
Evans, Chris D.; Jones, Tim G.; **Burden, Annette**; **Ostle, Nick**; Zielinski, Piotr; **Cooper, Mark D.A.**; **Peacock, Mike**; Clark, Joanna M.; **Oulehle, Filip**; **Cooper, David**; Freeman, Chris. 2012 Acidity controls on dissolved organic carbon mobility in organic soils. *Global Change Biology*, 18 (11). 3317-3331. 10.1111/j.1365-2486.2012.02794.x

Acidity controls on dissolved organic carbon mobility in organic soils

Running title: Acidity controls on DOC mobility

Chris D. Evans[a*], Tim G. Jones[b], Annette Burden[a], Nick Ostle[c], Piotr Zieliński[b,d], Mark D.A. Cooper[a,b], Mike Peacock[b], Joanna M. Clark[e], Filip Oulehle[a,f], David Cooper[a], Chris Freeman[b]

[a]Centre for Ecology and Hydrology, Environment Centre Wales, Deiniol Road, Bangor, LL57 2UW, UK

[b]School of Biological Sciences, Bangor University, Deiniol Road, Gwynedd, LL57 2UW, UK

[c]Centre for Ecology and Hydrology, Lancaster University, Lancaster, LA1 4AP, UK

[d]Institute of Biology, University of Bialystok, Swierkowa 20B, 15-950 Bialystok, Poland

[e]Soils Research Centre, Department of Geography and Environmental Science, University of Reading, Reading, RG6 6DW, UK

[f]Global Change Research Centre AS CR, v.v.i., Bělidla 986/4a, 603 00 Brno, Czech Republic

*Corresponding author. Email cev@ceh.ac.uk, Tel. +44 1248 374500.

Abstract

Dissolved organic carbon (DOC) concentrations in surface waters have increased across much of Europe and North America, with implications for the terrestrial carbon balance, aquatic ecosystem functioning, water treatment costs and human health. Over the past decade, many hypotheses have been put forward to explain this phenomenon, from changing climate and land-management to eutrophication and acid deposition. Resolution of this debate has been hindered by a reliance on correlative analyses of time-series data, and a lack of robust experimental testing of proposed mechanisms. In a four-year, four-site replicated field experiment involving both acidifying and de-acidifying treatments, we tested the hypothesis that DOC leaching was previously suppressed by high levels of soil acidity in peat and organo-mineral soils, and therefore that observed DOC increases a consequence of decreasing soil acidity. We observed a consistent, positive relationship between DOC and acidity change at all sites. Responses were described by similar hyperbolic relationships between standardised changes in DOC and hydrogen ion concentrations at all sites, suggesting potentially general applicability. These relationships explained a substantial proportion of observed changes in peak DOC concentrations in nearby monitoring streams, and application to a UK-wide upland soil pH dataset suggests that recovery from acidification alone could have led to soil solution DOC increases in the range 46-126% by habitat type since 1978. Our findings raise the possibility that changing soil acidity may have wider impacts on ecosystem carbon balances. Decreasing sulphur deposition may be accelerating terrestrial carbon loss, and returning surface waters to a natural, high-DOC condition.

Introduction

Dissolved organic carbon (DOC) is an integral component of soils and natural waters. It provides the major pathway for carbon transfer from terrestrial to aquatic ecosystems, contributes to heterotrophic processes in streams, lakes and coastal oceans, and provides a significant indirect source of CO_2 emission to the atmosphere (e.g. Cole et al., 2007; Battin et al., 2007; Wehenmeyer et al., 2011; Bianchi, 2011). During the last three decades, DOC concentrations have increased in surface waters draining semi-natural ecosystems in many areas including the United Kingdom (Evans et al., 2005; Worrall & Burt, 2007; Dawson et al., 2008; Chapman et al., 2010), Fennoscandia (Hongve et al., 2004; De Wit et al., 2007; Sarkkola et al., 2009; Arvola et al., 2010), the Baltic States (Pärn and Mander, 2012), Central Europe (Hejzlar et al., 2003; Oulehle & Hruska, 2009), the North-eastern United States (Findlay, 2005; Stoddard et al., 2003; SanClements et al., 2012) and Eastern Canada (e.g. Couture et al., 2011). In the United Kingdom, DOC concentrations have approximately doubled since the 1980s in areas dominated by organic soils (Evans et al., 2005). In the water industry, the high cost of DOC removal, and associated health risks through trihalomethane formation (e.g. Chow et al., 2003), result in it being widely viewed as a pollutant. Changes in DOC export to surface waters also affect aquatic energy supply and light regime (due to the chromophoric properties of organic compounds), with potentially major consequences for the functioning of aquatic ecosystems (Cole et al., 2001; Battin et al., 2009; Karlsson et al., 2010). When first detected, DOC increases were thought to be a consequence of climate change (Freeman et al., 2001; Hejzlar et al., 2003; Worrall & Burt, 2007; Hongve et al., 2004), and thus evidence of ecosystem destabilisation, contributing to terrestrial carbon losses (Bellamy et al., 2005). Some recent studies also suggest high climate-sensitivity of DOC leaching (e.g. Larssen et al., 2011; Fenner & Freeman, 2011). Other studies have linked elevated DOC to land-management factors such as moorland burning (Yallop et al., 2010) and drainage (e.g. Armstrong et al., 2010), or to the eutrophying effects of nitrogen deposition (Findlay, 2005; Pregitzer et al., 2004). Again, these factors all imply a response to ecosystem degradation. However, other research suggests that rising DOC is instead linked to declining acid deposition (Evans et al., 2006a; Monteith et al., 2007). If correct, this would have very different implications, as it implies that acid-sensitive waters are simply recovering towards their high-DOC, pre-industrial state as sulphur deposition declines. Numerous studies have since been published both supporting (e.g. De Wit et al., 2007; Oulehle & Hruska, 2009; Chapman et al., 2010; Arvola et al., 2010; Clark et al., 2011; Ekström et al., 2011; SanClements et al., 2012) and challenging (e.g. Roulet & Moore, 2006; Eimers et al., 2008; Worrall et al., 2008; Clair et al., 2008; Sarkkola et al., 2009; Sarkkola et al., 2009; Zhang et al., 2010; Couture et al., 2011; Löfgren and Zetterberg, 2011; Pärn & Mander, 2012) the hypothesis that rising trends in surface water DOC are due to declining acid deposition. Although attempts have been made to reconcile conflicting arguments by noting the different temporal scales over which climatic and depositional drivers operate (Clark et al., 2010), there remains no overall scientific consensus on the mechanisms controlling DOC leaching. This has, in turn, led to inconsistency and confusion in land-management and water treatment policy in regions where DOC is increasing.

One of the major barriers to resolution of the debate regarding drivers of long-term DOC increase has been the widespread reliance of nearly all of the published studies on long-term monitoring data (Roulet & Moore, 2006). While monitoring has been crucial to the detection of DOC trends, identification of causative relationships from correlative analysis of time series data is problematic, especially since at many sites more than one of the proposed driving variables, namely atmospheric deposition, climate and land-use, have changed over the time-periods for which data are available. A further source of uncertainty in interpreting surface water DOC trends is the relative scarcity, and typically shorter duration, of DOC monitoring data from soils. Soils, in particular shallow organic soil horizons, are the main source of DOC found in most headwater catchments (e.g. Evans et al., 2007), therefore it follows that an increasing trend in surface water DOC should be matched by an increasing trend in soil water DOC concentrations. However, available long-term soil solution data provide a mixed picture; while the majority of studies reporting DOC trends in organic horizons suggest an increase similar to that observed in surface waters (Hruška et al., 2009; Vanguelova et al., 2010; Borken et al., 2011; Stutter et al., 2011), more variable results have been reported for mineral horizons, with evidence of increases at some sites (Hruška et al., 2009; Stutter et al., 2011) but decreases at others (Löfgren et al., 2010; Wu et al., 2010; Borken et al., 2011; Löfgren and Zetterberg, 2011; Stutter et al., 2011). This apparent discrepancy between mineral soil and surface water DOC trends led Löfgren and Zetterberg (2011) to conclude that surface water DOC concentrations must be determined by processes taking place in the riparian zone.

Results from the limited number of acidity manipulations from which DOC responses have been reported are also somewhat equivocal. In the HUMEX catchment-scale acidification experiment in Norway, surface water organic acid concentrations were observed to decrease (Lydersen et al., 1996), as were organic soil solution DOC concentrations (Vogt et al., 1992), but changes in surface water DOC were not detected (Lydersen et al., 1996; Hessen et al., 1997). A catchment-scale ‘clean rain’ experiment at Risdalsheia, Norway, recorded increases in organic acids during recovery from acidification, but no clear change in DOC (Wright, 1989), whilst a similar plot-scale study at Solling, Germany recorded an increase in DOC, along with rising pH, in shallow soil solution (Corre and Lamersdorf, 2004). Ten years after experimental liming of a Swedish forest plot, Nilsson et al. (2001) recorded significantly higher DOC concentrations in the organic horizon and upper mineral soil leachates, but less change at depth. Schindler et al. (1992) recorded DOC decreases in bog pools after experimental acid additions to a bog in Ontario, as well as DOC reductions in a lake that was directly acidified to pH < 5.0. More recently, DOC responses at a number of field nitrogen addition experiments were evaluated, and found to be consistent with treatment-induced acidity changes, rather than nutrient effects (Evans et al., 2008). Ekström et al. (2011) applied sulphuric acid to forest plots in Sweden and observed reductions in organic horizon DOC concentrations, as well as qualitative changes indicative of reduced aromaticity, molecular weight and colour of the leached organic matter.

Here, we present a comprehensive, field experimental test of the hypothesis that DOC leaching was previously suppressed by high levels of acidity, and therefore that recently observed DOC increases are the result of declining acid deposition, based on a four-site, four-year field manipulation study. Parallel, replicated field experiments were established on two different soil types at two locations in the United Kingdom: one peat and one podzol site in a high-deposition area, the Peak District in Northern England; and a second peat and podzol located in a less polluted region, the Migneint in North Wales. Both locations have seen an approximately threefold reduction in sulphur deposition since 1970, whilst DOC concentrations in nearby surface water monitoring sites have increased by a factor of 2.94 (Peak District) and 1.89 (Migneint) since 1989 (see Supplementary Information).

Materials and methods

Sites and experimental design

Four parallel acidity manipulation experiments were established in 2007, at two moorland locations selected to represent major UK upland soil types and contrasting deposition levels. The soil types studied were i) blanket peats (histosols according to the FAO classification; FAO, 2006) which occupy around 13% of the UK land area (JNCC, 2010) in areas of high rainfall and low relief; and ii) peaty podzols (FAO histic podzol), which represent the most extensive organo-mineral soil type in the UK. Organo-mineral soils (i.e. soils with an organic horizon of < 40 cm) generally form in areas of high rainfall and moderate drainage, and occupy around 19% of the UK land area. Together, peats and organo-mineral soils support the large majority of the UK's surviving semi-natural habitat area, and are the dominant soil types in the upland catchments where freshwater DOC concentrations have been observed to increase (e.g. Evans et al., 2005; Worrall et al., 2004), as well as being prevalent in other areas with increasing DOC such as Scandinavia and Northeast North America.

