1):G01002

Donahue WF, Schindler DW, Page SJ, Stainton MP (1998) Acid induced changes in DOC quality in an experimental whole-lake manipulation. Environ Sci Technol 32(19): 2954–2960

Dytham C (2011) Choosing and using statistics: a biologist's guide, 3rd edn. Wiley-Blackwell, Chichester

Eimers MC, Watmough SA, Buttle JM (2008a) Long-term trends in dissolved organic carbon concentration: a cautionary note. Biogeochemistry 87(1):71–81

Eimers MC, Watmough SA, Buttle JM, Dillon PJ (2008b) Examination of the potential relationship between droughts, sulphate and dissolved organic carbon at a wetland-draining stream. Glob Change Biol 14(4):938–948

Evans CD, Freeman C, Monteith DT, Reynolds B, Fenner N (2002) Climate change—terrestrial export of organic carbon—reply. Nature 415(6874):862

Evans CD, Chapman PJ, Clark JM, Monteith DT, Cresser MS (2006) Alternative explanations for rising dissolved organic carbon export from organic soils. Glob Change Biol 12(11):2044–2053

Evans C, Goodale C, Caporn S, Dise N, Emmett B, Fernandez I, Field C, Findlay S, Lovett G, Meesenburg H, Moldan F, Sheppard L (2008) Does elevated nitrogen deposition or ecosystem recovery from acidification drive increased dissolved organic carbon loss from upland soil? A review of evidence from field nitrogen addition experiments. Biogeochemistry 91(1):13–35

Fenner N, Freeman C, Reynolds B (2005) Hydrological effects on the diversity of phenolic degrading bacteria in a peatland: implications for carbon cycling. Soil Biol Biochem 37(7):1277–1287

Freeman C, Lock MA, Reynolds B (1993) Fluxes of CO_2, CH_4 and N_2O from a Welsh peatland following simulation of water-table draw-down-potential feedback to climatic-change. Biogeochemistry 19(1):51–60

Freeman C, Evans CD, Monteith DT, Reynolds B, Fenner N (2001a) Export of organic carbon from peat soils. Nature 412(6849):785

Freeman C, Ostle N, Kang H (2001b) An enzymic 'latch' on a global carbon store—a shortage of oxygen locks up carbon in peatlands by restraining a single enzyme. Nature 409(6817):149

Freeman C, Fenner N, Ostle NJ, Kang H, Dowrick DJ, Reynolds B, Lock MA, Sleep D, Hughes S, Hudson J (2004) Export of dissolved organic carbon from peatlands under elevated carbon dioxide levels. Nature 430(6996):195–198

Glatzel S, Lemke S, Gerold G (2006) Short-term effects of an exceptionally hot and dry summer on decomposition of surface peat in a restored temperate bog. Eur J Soil Biol 42(4):219–229

Goldhammer T, Blodau C (2008) Desiccation and product accumulation constrain heterotrophic anaerobic respiration in peats of an ombrotrophic temperate bog. Soil Biol Biochem 40(8):2007–2015

Gorham E (1991) Northern peatlands: role in the carbon cycle and probable responses to climate warming. Ecol Appl 1: 182–195

Heal OW, Smith RAH (1978) Introduction and site description. In: Heal OW, Perkins DF (eds) Production ecology of British moors and montane grasslands. Springer, Berlin, pp 2–16

Heinemeyer A, Croft S, Garnett MH, Gloor E, Holden J, Lomas MR, Ineson P (2010) The MILLENNIA peat cohort model: predicting past, present and future soil carbon budgets and fluxes under changing climates in peatlands. Clim Res 45:207–226

Hemond HF (1990) Acid neutralizing capacity, alkalinity, and acid-base status of natural-waters containing organic acids. Environ Sci Technol 24(10):1486–1489

Hope D, Billett MF, Cresser MS (1994) A review of the export of carbon in river water—fluxes and processes. Environ Pollut 84(3):301–324

Hruska J, Kram P, McDowell WH, Oulehle F (2009) Increased dissolved organic carbon (DOC) in Central European streams is driven by reductions in ionic strength rather than climate change or decreasing acidity. Environ Sci Technol 43(12):4320–4326

Hughes S, Freeman C, Reynolds B, Hudson JA (1998) The effects of increased drought frequency on sulphate and dissolved organic carbon in peatland dominated catchments. In: Lemmela R, Helenius N (eds) Proceedings of the second international conference on climate and water, vols 1–3, pp 311–319

IPCC (2007) Climate exchange 2007: the physical science basis. Cambridge University Press, Cambridge

Ise T, Dunn AL, Wofsy SC, Moorcroft PR (2008) High sensitivity of peat decomposition to climate change through water-table feedback. Nat Geosci 1(11):763–766

Jager DF, Wilmking M, Kukkonen JVK (2009) The influence of summer seasonal extremes on dissolved organic carbon export from a boreal peatland catchment: evidence from one dry and one wet growing season. Sci Total Environ 407(4):1373–1382

Kalbitz K, Schmerwitz J, Schwesig D, Matzner E (2003) Biodegradation of soil-derived dissolved organic matter as related to its properties. Geoderma 113(3–4):273–291