Two experiments were located in the Peak District. This peat-dominated upland area is located close to major industrial centres, and has experienced amongst the highest historic levels of S and N deposition in Europe. Soils and surface waters are strongly acidified (Evans et al., 2000) and nitrogen saturated (Curtis et al., 2005; Helliwell et al., 2007). Two sets of experimental plots were established at around 440m above sea level (1° 54.5' W, 53° 28.3' N) on an area of blanket peat, and on a nearby peaty podzol. The site receives a mean annual rainfall of 1.0 m and has an average annual temperature of 8 °C. Non-marine S deposition (estimated from 5km gridded CEH Edinburgh moorland deposition data for 2006-08, adjusted for on-site wet deposition measurements over the same period) is estimated at around 26 kg S ha^{-1} yr^{-1}. Deposition estimates from the FRAME model (Dore et al., 2007) suggest that S deposition decreased by 69% between 1970 and 2005. Surface water monitoring data from the River Etherow Acid Waters Monitoring Network (AWMN) catchment, which is located 6 km from the experimental site (Evans et al., 2006a; Supplementary Figure S1) show a 194% increase in annual mean DOC concentrations over the 1989-2009 period. The deep peat experimental site is covered by a degraded vegetation of Eriophorum vaginatum, Calluna vulgaris and Vaccinium myrtillus; Sphagnum mosses are largely absent from the area, thought to be the result of historic S pollution (Tallis, 1987). Mean peat depth across the site is 2.3 m and the mean measured water table depth over the experimental period was 13 cm. The podzol site has a 5-8 cm organic horizon, overlying a 20-40 cm sandy E horizon and stony B horizon. Vegetation is mainly Festuca Ovina and Vaccinium myrtillus.

A second set of experiments were established on the Migneint, an extensive blanket peat in relatively good condition located in North Wales. Again, two sets of manipulation plots were established, on adjacent peats and peaty podzol sites (3° 48.8' W, 52° 59.6' N). This area has received somewhat lower historic levels of S and N deposition, although significant acidification is thought to have occurred (Evans et al., 2006b). Annual rainfall is 2.4 m, and present-day S deposition is 15 kg S ha^{-1} yr^{-1}. FRAME modelled estimates suggest that S deposition decreased by 66% between 1970 and 2007. Surface water monitoring data from the nearby Llyn Llagi AWMN site record an 89% increase in annual mean DOC concentrations between 1989 and 2009 (Supplementary Figure S1b). At the Afon Gwy AWMN site, 50 km to the south, DOC has increased by 51% over the same period

(Supplementary Figure S1c). The Migneint peat experimental site, at 460 m a.s.l., is dominated by Calluna vulgaris, with Eriophorum Vaginatum above a deep Sphagnum layer. The mean peat depth across the site is 2.0 m and mean water table depth during the study period was 9 cm. The podzol site was established on a small hill emerging from the blanket bog, at 486 m a.s.l. At this site a peaty organic horizon of 5-18 cm depth overlies shallow, stony E and B horizons over bedrock. Vegetation is dominated by the graminoids Juncus squarrosus and Festuca ovina, with some Galium saxatile, and mosses including Polytrichum commune and Pleurozium shreberii.

Experimental design and operation

At each of the four experimental sites, soil acidity was manipulated for more than three years by regular addition of acid and alkaline treatment solutions. At each experiment, twelve 3x3 m plots were assigned to control, acid and alkaline treatments in a randomised blocked design, giving four replicates per treatment. All plots were established in August 2007, and treatments began in April 2008 following a period of pre-treatment measurements. Acid treatments comprised 4-weekly additions of sulphuric acid (H_2SO_4), mixed with ambient rainwater collected at each site and applied evenly across the plots using watering cans in 20 l of water, followed by a 10 l 'rinse' with ambient rainwater to ensure that the treatment solution entered the soil, and to minimise any direct effects on the vegetation. The initial annual treatment dose was 25 kg S ha^{-1} yr^{-1}, while the additional water addition (3.3 l m^{-2} per treatment application, or 43 mm yr^{-1}). was equivalent to 1.8% of average annual rainfall at the Migneint, and 4.3% at the Peak District sites. In January 2009, after no detrimental impacts on vegetation had been observed in the 2008 growing season, the treatment was increased to 50 kg S ha^{-1} yr^{-1} (SO_4 concentration in solution 7.2 meq l^{-1}), and in September 2009 the dosage at the peat plots was increased to 100 kg S ha^{-1} yr^{-1} (SO_4 concentration in solution 14.4

meq l^{-1}). Dosages were increased to ensure a measurable pH change within the duration of the experiment, with a higher dose found to be required at the peat plots due to SO_4reduction. We emphasise that the aim of the experiment was to evaluate DOC responses to a pH change, rather than the response to a specific S application rate, and that acidification (and its reversal) represent gradual responses to a cumulative deposition dose. Thus, the increases in dosage (having first ensured that direct toxicity to vegetation was not occurring) represented an acceleration of the experiment rather than a change in design. The maximum, 100 kg S ha^{-1} yr^{-1} treatment level applied is of a similar order to ambient sulphur deposition in the Peak District during the 1970s, and thus within a realistic environmental range for the ecosystems studied. Alkaline treatments comprised additions of sodium hydroxide (NaOH) and magnesium chloride ($MgCl_2$), intended to obtain a molar OH^- concentration equivalent to the H^+ concentration in the acid treatments, and a Na/Mg ratio similar to sea-salt. Alkaline dosages were increased in parallel to those in the acid treatments, and all treatment rates remained constant during the last two full years, 2010 to 2011 (total base cation concentrations in treatment solution 7.2 meq l^{-1} and 14.4 meq l^{-1} to podzol and peat sites respectively).

Soil solution sampling and analysis

Measurements were made 4-weekly, immediately before the treatments were applied (i.e. 4 weeks after the preceding treatment). This ensured that measured changes reflected a sustained alteration to plot pH, rather than a transient response to treatment application. Soil-water samples were collected using Rhizon® suction samplers (Van Walt Ltd.), comprising 10 cm long, 2.5 mm diameter porous membranes attached to 20 ml syringes, which were used to apply suction and collect samples. Four samplers were inserted diagonally into the surface organic horizon of each plot, at the start of the study, and samples were collected by applying suction overnight, and bulking samples the following morning to give one composite sample per plot. Samples were stored at 4°C and within 24 hours they were analysed for pH using an Orion 720A pH meter. The remaining sample was filtered using pre-rinsed 0.45 μm cellulose acetate syringe filters, and DOC analysed with a Thermalox 5001.03 (Analytical Sciences Limited) carbon analyser using the Non-Purgable Organic Carbon (NPOC) method, whereby samples were acidified to pH 2.0 and purged with oxygen to drive off any inorganic carbon prior to analysis for total carbon.

Data analysis

After testing the data for normal distribution and equal variance, pH and DOC data were analysed for the pre-treatment period (August 2007 to April 2008) and for each full year of manipulation data (i.e. 2009, 2010 and 2011) using linear mixed effects models (lme) analysed by ANOVA using R version 2.12.1 as lme(DOC~treatment*date, random = ~1|plot) for each of the four experimental sites and for each time period. This approach was used to enable the raw data to be analysed accounting for replication at the level of the experimental unit, or plot (n = 12). The four sites were then combined within a linear mixed effects model as (schematically) lme(DOC~site_soil+treatment, random = ~1|fullplot), again analysed for the four time periods, with location indicating the four site/soil combinations. This analysis provides estimates of treatment differences and also, in principle, soil differences. However, the test for soil differences ($F_{1,1}$) is very weak and does not lead to the rejection of the hypothesis of no difference between peat and podzol (i.e. $p > 0.05$) for either pH or DOC for any period. The site effect (Peak District vs Migneint) is treated as random in the model.

The four experimental sites had different characteristic DOC concentrations and acidity levels (control plot mean DOC range 25-58 mg l^{-1}, pH range 3.9 to 4.4). In addition, the Peak District peat and Migneint podzol sites exhibited some pre-treatment differences in mean DOC concentrations between control and treatment plots (Figure 1, Table 1). To explore underlying relationships between DOC and pH change, we therefore standardised DOC concentrations by dividing mean DOC for each treatment at each site and sampling interval by the corresponding pre-treatment mean. Deviation from this initial level due to treatment was quantified as the ratio of mean standardised

DOC concentrations from the treatment and control plots, calculated for each sample set collected. The resulting ratio can be considered an estimate proportional change in DOC due to treatment, corrected for pre-treatment differences, and expressed (as change relative to control) as:

$$\mathrm{RDOC_{std}t} = \frac{\mathrm{DOCt_{treatment}} \times \mathrm{DOCpre_{control}}}{\mathrm{DOCt_{\,control}} \times \mathrm{DOCpre_{treatment}}} \qquad (1)$$

Where $DOCt_x$ is the mean DOC concentration for the treatment or control plots at time t, and $DOCpre_x$ is the corresponding pre-treatment mean concentration. This definition is conceptually similar to the %ΔDOC term previously used to compare proportional DOC changes across long-term monitoring sites and experimental mesocosms with differing initial DOC concentrations, in order to detect effects of changing sulphur deposition across a range of contrasting monitoring sites or experimental mesocosms (Monteith et al., 2007; Clark et al., 2011). The standardised ratio of treatment/control change in hydrogen ion concentration (RH_{std}) was calculated using an identical procedure.

Relationships between DOC and acidity change at each experiment were evaluated by plotting $RDOC_{std}$ against RH_{std}, and fitting a hyperbolic function of the form:

$$\mathrm{RDOC_{std}} = \frac{}{(\mathrm{RH_{std}})^{\mathrm{b}}} \qquad (2)$$

Where the parameter b is fitted to the data. This function was used because i) results showed apparently non-linear relationships between $RDOC_{std}$ and RH_{std}; ii) it passes through the point $RDOC_{std} = 1$, $RH_{std} = 1$ (i.e. no experimentally induced change in DOC where there was no change in acidity); and iii) it is reversible, i.e. an increase in H concentration from X to Y, followed by a decrease from Y to X, will return DOC concentration to its initial value, regardless of the value of b (this would not be the case, for example, if a linear fit were applied). The exponent b was fitted to the data using the Microsoft Excel Solver function to minimise the sum of squared errors, multiplied by a weighting factor equal to $1/(RDOC_{std})^2$. This weighting factor was found to result in an improved fit to the larger treatment-induced changes in $RDOC_{std}$ associated with the most acidic samples from the acid treatment plots.

Estimation of long-term change in organic soil DOC concentrations

Experimentally observed relationships between $RDOC_{std}$ and RH_{std} were used to estimate the magnitude of organic horizon DOC change that could be accounted for by observed changes in organic soil pH, for comparable soils at larger scales. Relationships were applied first to data from two nearby long-term monitoring streams: the River Etherow in the Peak District, and the Afon Gwy in Wales (See above, Supplementary Material). For these upland streams, which both drain peat and podzolic soils comparable to the experimental sites, runoff chemistry approaches that of the upper organic horizon during high flow conditions, at which time acidity and DOC concentrations tend to be highest (e.g. Hinton et al, 1997; Hood et al., 2006; Austnes et al., 2009; Raymond et al., 2010). Therefore, near-surface organic soil solution DOC and H concentrations were inferred from the 90th percentile stream concentrations for two five year periods at the beginning and end of monitoring, namely 1989-1994 and 2005-2009. The change in observed hydrogen ion concentrations between the two periods was used to calculate RH_{std}, with the first period treated as the ‘control’ and the second as the ‘treatment’, and relationships obtained from the experiments in the respective regions used to predict $RDOC_{std}$, and thereby the predicted percentage change in organic horizon DOC concentrations over the monitoring period. These results were compared to the observed change in 90th percentile DOC concentrations at the two streams.

Second, to provide estimates of the magnitude of DOC change potentially associated with recovery from acidification in comparable soils at a UK scale, we analysed data from the UK Countryside Survey (CS, Emmett et al., 2010), in which the pH of ‘topsoil’ (0-15 cm) samples was measured in 1978, and again in 2007, in both cases using a slurry with a 1:2.5 soil:water ratio by weight. An analysis of parallel measurements of mean soil water and soil-water slurry pH at a set of 18 UK monitoring sites (F. Oulehle, unpublished data) showed a 1:1 relationship between the two pH measurements ($R^2 = 0.75$), suggesting that one pH measure could reasonably be used as a proxy for the other. We estimated changes in soil water DOC concentrations in unforested semi-natural habitats that characteristically occur on acidic peat or organo-mineral soils (i.e. those considered reasonably comparable to the experimental sites in terms of vegetation, soil type and acidity), using data from the CS Bog, Dwarf Shrub Heath, Acid Grass and Bracken broad habitat categories. All habitats showed an increase in mean pH between the two surveys, and these mean values were used to calculate RH_{std} as above, and to predict mean percentage increase in DOC concentration by habitat class using the $RDOC_{std}$ - RH_{std} relationships obtained from the experiments, using data from the most appropriate soil type. Thus, predictions for Acid Grass and Bracken were based on the combined podzol data, and predictions for Bog on the combined peat data. Dwarf Shrub Heath occurs on both peats and podzols, and predictions for this habitat were therefore based on the full set of experimental data.

Results

Four-weekly experimental additions of acidic (sulphuric acid) and alkaline (sodium hydroxide) solutions led to changes in soil water pH at all four sites (Figure 1a-d). The magnitude of re-acidification due to acid addition ranged from a pH reduction of 0.06 units at the Migneint peat to 0.20 units at the Peak District peat (based on 2010-11 means). Alkali additions led to only a marginal pH increase at the Migneint peat (0.03 units), while increases ranged from 0.07 to 0.29 units at the other sites. DOC responses to pH manipulations were consistent for both soils at both sites (Figure 1e-h). In all experiments, 2010-11 mean DOC was lower in the acid treatments than in the controls, and it was higher in all alkaline treatments except for the Migneint peat, where the absence of a DOC change coincided with the very small treatment-induced pH change. Analysis of variance revealed significant ($p < 0.05$) treatment effects on pH at all sites except the Migneint peat by 2010, and for all four sites by 2011. For DOC, significant differences were observed between treatments for the two Peak District sites in 2010, and additionally for the Migneint podzol site in 2011 (Table 1).

Inherent natural background differences in DOC concentrations during the pre-treatment period slightly obscured treatment responses at some sites, notably the Peak District peat where pre-treatment DOC was apparently higher in the 'acid' plots, a pattern which had completely reversed by 2010 (Figure 1d). The effect of treatment on pH for the combined dataset was highly significant ($p < 0.001$) in all three treatment years, and separate analysis of the acid and alkaline treatments also revealed significant pH responses to each treatment across the four-site dataset in each treatment year. The effect of treatment on DOC for the combined dataset was also significant ($p \leq 0.002$) in all three treatment years, while the individual acid treatments showed a significant DOC response in 2010 and 2011, and the alkaline treatments from 2009 to 2011 (Table 1).

Ratios of treatment/control standardised DOC and hydrogen ion concentration, $RDOC_{std}$ and RH_{std}, were computed for all samples collected during 2009-2011. Plots of $RDOC_{std}$ versus RH_{std}, combining acid and alkaline treatment data, reveal a strong, negative and non-linear relationship between treatment-induced acidity and DOC changes for each of the four experimental sites (Figure 2, Table 2). The hyperbolic function $RDOC_{std} = 1/(RH_{std}{}^{b})$ was fitted to each individual experimental dataset, to data merged by region and soil type (Supplementary Figure S2, Table 2), and to the full dataset (Figure 3, Table 2). All relationships were significant at $p < 0.001$; R^2 values for predicted versus observed $RDOC_{std}$ ranged from 0.14 to 0.60. Relationships across the four sites remained significant if the acid and alkaline treatments were considered separately. As would be expected from the ANOVA results, the DOC-H relationship was weakest at the Migneint peat site, where little treatment-induced acidity change occurred. Fitted values for the coefficient b were largest at the Peak District sites, where the strength of the DOC-H relationship was also greatest.

At the Migneint podzol site, a large group of apparent outliers were observed for the alkaline treatment, in which DOC differed little from the controls despite treatment-induced reductions in acidity (circled area of Figure 2d). This site had the highest pre-treatment pH of those studied, and showed the largest pH increase in response to alkaline treatment (Figure 1). For samples from this treatment, we noted a significant, positive relationship in the residual of predicted versus observed DOC concentrations (based on the best-fit relationship shown in Figure 2d), and mean measured pH (R^2 = 0.20, p = 0.006). Above pH 4.63, all residuals were positive. In other words, the relationship between $RDOC_{std}$ and RH_{std} observed for the remainder of the data at this site, and at all other sites, appeared to break down at the highest recorded pH values; possible reasons for this are discussed below. To assess the influence of these samples on results, we re-analysed the Migneint podzol dataset based on the acid treatment data only, and also re-analysed the combined Migneint, podzol and full datasets with the Migneint podzol alkaline treatment data excluded (Table 2; dashed best fit lines in Figures 2, 3 and S2). In all cases, excluding these data strengthened the relationship between $RDOC_{std}$ and RH_{std} for the remaining data, and gave higher (and convergent) values of the coefficient b.

The observed relationships between $RDOC_{std}$ and RH_{std} from the experiments were used to estimate the amount of DOC change that could be accounted for by changing acidity for i) nearby stream monitoring sites, and ii) UK-wide soil pH chemistry data from the Countryside Survey (Emmett et al., 2010). For the streams, as described above, changes in 90th percentile stream H and DOC concentrations were assumed to reflect changes in acid, high-DOC runoff from surface organic horizons, comparable to the data from the experimental sites. Results suggest that reductions in organic soil acidity could account for 48% of the observed high flow DOC increase at the Peak District monitoring stream (based on combined Peak District dataset), and 51-94% of the (smaller) high flow DOC increases at the Welsh site (Figure 4; lower estimate based on full Migneint dataset, higher estimate on Migneint dataset with podzol alkaline treatment data omitted). Scaling predictions up to a national level, based on Countryside Survey data, we estimate that soil pH increases observed since 1978 could have generated average DOC increases of 46% to 126% in habitat types similar to our experimental sites (Figure 5).

Discussion

At all sites except the Migneint peat, our acidity manipulations generated a pH range of at least 0.3 units (comparing 2011 means for acid and alkaline treatments at each site), equating to a hydrogen ion concentration range of 50 – 110 μeq l^{-1}. This magnitude of treatment-induced change in soil solution acidity is comparable to recorded pH increases in the range 0.2 to 0.5 units recorded between 1978 and 2007 at the analogous Countryside Survey broad habitats (Figure 5). Our results suggest that DOC concentrations in organic soil porewaters were strongly, and consistently, sensitive to these acidity changes. In the strongly acidified Peak District region, DOC responded to both acid and alkaline manipulations, with the alkaline treatments leading to particularly large increases in DOC in both the peat and podzol plots (Figure 1a-b, e-f). DOC decreases in the acid treatments were smaller, particularly in the peat plots, suggesting that further pH reductions in these already highly acidic organic soils (pre-treatment pH 3.9 to 4.0) may have a limited additional impact on DOC leaching. This interpretation is supported by measurements on a subset of samples (Oulehle et al., in prep.) indicating that organic acids are mostly protonated at these low pH levels, and thus that there is limited scope for further suppression of organic matter solubility. On the other hand, at the Migneint podzol site, with a much higher pre-treatment pH of 4.4, the acid treatment led to strong reductions in DOC concentrations (Figure 1c,g), whereas further pH increases in the alkaline treatment generated only a slight additional increase in DOC concentrations. Collectively, these results suggest a peak sensitivity of DOC leaching to pH in the approximate range 4.0 to 4.5, close to the typical average dissociation constant (pKa) value of carboxyl functional groups in bulk samples of organic rich acid waters (e.g. Hruška et al., 2003, Kortelainen et al., 1992). At pKa = pH, 50% of carboxyl functional groups are dissociated, and small changes in pH are likely to lead to large changes in dissociation.

The apparently decreasing sensitivity of DOC concentration to further pH increases at the Migneint podzol site is consistent with this physico-chemical control on DOC leaching, and may explain the divergence of samples with pH > 4.6 (all from the alkaline treatment) from the $RDOC_{std}$ versus RH_{std} curve observed for the remainder of the dataset (Figure 2d). This site also had the lowest organic horizon carbon content, and highest graminoid cover, of the four experimental sites studied; it is therefore also possible that, at the high pH levels obtained in the alkaline treatment, the rate of DOC production may have becoming limiting for porewater DOC concentrations, rather than subsequent pH-dependent solubility. Indeed, the large treatment-induced pH increases observed in the Migneint alkaline treatment can in part be attributed to the exhaustion of buffering by organic acids. This hypothesised shift from 'solubility controlled' to 'supply controlled' DOC leaching would, if correct, have implications for both the spatial extent and future trajectory of DOC trends. For example, as DOC leaching becomes less restricted by soil acidity, it may become more sensitive to processes influencing DOC production, such as climate and land-management.

At the Migneint peat site, the non-significant DOC response is largely attributable to the comparatively weak response of pH to the treatment at this site, rather than a lack of DOC response to acidity change per se. The Migneint peat receives lower ambient deposition than the Peak District peat, and has higher rainfall and a higher mean water table, all of which would favour greater retention of applied SO_4 in the acid treatments, and of base cations in alkaline treatments. Treatment-induced acidification at this site was largely observed during dry periods, when S retained due to SO_4 reduction was re-oxidised and leached, leading to transient periods of higher acidity, which were also associated with lower DOC concentrations relative to controls. However, these transient treatment responses were insufficient to generate significant changes in mean pore water chemistry.