Knorr KH, Lischeid G, Blodau C (2009) Dynamics of redox processes in a minerotrophic fen exposed to a water table manipulation. Geoderma 153(3–4):379–392

Mitchell G, McDonald AT (1992) Discoloration of water by peat following induced drought and rainfall simulation. Water Res 26(3):321–326

Mulder J, Pijpers M, Christophersen N (1991) Water-flow paths and the spatial-distribution of soils and exchangeable cations in an acid-rain impacted and a pristine catchment in Norway. Water Resour Res 27(11):2919–2928

Neal C, Reynolds B, Robson AJ (1999) Acid neutralisation capacity measurements within natural waters: towards a standardised approach. Sci Total Environ 244:233–241

Pastor J, Solin J, Bridgham SD, Updegraff K, Harth C, Weishampel P, Dewey B (2003) Global warming and the export of dissolved organic carbon from boreal peatlands. Oikos 100(2):380–386

Patrick S, Waters D, Juggins S, Jenkins A (1991) The United Kingdom Acid Waters Monitoring Network: site descriptions and methodology report. ENSIS Ltd., London

Preston MD, Eimers MC, Watmough SA (2011) Effect of moisture and temperature variation on DOC release from a peatland: conflicting results from laboratory, field and historical data analysis. Sci Total Environ 409(7): 1235–1242

Schiff S, Aravena R, Mewhinney E, Elgood R, Warner B, Dillon P, Trumbore S (1998) Precambrian shield wetlands: hydrologic control of the sources and export of dissolved organic matter. Clim Change 40(2):167–188

Schindler DW, Curtis PJ, Bayley SE, Parker BR, Beaty KG, Stainton MP (1997) Climate-induced changes in the dissolved organic carbon budgets of boreal lakes. Biogeochemistry 36(1):9–28

Scott MJ, Jones MN, Woof C, Tipping E (1998) Concentrations and fluxes of dissolved organic carbon in drainage water from an upland peat system. Environ Int 24(5–6): 537–546

Sowerby A, Emmett BA, Williams D, Beier C, Evans CD (2010) The response of dissolved organic carbon (DOC) and the ecosystem carbon balance to experimental drought in a temperate shrubland. Eur J Soil Sci 61(5):697–709

Sparks DL (2003) Environmental soil chemistry. Academic Press, San Diego

Strack M, Waddington JM, Bourbonniere RA, Buckton EL, Shaw K, Whittington P, Price JS (2008) Effect of water table drawdown on peatland dissolved organic carbon export and dynamics. Hydrol Process 22(17):3373–3385

Tallis JH (1994) Pool-and-hummock patterning in a southern Pennine blanket mire. 2. The formation and erosion of the pool system. J Ecol 82(4):789–803

Thacker SA, Tipping E, Gondar D, Baker A (2008) Functional properties of DOM in a stream draining blanket peat. Sci Total Environ 407(1):566–573

Thurman EM (1985) Organic geochemistry of natural waters. Kluwer, Dordrecht

Tipping E, Woof C, Rigg E, Harrison AF, Ineson P, Taylor K, Benham D, Poskitt J, Rowland AP, Bol R, Harkness DD (1999) Climatic influences on the leaching of dissolved organic matter from upland UK Moorland soils, investigated by a field manipulation experiment. Environ Int 25(1):83–95

Tipping E, Smith EJ, Lawlor AJ, Hughes S, Stevens PA (2003) Predicting the release of metals from ombrotrophic peat due to drought-induced acidification. Environ Pollut 123(2): 239–253

Toberman H, Freeman C, Artz RRE, Evans CD, Fenner N (2008) Impeded drainage stimulates extracellular phenol oxidase activity in riparian peat cores. Soil Use Manag 24(4):357–365

Waiser MJ (2006) Relationship between hydrological characteristics and dissolved organic carbon concentration and mass in northern prairie wetlands using a conservative tracer approach. J Geophys Res Biogeosci 111(G2): G02024

Watts CD, Naden PS, Machell J, Banks J (2001) Long term variation in water colour from Yorkshire catchments. Sci Total Environ 278(1–3):57–72

Weishaar JL, Aiken GR, Bergamaschi BA, Fram MS, Fujii R, Mopper K (2003) Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. Environ Sci Technol 37(20):4702–4708

Wickland KP, Neff JC, Aiken GR (2007) Dissolved organic carbon in Alaskan boreal forest: sources, chemical characteristics, and biodegradability. Ecosystems 10(8): 1323–1340

Worrall F, Burt TP (2008) The effect of severe drought on the dissolved organic carbon (DOC) concentration and flux from British rivers. J Hydrol 361(3–4):262–274

Worrall F, Burt T, Shedden R (2003) Long term records of riverine dissolved organic matter. Biogeochemistry 64(2):165–178

Worrall F, Harriman R, Evans CD, Watts CD, Adamson J, Neal C, Tipping E, Burt T, Grieve I, Monteith D, Naden PS, Nisbet T, Reynolds B, Stevens P (2004) Trends in dissolved organic carbon in UK rivers and lakes. Biogeochemistry 70(3):369–402