Normalising the treatment data as RH_{std} and $RDOC_{std}$ revealed that, to a large extent, DOC leaching responses to acidity change were fundamentally similar among sites and over time. There is some evidence, based on the larger fitted 'b' coefficient values in the hyperbolic $RDOC_{std}$-RH_{std} relationships for individual sites, that the Peak District soils are more sensitive to acidity change than those of the Migneint. This would be consistent with laboratory experiments on peat cores collected from the same areas (Clark et al., 2011), and with the greater observed DOC increases in Peak District surface waters compared to those in Wales generally (Figure 5, S1). On the other hand, the 'b' value obtained from the acid plots alone at the Migneint podzol site (-0.871) is similar to that obtained from the full Peak District dataset (-0.794), suggesting that more acidic soils (i.e. those with pH < 4.6) may behave similarly in different locations, and therefore that a reasonably generic overall relationship may exist between acidity change and DOC change in organic soils across larger spatial scales. Taking the fitted b value of -0.540 for the entire experimental dataset, we estimate that a 0.3 unit increase in pH (equivalent to a halving of hydrogen ion concentrations) would lead to a 45% increase in DOC concentrations. Excluding data from the Migneint podzol alkaline treatment (b = -0.753) gives a predicted DOC increase of 68%. On the same basis, the pH increase required to double DOC concentrations would be 0.56 units based on the full dataset, or 0.40 units with the Migneint podzol alkaline treatment data excluded.

Applying our experimental results to observations of long-term pH change in UK soils and surface waters (Figures 4-5) suggests that reductions in acid deposition, and subsequently observed pH increases, may be sufficient to explain a large proportion of the observed increase in surface water DOC concentrations. The range of predicted DOC increases for the acidic upland habitat classes of the Countryside Survey (46-126%) is of the same order as observed (mean 91%) DOC increases in UK surface waters (Evans et al., 2005), albeit over a longer time period (1978-2007 versus 1988-2007). Since the Countryside Survey encompasses the entire UK, including remote areas such as Northwest Scotland that were not subject to significant acidification, it is likely that pH changes in more deposition-impacted areas (including our study sites) significantly exceeded the national means reported, and that acidity reductions thus generated larger DOC increases in these regions. The comparatively small predicted DOC increase for bogs appears to reflect the extent to which pH change in peats has been buffered by other processes such as sulphate (SO_4) reduction (as in the Migneint peat experiment), and the relatively high proportion of the total UK bog area located in less pollution-impacted north-western areas. On the other hand, there is some recent evidence that acidification of peatlands in the UK was at least partly caused by deposition of hydrochloric acid which, unlike sulphuric acid, remains mobile under the reducing conditions associated with waterlogged peats (Evans et al., 2011). Clark et al (2011) showed that laboratory additions of chloride, even as neutral sea-salt, could have a similar effect on peat porewater pH and DOC concentrations to sulphuric acid. This would potentially enhance the magnitude of pH (and therefore DOC) change in areas of high SO_4retention such as the Migneint peat plots.

To our knowledge, relationships between DOC trends and acidity have only previously been inferred from long-term monitoring data (e.g. Monteith et al., 2007), laboratory experiments (Clark et al., 2011), indirect interpretation of results from field N addition experiments (Evans et al., 2008), and from the acidification experiment by Ekström et al. (2011). As noted earlier, monitoring data are susceptible to differing interpretations under conditions where multiple environmental changes are occurring simultaneously, whereas experiments are limited by the need to obtain measurable ecosystem responses during comparatively short manipulation periods, and the accompanying risks of experimental artefacts. By combining monitoring, laboratory and field experimental data, the limitations of each method are to some extent overcome, and the consistent results obtained provide overall support for the hypothesis that DOC increases are attributable to declining acid deposition. The general consistency of our findings (over time at individual sites, for both acid and alkaline treatments, and between four sites with differing soils, vegetation, ambient deposition and acidity), as well as the rapidity of DOC response to pH change, appear best explained by a direct, physico-chemical mechanistic influence of acidity on organic matter solubility. This interpretation is supported by earlier laboratory experiments (e.g. Vance & David, 1989; Tipping and Woof, 1989; Lofts et al., 2001), which derived relationships between DOC and acidity in soil cores, across wide pH ranges. Our data demonstrate that such relationships also operate under vegetated, field conditions, and across the pH range (approximately 3.8 to 4.6) within which much of the observed change in UK upland soil acidity during the last 30 years has taken place (e.g. Emmett et al., 2010; Kirk et al., 2010).

While our results thus point towards a physico-chemical control of DOC leaching from organic soils by acidity (and therefore, indirectly, by acid deposition), several areas of uncertainty remain. Firstly, there are several related physico-chemical mechanisms linked to deposition change that could affect DOC leaching; in addition to acidity, organic matter solubility may also be influenced by ionic strength, complexation with specific metal ions such as aluminium, and anion adsorption. Aluminium (Al) complexation can largely be discounted in ombrotrophic peat where Al concentrations are low, but may be significant in some organo-mineral soils or in peats receiving some lateral water inputs from mineral soils (Clark et al., 2011), and along with anion adsorption may be important in underlying mineral horizons (see below). Mean measured Al concentrations on three sets of samples collected during 2011 were below 2 μmol l^{-1} at both Migneint sites, but somewhat higher at the Peak District sites (6.3 and 11.5 μmol l^{-1} in the podzol and peat sites respectively). Higher Al concentrations in the Peak District sites could help to explain their greater observed sensitivity to acidity manipulation, as suggested by Clark et al. (2011). Ionic strength has been invoked as the main driver of rising DOC trends by Hruška et al. (2009), but in studies of the effects of ambient deposition change it is difficult to distinguish between acidity and ionic strength effects, because the two generally co-vary. It is also difficult to apply a treatment of either acidity or ionic strength without affecting the other, even under controlled laboratory experiments; in the simple laboratory experiments of Clark et al. (2011), addition of H_2SO_4 increased ionic strength in solution, whilst addition of neutral 'seasalt' caused a decrease in solution pH due to displacement of soil exchangeable hydrogen ions by Na and Mg. Our alkaline treatment offers some insight into the relative role of acidity versus ionic strength, as it increased the solute load but simultaneously reduced acidity. The observation that DOC generally increased under the alkaline treatments despite increases in measured ionic strength at all four sites suggests that the acidity effect dominates (Oulehle et al., in prep.). Nevertheless, we cannot exclude the possibility of an ionic strength effect, which could help to explain why overall DOC responses to the acid treatment (in which acidity and ionic strength would have had been reinforcing) appeared somewhat stronger than DOC responses to the alkaline treatments (in which the two effects would have would have been opposing) (Figures 2-3). If this were the case, the empirical relationships obtained from the experiments may under-estimate the magnitude of DOC change due to reduced acid deposition.

In this study, we have focused on quantitative changes in DOC concentration, but qualitative changes in dissolved organic matter composition may also have important consequences, for example in relation to water colour and drinking water treatment. Other studies have demonstrated compositional changes in DOM alongside rising DOC trends in long-term surface water datasets (e.g. De Wit et al., 2007; Dawson et al, 2009) and in response to field and laboratory experimental acidity manipulations (Clark et al., 2011; Ekström et al., 2011), with which results from our experimental study appear consistent (Oulehle et al., in prep.). The inference from the Migneint podzol site that DOC-pH relationships may break down at higher pH values, or that limitations to DOC supply may begin to outweigh controls on solubility, requires further investigation. Similarly, our study focused only on organic soil horizons, whereas controls on organic matter solubility within mineral soils, associated with adsorption and binding to mineral surfaces, and interactions with metal ions such as aluminium and iron, may lead to more complex responses (e.g. Zech et al., 1994; Kalbitz et al., 2000; Lofts et al., 2001; Löfgren et al., 2010; Mikkuta & Kaiser, 2011). These interactions may help to explain the more heterogeneous, and in some cases divergent, DOC trends observed in monitoring data from mineral soils, noted earlier. In particular, competition for anion adsorption sites between SO_4 and DOC appears to explain decreasing DOC trends in more weathered, iron-rich mineral horizons (e.g. Borken et al., 2011; Wu et al., 2010), a conclusion supported by results from the Solling field experiment in Germany, where $(NH_4)_2SO_4$ additions led to large DOC reductions in the mineral soil (Evans et al., 2008). In the more organic soils of the UK uplands, on the other hand, SO_4 adsorption capacity is relatively low, and competition between SO_4 and DOC for adsorption sites appears limited (Hughes et al., 2012). In these soils, the effects of acid deposition on DOC leaching may even be amplified by passage through mineral horizons, due to the strong negative effect of Al mobilisation on DOC solubility (Kennedy et al., 1996; Lofts et al., 2001; Chapman et al., 2010). Because Al solubility declines above pH 4.6-4.9 (Nordstrom & Ball, 1987), its effect on DOC solubility in mineral soils may diminish over a similar pH range to the decrease in direct pH effects on DOC solubility in the organic horizon, as inferred from the Migneint podzol data. Although UK soil solution time series data remain insufficient to draw firm conclusions on organic versus mineral horizon trends, our results do not suggest that there is necessarily a disconnection between DOC changes in organic soils and DOC changes in surface waters.

Finally, while our data support a physico-chemical control on DOC mobility, it seems likely that this may be reinforced, over longer periods, by the effects of biologically-mediated responses to pH change. Many aspects of soil biological activity, including microbial abundance and activity, decomposition rates and enzyme activity have all been shown to be constrained by low pH (e.g. Baath et al., 1980; Fierer and Jackson, 2006; Sinsabaugh, 2011; Oulehle et al., 2011), therefore a change in DOC production due to pH change might be expected. During the experiment, we made regular measurements of a number of indicators of soil biological activity, including soil enzyme activities and soil CO_2 respiration, but were unable to detect any treatment effects (T. Jones, unpublished data). At this stage, therefore, we have to attribute observed DOC responses to physico-chemical factors, but do not rule out a more gradual biological response. Longer-term experimental manipulation studies and monitoring of DOC production processes will be required to elucidate this further.

Overall, based on our results, we conclude that decreasing acid deposition represents a highly plausible driver of the surface water DOC increases observed across many areas. While we would caution against extrapolating results too far from the moorland areas of the UK in which the experiments were undertaken, we note that the soil types they represent, histosols and podzols, occupy substantial areas of Northern and Central Europe, and of Northeast North America, namely those regions in which rising trends in DOC have been recorded. We recognise that our results do not preclude the influence of climatic factors such as discharge, temperature and solar radiation, and indeed there is little doubt that these affect episodic, seasonal, and inter-annual variations, as has been demonstrated in many previous studies (e.g. Erlandsson et al., 2008; Sarkkola et al., 2009; Zhang et al., 2010; Clark et al., 2010). In areas not subject to historic acid deposition these drivers may dominate DOC variability, and where they exhibit long-term changes, factors such as climate may also have led to observed changes in DOC (e.g. Schindler et al., 1997; Striegl et al., 2005) or may be expected to do so in the future (Larssen et al., 2011). Similarly, land-use factors may contribute to spatial DOC variations and, in cases where land-use has changed, to long-term trends. On the other hand, few if any of these drivers have exhibited consistent long-term changes over the last 20-30 years, across the full area over which DOC has increased. Based on our results, we do not believe that it is necessary to invoke these additional factors in order to explain the general magnitude and spatial extent of rising DOC trends that have been observed to date (almost exclusively) in areas historically affected by acid deposition (Monteith et al., 2007). The often-cited view that there has been no universal driver of rising DOC trends (e.g. Roulet & Moore, 2007; Zhang et al., 2010; Preston et al., 2011), despite their consistency across large areas, must therefore be open to question.

The observed sensitivity of DOC leaching to pH also raises wider questions about the importance of acidity to other aspects of the carbon cycle. Previous studies have suggested that acidity changes may have contributed to observed soil carbon changes in the UK (Evans et al., 2007; Emmett et al., 2010). Experimental liming studies have shown increased soil respiration, enhanced microbial activity and long-term changes in the distribution of soil C, concurrent with pH and DOC increases (Nilsson et al., 2001; Andersson and Nilsson 2001), while methanogenesis may also be sensitive to pH change (Ye et al., 2012). Recent measurements suggest that decreased acid deposition loadings may have caused a 40% loss of organic horizon carbon at a Czech forest monitoring plot (Oulehle et al., 2011). Acidity dynamics are rarely incorporated in carbon models, or considered as a driver of change in carbon fluxes, yet many of the measurements from which process understanding and models have been developed and tested have taken place in Europe and North America against a background of dramatically changing sulphur deposition. Further work is required to establish the impacts of changing soil acidity on the wider carbon cycle, and to ensure that observed changes in terrestrial carbon cycling, particularly those based on measurements in industrialised regions, are not erroneously attributed to other drivers.

ACKNOWLEDGEMENTS

This research was funded by the UK Natural Environment Research Council, Grant No. NE/E011837/1, with additional support for the Peak District experiments from the Department of Environment, Food and Rural Affairs (Contract No. AQ0803). We are grateful to all who supported the fieldwork, notably James Hall, Adriana Raveau and Jacky Teshome, to Don Monteith and Ed Tipping for discussions and advice on data interpretation, and to two anonymous reviewers for their constructive comments.

References

Andersson S, Nilsson SI (2001) Influence of pH and temperature on microbial activity,substrate availability of soil-solution bacteria and leaching of dissolved organic carbon in a mor humus. Soil Biol. Biochem. 33: 1181-1191.

Armstrong A, Holden J, Kay P et al. (2010) The impact of peatland drain-blocking on dissolved organic carbon loss and discolouration of water; results from a national survey. J. Hydrol. 381: 112-120.

Arvola L, Rask M, Ruuhijärvi J, Tulonen T, Vuorenmaa J, Ruoho-Airola T, Tulonen J (2010) Long-term patterns in pH and colour in small acidic boreal lakes of varying hydrological and landscape settings. Biogeochemistry 101: 269-279.

Austnes K, Evans CD, Eliot-Laize C, Naden PS, Old GH (2009). Effects of storm events on mobilisation and in-stream processing of dissolved organic matter (DOM) in a Welsh peatland catchment. Biogeochemistry 99: 157-173.

Baath E, Berg B, Lohm U et al. (1980) Effects of experimental acidification and liming on soil organisms and decomposition in a Scots pine forest. Pedobiologia, 20, 85-100.

Battin TJ, Luyssaert S, Kaplan LA et al. (2009) The boundless carbon cycle. Nature Geosci. 2: 598-600.

Bellamy PH, Loveland PJ, Bradley RI, Lark MR, Kirk G (2005) Carbon losses from all soils across England and Wales 1978-2003. Nature 437: 245-248.

Bianchi TS (2011) The role of terrestrially derived organic carbon in the coastal ocean: A changing paradigm and the priming effect. Proc. Nat. Acam. Sci. 108: 19473–19481.

Borken W, Ahrens B, Schulz C, Zimmermann L (2011) Site-to-site variability and temporal trends of DOC concentrations and fluxes in temperate forest soils. Global Change Biol. 17: 2428-2443

Chapman PJ, McDonald AT, Tyson R, Palmer SM, Mitchell G, Irvine B (2010) Changes in water colour between 1986 and 2006 in the headwaters of the River Nidd, Yorkshire, UK. Biogeochemistry 101: 281-294.

Chow AT, Tanji KK, Gao S (2003) Production of dissolved organic carbon (DOC) and trihalomethane (THM) precursor from peat soils. Water Res. 37: 4475-4485.

Clair TA, Dennis IF, Vet R, Laudon H (2008) Long-term trends in catchment organic carbon and nitrogen exports from three acidified catchments in Nova Scotia, Canada. Biogeochemistry 87: 83-97.

Clark JM, Bottrell SM, Evans CD et al. (2010) The importance of the relationship between scale and process in understanding long-term DOC dynamics. Sci. Total Environ 408: 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. doi: 10.1111/j.1365-2389.2010.01344.x.

Cole JJ, Prairie YT, Caraco NF et al. (2007) Plumbing the Global Carbon Cycle: Integrating Inland Waters into the Terrestrial Carbon Budget. Ecosystems 10: 171-184

Corre MD, Lamersdorf NP (2004). Reversal of nitrogen saturation after long-term deposition reduction: Impact on soil nitrogen cycling. Ecology 85: 3090-3104.

Couture S, Houle D, Gagnon C (2011) Increases of dissolved organic carbon in temperate and boreal lakes in Quebec, Canada. Environ. Sci. Pollut. Res. DOI 10.1007/s11356-011-0565-6.

Curtis CJ, Emmett BA, Grant H et al. (2005) Nitrogen saturation in UK moorlands: the critical role of bryophytes and lichens in determining retention of atmospheric N deposition. J. Appl. Ecol. 42: 507–517.

Dawson JJC, Soulsby C, Tetzlaff D, Hrachowitz M, Dunn SM, Malcolm IA (2008). Influence of hydrology and seasonality on DOC exports from three contrasting upland catchments. Biogeochemistry, 90: 93-113

Dawson JJC, Malcolm IA, Middlemass SJ, Tetzlaff D, Soulsby C (2009). Is the composition of dissolved organic carbon changing in upland acidic streams? Environ. Sci. Technol. 43: 7748-7753

De Wit HA, Mulder J, Hindar A, Hole L (2007) Long-term increase in dissolved organic carbon in streamwaters in Norway Is response to reduced acid deposition. Environ. Sci. Technol. 41, 7706-7713.

Dore AJ, Vieno M, Tang YS, Dragosits U, Dosio A, Weston KJ, Sutton MA (2007) Modelling the atmospheric transport and deposition of sulfate and nitrogen over the United Kingdom and assessment of the influence of SO_2 emissions from international shipping. Atmos. Environ. 41: 2355-2367.

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

Ekström SM, Kritzberg ES, Kleja DB, Larsson N, Nilsson PA, Graneli W, Bergkvist B (2011) Effect of acid deposition on quantity and quality of dissolved organic matter in soil-water. Environ. Sci. Technol. 45, 4733-4739.

Emmett BA, Reynolds B, Chamberlain PM et al. (2010) Countryside Survey: Soils Report from 2007. Technical Report No. 9/07, NERC/Centre for Ecology & Hydrology.

Erlandsson M, Buffam I, Fölster J, Laudon H, Temnerud J, Weyhenmeyer G, Bishop K (2008). Thirty-five years of synchrony in the organic matter concentrations of Swedish rivers explained by variation in flow and sulphate. Global Change Biol. 14, 1191-1198.

Evans CD, Jenkins A, Wright RF (2000) Surface water acidification in the South Pennines. 1. Current status and spatial variability. Environ. Pollut. 109: 11-20

Evans, CD, Monteith DT, Cooper DM (2005) Long-term increases in surface water dissolved organic carbon: Observations, possible causes and environmental impacts. Environ. Pollut. 137: 55-71.

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

Evans CD, Cooper DM, Juggins S, Jenkins A, Norris D (2006b) A linked spatial and temporal model of the chemical and biological status of a large, acid-sensitive river network. Sci. Total Environ. 365: 167-185.

Evans CD, Freeman C, Cork LG et al. (2007) Evidence against recent climate-induced destabilisation of soil carbon from ^{14}C analysis of riverine dissolved organic matter. Geophys Res. Lett. 34: L07407, doi:10.1029/2007GL029431.

Evans CD, Goodale CL, Caporn SJM et al. (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 additions experiments. Biogeochemistry 91: 13-35.

Evans CD, Monteith DT, Fowler D, Cape JN, Brayshaw S (2011). Hydrochloric acid: An overlooked driver of environmental change. Environ. Sci. Technol., 45, 1887-1894.

Fenner N & Freeman C (2011) Drought-induced carbon loss in peatlands. Nature Geosci. 4: 895-900.

FAO (2006) World reference base for soil resources. A framework for international classification, correlation and communication. World Soil Resources Reports 103, Food and Agriculture Organisation of the United Nations, 145 pp.

Findlay SEG (2005) Increased carbon transport in the Hudson River: unexpected consequence of nitrogen deposition? Front. Ecol. Environ. 3: 133-137.

Fierer N, Jackson RB (2006) The diversity and biogeography of soil bacterial communities. Proc. Nat. Acad. Sci. 103: 626-631.

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

Hejzlar J, Dubrovsky M, Buchtele J, Ruzicka M (2003) The apparent and potential effects of climate change on the inferred concentration of dissolved organic matter in a temperate stream (the Malse River, South Bohemia). Sci. Total Environ. 310: 142-152.

Helliwell RC et al. (2007) The role of catchment characteristics in determining surface water nitrogen in four upland regions in the UK. Hydrol. Earth Syst. Sci. 11: 356-371.

Hessen DO, Gjessing ET, Knulst J, Fjeld E (1997). TOC fluctuations in a humic lake as related to catchment acidification, season and climate. Biogeochemistry 36: 139-151.

Hinton MJ, Schiff SL, English MC. The significance of storms for the concentration and export of dissolved organic carbon from two Precambrian Shield catchments, Biogeochemistry 36: 67-88.

Hongve D, Riise G, Kristiansen JF (2004) Increased colour and organic acid concentrations in Norwegian forest lakes and drinking water – a result of increased precipitation? Aquat. Sci. 66: 231-238.

Hood E, Gooseff MN, Johnson SL (2006) Changes in the character of stream water dissolved organic carbon during flushing in three small watersheds, Oregon. J Geophys Res. 111: G01007, doi:10.1029/2005JG000082.

Hruška J, Köhler S, Laudon H, Bishop K (2003). Is a universal model of organic acidity possible: Comparison of acid/base properties of dissolved organic carbon in the boreal and temperate zones. Environ. Sci. Technol. 37: 1726-1730.

Hruška J, Krám 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: 4320-4326.

Hughes S, Reynolds B, Norris DA, et al. (2012) Recovery of sulfate saturated soils in the Plynlimon catchments, mid-Wales following reductions in atmospheric S inputs from the 1980s to 2011. J Env. Monitor. 14: 1531-1541.

Kalbitz K, Solinger S, Park JH, Michalzik B, Matzner E (2000) Controls on the dynamics of dissolved organic matter in soils: A review. Soil Science 165: 277-304.

Karlsson J, Byström P, Ask J, Ask P, Persson L, Jansson M (2010) Light limitation of nutrient-poor lake ecosystems. Nature 460: 506-510.

Kennedy J, Billett MF, Duthie D, Fraser AR, Harrison AF (1996) Organic matter retention in an upland humic podzol: the effect of pH and solute type. Eur. J. Soil Sci. 47: 615-625.

Kortelainen P, David MB, Roila T, Mäkinen I (1992) Acid-base characteristics of organic carbon in the HUMEX lake Skjervatjern. Env. Int. 18: 621-629.Kirk GJD, Bellamy PH, Lark RM (2010) Changes in soil pH across England and Wales in response to decreased acid deposition. Global Change Biol. 16: 3111-3119.

Larssen S, Andersen T, Hessen DO (2011) Climate change predicted to cause severe increase of organic carbon in lakes. Global Change Biol. 17: 1186-1192.

Löfgren S, Zetterberg T (2011) Decreased DOC concentrations in soil water in forested areas in southern Sweden during 1987–2008. Sci. Total Environ. 409: 1916-1926.

Löfgren S, Gustafsson JP, Bringmark L (2010) Decreasing DOC trends in soil solution along the hillslopes at two IM sites in southern Sweden - Geochemical modeling of organic matter solubility during acidification recovery. Sci. Total Environ. 409: 201-210.

Lofts S, Simon BM, Tipping E, Woof C (2001) Modelling the solid-solution partitioning of organic matter in European forest soils. Eur. J. Soil Sci. 52: 215-226.

Lumsdon DG, Stutter MI, Cooper RJ, Manson JR (2005) Model assessment of biogeochemical controls on dissolved organic matter partitioning in an acid organic soil. Environ. Sci. Technol. 39: 8057-8063.

Lydersen E, Fjeld E, Gjessing ET (1996). The Humic Lake Acidification Experiment (HUMEX): Main physico-chemical results after five years of artificial acidification. Environ. Int. 22: 591-604.

Monteith DT, Stoddard JL, Evans CD et al. (2007) Dissolved organic carbon trends resulting from changes in atmospheric deposition chemistry. Nature 450: 537–41.

Mikutta R & Kaiser K. (2011) Organic matter bound to mineral surfaces: Resistance to chemical and biological oxidation. Soil Biol. Biochem. 43: 1738-1741.

Nilsson SI, Andersson S, Valeur I, Persson T, Bergholm J, Wirén A (2001). Influence of dolomite lime on leaching and storage of C, N and S in a Spodosol under Norway spruce (Picea abies (L.) Karst.). Forest Ecol. Manage. 146: 55-73.

Nordstrom DK & Ball JW (1987). The geochemical behaviour of aluminum in Acidified surface waters. Science, 232, 54-56.

Oulehle F, Hruška J (2009) Rising trends of dissolved organic matter in drinking-water reservoirs as a result of recovery from acidification in the Ore Mts., Czech Republic. Environ. Pollut. 157: 3433-3439.

Oulehle F, Evans CD, Hofmeister J et al. (2011) Major changes in forest carbon and nitrogen cycling caused by declining sulphur deposition. Global Change Biol. 17: 3115-3129.

Pärn J, Mander U (2012) Increased organic carbon concentrations in Estonian rivers in the period 1992–2007 as affected by deepening droughts. Biogeochemistry 108: 351-358.

Pregitzer KS, Zak DR, Burton AJ, Ashby JA, MacDonald NW (2004) Chronic nitrate additions dramatically increase the export of carbon and nitrogen from northern hardwood ecosystems. Biogeochemistry 68: 179-197

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., doi:10.1016/j.scitotenv.2010.12.027.

R Development Core Team, 2011. R: A Language and Environment for Statistical Computing. 3-900051-07-0. R Foundation for Statistical Computing, Vienna, Austria. http://www.R-project.org.

Raymond PA, Saiers JE, 2010. Event controlled DOC export from forested watersheds. Biogeochemistry 100: 197-209

Roulet N, Moore TR (2006) Browning the waters. Nature 444: 283-284.

SanClements MD, Oelsner GP, McKnight DM, Stoddard JL, Nelson SJ (2012) New insights into the source of decadal increases of dissolved organic matter in acid-sensitive lakes of the Northeastern United States. Environ. Sci. Technol. 46: 3212-3219.

Sarkkola S, Koivusalo H, Laurén A et al. (2009) Trends in hydrometeorological conditions and stream water organic carbon in boreal forested catchments. Sci. Total Environ. 408: 92-101.

Schindler DW, Bayley SE, Curtis PJ, Parker BR, Stainton MP, Kelly CA (1992). Natural and man-caused factors affecting the abundance and cycling of dissolved organic substances in precambrian shield lakes. Hydrobiologia 229: 1-21.

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: 9-28.

Sinsabaugh RL (2010). Phenol oxidase, peroxidase and organic matter dynamics of soil. Soil Biol.. Biochem. 42: 391-404.

Stoddard JL, Kahl JS, Deviney FA et al. (2003). Response of Surface Water Chemistry to the Clean Air Act Amendments of 1990. Report EPA 620/R-03/001, United States Environmental Protection Agency, North Carolina.

Striegl RG, Aiken GR, Dornblaser MM, Raymond PA, Wickland KP (2005). A decrease in discharge-normalized DOC export by the Yukon River during summer through autumn. Geophys. Res. Lett. 32: L21413, doi:10.1029/2005GL024413.

Stutter MI, Lumsdon DG, Rowland AP (2011). Three representative UK moorland soils show differences in decadal release of dissolved organic carbon in response to environmental change. Biogeosciences 8: 3661-3675.

Tallis JH (1987) Fire and flood at Holme Moss: erosion processes in an upland blanket mire. J. Ecol. 75: 1099-1129.

Tipping E, Woof C (1990). Humic substances in acid organic soils: modelling their release to the soil solution in terms of humic charge. J. Soil Sci. 41: 573-586.

Vance GF, David MB (1989). Effect of acid treatment on dissolved organic carbon retention by a spodic horizon. Soil. Sci. Soc. Am. J. 53: 1242-1247.

Vanguelova E, Pitman R, Luiro J, Helmisaari H-S (2010) Long term effects of whole tree harvesting on soil carbon and nutrient sustainability in the UK. Biogeochemistry 101: 43-59.

Vogt RD, Seip HM, Ranneklev S (1992). Soil and soil water studies at the HUMEX site. Environ. Int. 18: 555-564.

Worrall F., Burt TP (2007) The flux of dissolved organic carbon from UK rivers. Global Biogeochem. Cycl. 21: GB1013.

Worrall F et al (2004). Trends in dissolved organic carbon in UK rivers and lakes. Biogeochemistry 70: 369-402.

Worrall F, Burt TP, Adamson J (2008) Linking pulses of atmospheric deposition to DOC release in an upland peat-covered catchment. Global Biogeochem. Cycl. 22: GB4014.

Wu Y, Clarke N, Mulder N (2010) Dissolved organic carbon concentrations in throughfall and soil waters at Level II monitoring mlots in Norway: Short- and long-term variations. Water Air Soil Pollut. 205: 273-288.

Wright RF (1989). RAIN Project: Role of organic acids in moderating pH change following reduction in acid deposition. Water Air Soil Pollut. 46: 251-259.

Yallop AR, Clutterbuck B, Thacker J. (2010) Increases in humic dissolved organic carbon export from upland peat catchments: the role of temperature, declining sulfate deposition and changes in land management. Climate Res. 45: 43-56.

Ye R, jin Q, Bohannan B, Keller JK, McAllister SA, Bridgham SA (2012) pH controls over anaerobic carbon mineralization, the efficiency of methane production, and methanogenic pathways in peatlands across an ombrotrophic-minerotrophic gradient. Soil Biol. Biochem. 54: 36-47.

Zech W, Guggenberger G, Schulten H-R (1994) Budgets and chemistry of dissolved organic carbon in forest soil: effects of anthropogenic soil acidification. Sci Total Environ. 152:49–62

Zhang J, Hudson J, Neal R et al. (2010) Long-term patterns of dissolved organic carbon in lakes across eastern Canada: Evidence of a pronounced climate effect. Limnol. Oceanogr. 55: 30-42.

FIGURE CAPTIONS

Figure 1. Mean and standard error of soil solution pH and DOC at each experimental site for control, acid and alkaline treatment plots (n=4 per treatment and experimental site). Data are shown for the pre-treatment period (August 2007 to April 2008) and for the last three full years of manipulation. Significant treatment effects by site and time period denoted by * $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$ (Table 1)

Figure 2. Ratio of treatment to control standardised DOC ($RDOC_{std}$) versus ratio of treatment to control standardised hydrogen ion concentration (RH_{std}) for all samples collected in 2009-2011 from individual experiment sites. Filled circles represent samples from acid treatment plots, open circles samples from alkaline treatment plots (mean of 4 replicates in each case). Trendlines shown are of the form $RDOC_{std} = 1/(RH_{std}^{b})$, with b fitted to each dataset by weighted least squares regression (see Methods, Table 2). Solid trendlines show fit to full dataset, dashed trendlines show fit to data after excluding data from the Migneint podzol alkaline treatment. Circled area in d) illustrates the cluster of apparent outlier values associated with this treatment (see text for discussion). For merged relationships by region (Peak District and Migneint) and soil type (peat and podzol) see Supplementary Figure 2.

Figure 3. Ratio of treatment to control standardised DOC ($RDOC_{std}$) versus ratio of treatment to control standardised hydrogen ion concentration (RH_{std}) for all samples collected in 2009-2011 from all experimental sites and (acid and alkaline) treatments. Trendline shown is of the form $RDOC_{std} = 1/(RH_{std}^{b})$, with b fitted to each dataset by weighted least squares regression (see Methods, Table 2). Open circles represent samples from alkaline treatments, filled circles samples from acid treatments. Solid trendlines show fit to full dataset, dashed trendlines show fit to data after excluding data from the Migneint podzol alkaline treatment.

Figure 4. Observed changes in 90th percentile hydrogen ion concentrations, and observed and predicted changes in 90th percentile DOC concentrations, for the first and last 5 full years of data from two long-term Acid Waters Monitoring Network sites located near the experimental plots. Predicted changes are based on $RDOC_{std}$ vs RH_{std} regressions derived from experimental plots from each area (Table 2).

Figure 5. Observed changes in hydrogen ion concentrations, and predicted changes in DOC, between 1978 and 2007, for the four acidic moorland habitat classes in the UK Countryside Survey. Predicted changes are based on $RDOC_{std}$ vs RH_{std} regressions. Dwarf shrub heath predictions are based on the full dataset, and bog predictions on the combined peat data, both with the Migneint podzol alkaline treatment excluded from regressions. Predictions for the alkaline acid grass and bracken habitats are based on the combined podzol data. Because the pH of these habitats rose above 4.6 by 2007, predicted DOC changes are shown both with (light grey) and without (dark grey) the Migneint podzol alkaline treatment included in the regressions (See Table 2).

Table 1. Analysis of variance for pH and DOC for pre-treatment, 2009, 2010 and 2011 measurements. One-way analysis of variance against treatment carried out for individual sites, and two-way analysis of variance for the combined dataset against site and treatment (including a separate assessment for acid and alkaline treatments across the four sites). Significant effects ($p < 0.05$) highlighted in bold.

	Pre-treatment		2009		2010		2011	
Site	pH							
Peak District Podzol	$F_{2,9} = 0.12$	$p = 0.885$	$F_{2,9} = 3.84$	$p = 0.062$	$F_{2,9} = 9.85$	$p = 0.005$	$F_{2,9} = 11.23$	$p = 0.004$
Peak District Peat	$F_{2,9} = 2.96$	$p = 0.103$	$F_{2,9} = 2.57$	$p = 0.131$	$F_{2,9} = 34.22$	$p < 0.001$	$F_{2,9} = 35.38$	$p < 0.001$
Migneint Podzol	$F_{2,9} = 0.03$	$p = 0.970$	$F_{2,9} = 3.45$	$p = 0.077$	$F_{2,9} = 5.81$	$p = 0.024$	$F_{2,9} = 16.90$	$p = 0.001$
Migneint Peat	$F_{2,9} = 0.3$	$p = 0.747$	$F_{2,9} = 2.11$	$p = 0.177$	$F_{2,9} = 2.53$	$p = 0.134$	$F_{2,9} = 5.43$	$p = 0.028$
Combined data								
Treatment effect	$F_{2,42} = 0.075$	$p = 0.928$	$F_{2,42} = 9.67$	$p < 0.001$	$F_{2,42} = 17.93$	$p < 0.001$	$F_{2,42} = 39.92$	$p < 0.001$
Acid	$F_{1,27} = 0.041$	$p = 0.841$	$F_{1,27} = 5.52$	$p = 0.026$	$F_{1,27} = 22.98$	$p < 0.001$	$F_{1,27} = 26.39$	$p < 0.001$
Alkaline	$F_{1,27} = 0.065$	$p = 0.801$	$F_{1,27} = 5.14$	$p = 0.032$	$F_{1,27} = 5.89$	$p = 0.022$	$F_{1,27} = 18.06$	$p < 0.001$
Site	DOC							
Peak District Podzol	$F_{2,9} = 0.73$	$p = 0.509$	$F_{2,9} = 9.41$	$p = 0.006$	$F_{2,9} = 6.99$	$p = 0.015$	$F_{2,9} = 15.42$	$p = 0.001$
Peak District Peat	$F_{2,9} = 2.30$	$p = 0.157$	$F_{2,9} = 2.81$	$p = 0.113$	$F_{2,9} = 14.11$	$p = 0.002$	$F_{2,9} = 21.57$	$p < 0.001$
Migneint Podzol	$F_{2,9} = 0.67$	$p = 0.536$	$F_{2,9} = 0.53$	$p = 0.606$	$F_{2,9} = 2.53$	$p = 0.134$	$F_{2,9} = 6.67$	$p = 0.017$
Migneint Peat	$F_{2,9} = 0.08$	$p = 0.922$	$F_{2,9} = 0.51$	$p = 0.616$	$F_{2,9} = 2.00$	$p = 0.191$	$F_{2,9} = 0.05$	$p = 0.953$
Combined data								
Treatment effect	$F_{2,42} = 2.38$	$p = 0.105$	$F_{2,42} = 7.22$	$p = 0.002$	$F_{2,42} = 16.97$	$p < 0.001$	$F_{2,42} = 16.67$	$p < 0.001$
Acid treatments only	$F_{1,27} = 3.68$	$p = 0.066$	$F_{1,27} = 0.81$	$p = 0.377$	$F_{1,27} = 13.24$	$p = 0.001$	$F_{1,27} = 5.43$	$p = 0.028$
Alkaline treatments only	$F_{1,27} = 1.34$	$p = 0.257$	$F_{1,27} = 9.52$	$p = 0.005$	$F_{1,27} = 8.70$	$p = 0.007$	$F_{1,27} = 16.69$	$p < 0.001$

Table 2. Fitted coefficient (b) in equation $\mathrm{RDOC_{std}} = 1/(\mathrm{RH_{std}}^{b})$, based on a weighted least-squares regression, for individual experimental sites, combined data for each region, and full experimental dataset. R^2 and p values shown for simulated versus observed $\mathrm{RDOC_{std}}$. Left side of table shows results based on inclusion of all data, right side shows re-analysed results excluding the Migneint podzol alkaline treatment data (where relevant).

	Full dataset				Dataset excluding Migneint podzol alkaline treatment data			
Site	Coefficient	R^2	p	n	Coefficient	R^2	p	n
Peak District podzol	-0.645	0.60	< 0.001	67	-	-	-	-
Peak District peat	-0.989	0.43	< 0.001	74	-	-	-	-
Migneint podzol	-0.402	0.37	< 0.001	74	-0.871	0.38	< 0.001	37
Migneint peat	-0.231	0.14	< 0.001	84	-	-	-	-
Peak District combined	-0.794	0.51	< 0.001	141	-	-	-	-
Migneint combined	-0.386	0.30	< 0.001	158	-0.684	0.42	< 0.001	121
Peat combined	-0.773	0.33	< 0.001	158	-	-	-	-
Podzol combined	-0.468	0.39	< 0.001	141	-0.739	0.60	< 0.001	104
All sites combined	-0.540	0.34	<0.001	299	-0.753	0.47	<0.001	271

Figure 1

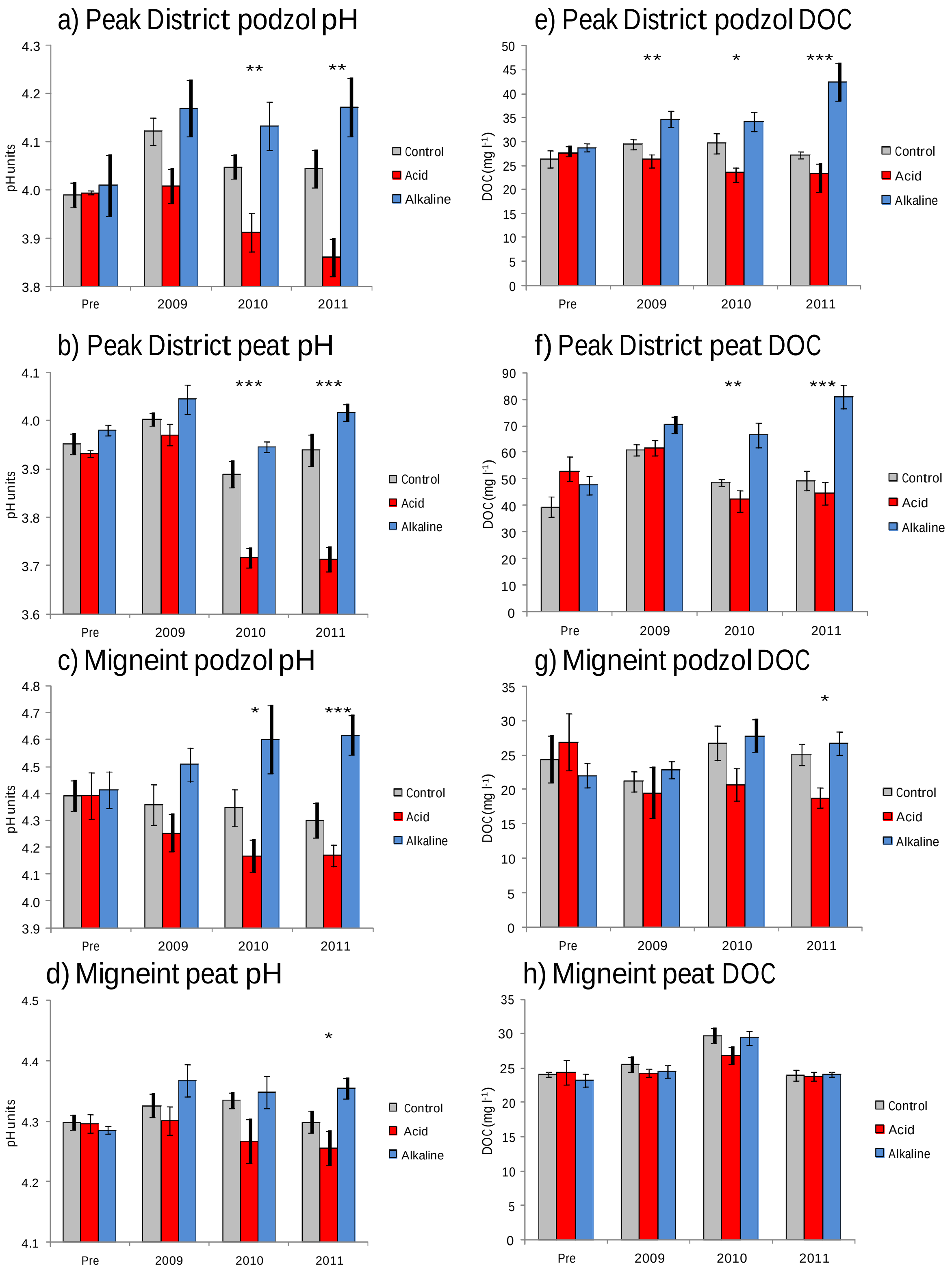

a) Peak District podzol pH
pH units
4.3
4.2
4.1
4.0
3.9
3.8
**
**
Pre
2009
2010
2011
Control
Acid
Alkaline
e) Peak District podzol DOC
DOC (mg l-1)
50
45
40
35
30
25
20
15
10
5
0
**
*
***
Pre
2009
2010
2011
Control
Acid
Alkaline
b) Peak District peat pH
pH units
4.1
4.0
3.9
3.8
3.7
3.6
***
***
Pre
2009
2010
2011
Control
Acid
Alkaline
f) Peak District peat DOC
DOC (mg l-1)
90
80
70
60
50
40
30
20
10
0
**
***
Pre
2009
2010
2011
Control
Acid
Alkaline
c) Migneint podzol pH
pH units
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
*
***
Pre
2009
2010
2011
Control
Acid
Alkaline
g) Migneint podzol DOC
DOC (mg l-1)
35
30
25
20
15
10
5
0
*
Pre
2009
2010
2011
Control
Acid
Alkaline
d) Migneint peat pH
pH units
4.5
4.4
4.3
4.2
4.1
*
Pre
2009
2010
2011
Control
Acid
Alkaline
h) Migneint peat DOC
DOC (mg l-1)
35
30
25
20
15
10
5
0
Pre
2009
2010
2011
Control
Acid
Alkaline

Figure 2

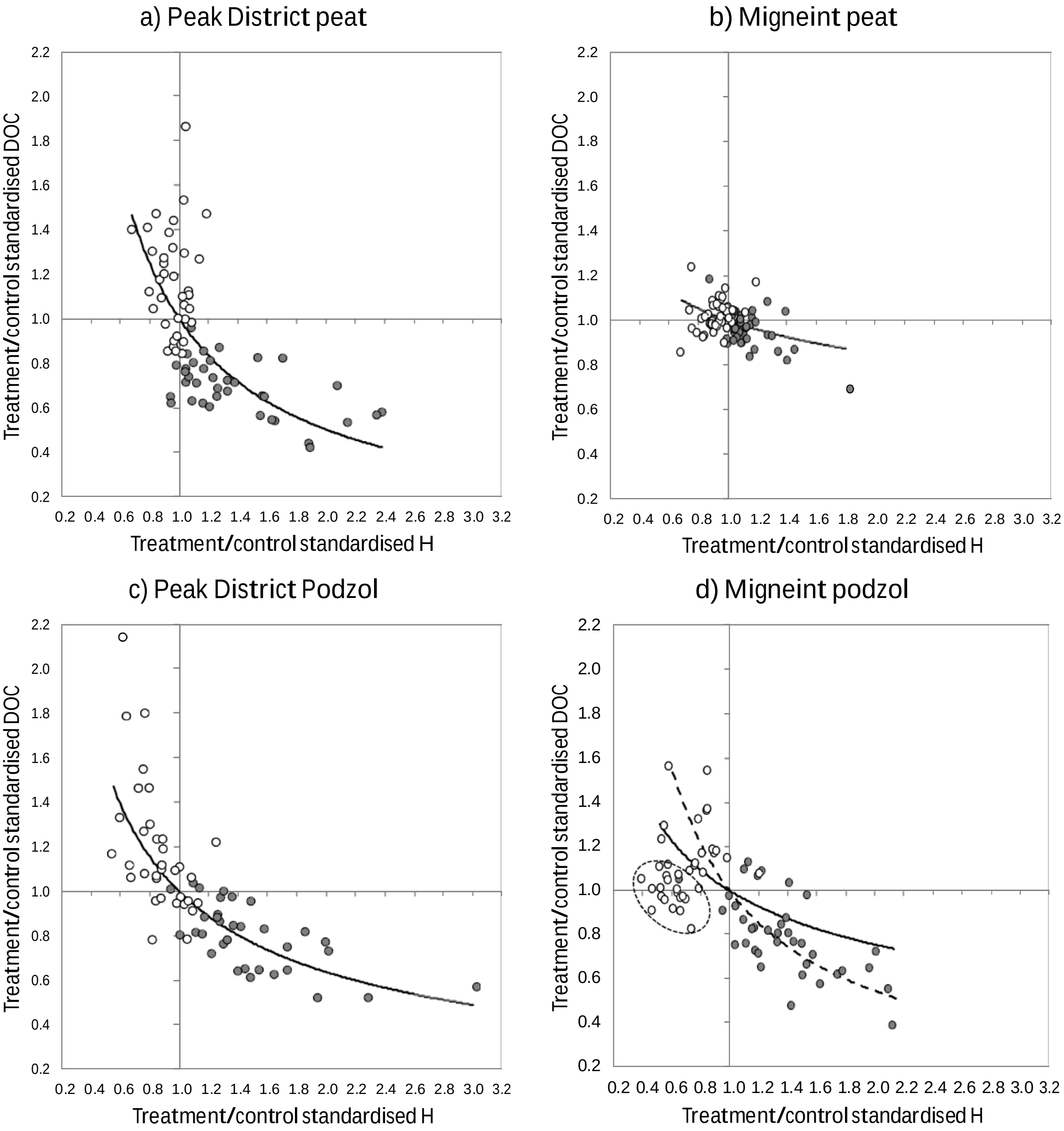

a) Peak District peat
b) Migneint peat
c) Peak District Podzol
d) Migneint podzol
Treatment/control standardised DOC
Treatment/control standardised H
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
3.2

Figure 3

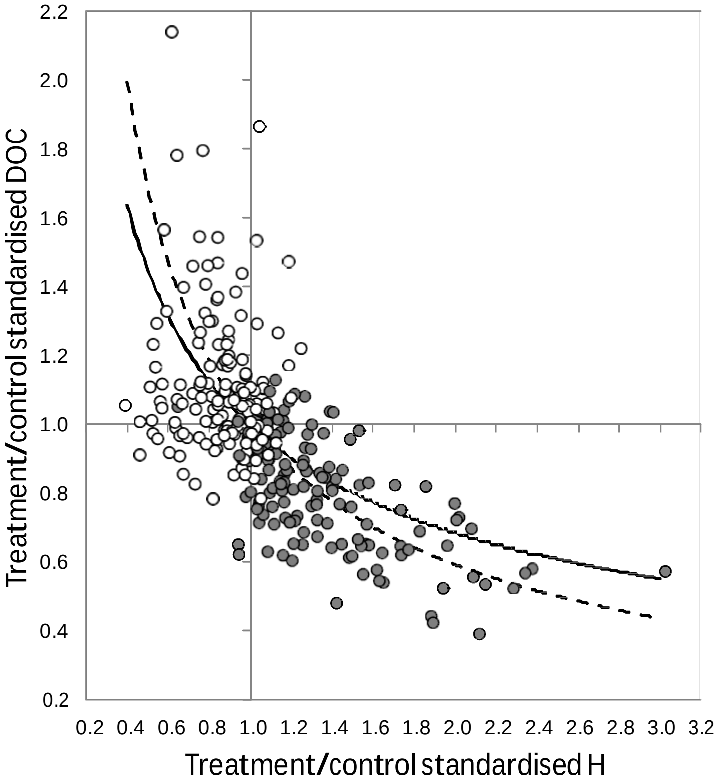
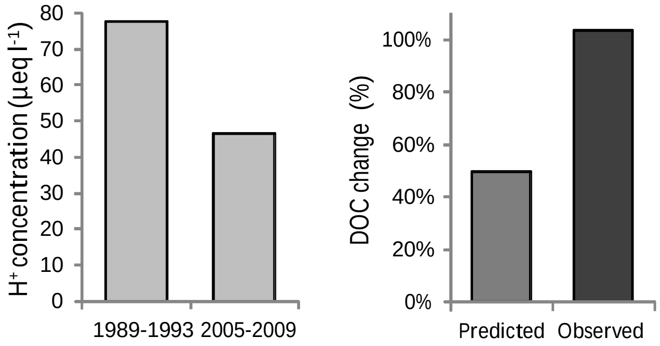

2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
Treatment/control standardised DOC
0.2 0.4 0.6 0.8 1.0 1.2 1.4 1.6 1.8 2.0 2.2 2.4 2.6 2.8 3.0 3.2
Treatment/control standardised H

Figure 4

a) River Etherow, Peak District



b) Afon Gwy, Wales

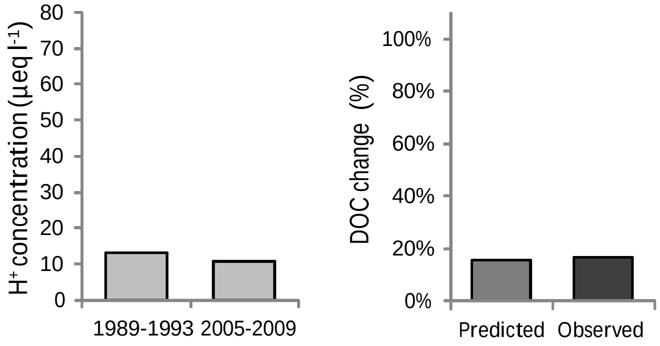
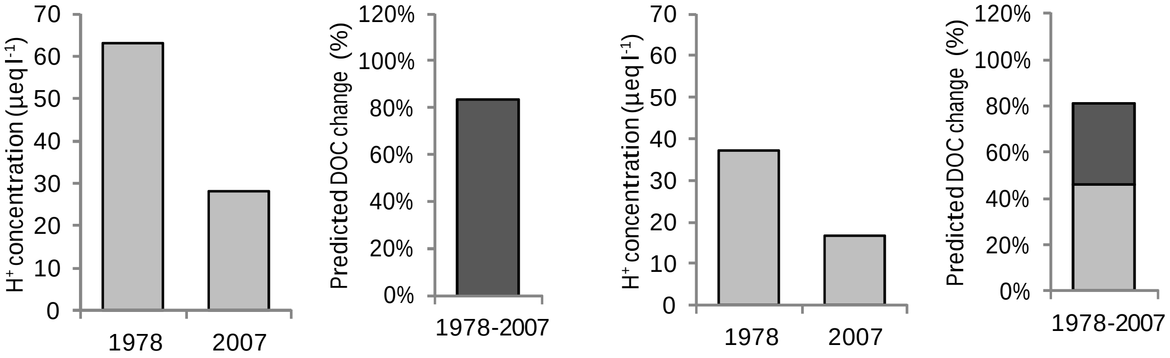
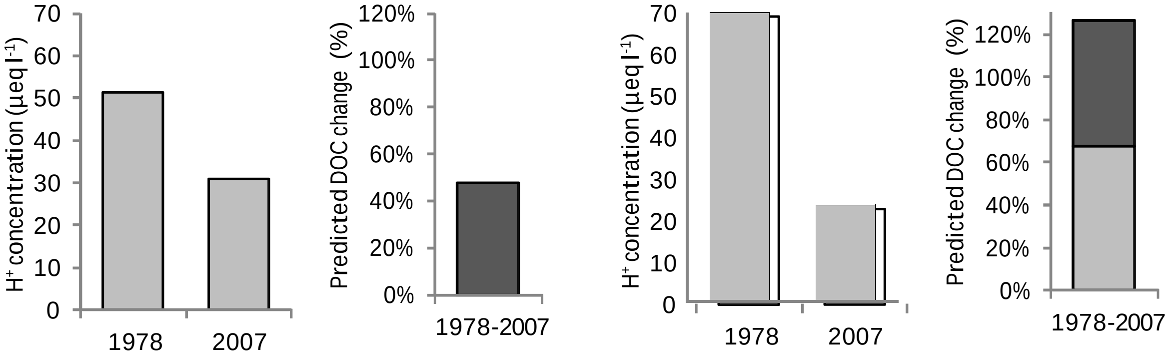


Figure 5



a) Dwarf shrub heath

b) Acid grass



c) Bog

d) Bracken