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1 Acidity controls on dissolved organic carbon mobility in organic soils

2 Running title: Acidity controls on DOC mobility

3

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20

21 Abstract

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

41

42 Introduction

43 Dissolved organic carbon (DOC) is an integral component of soils and natural waters. It provides the
44 major pathway for carbon transfer from terrestrial to aquatic ecosystems, contributes to
45 heterotrophic processes in streams, lakes and coastal oceans, and provides a significant indirect
46 source of CO₂ emission to the atmosphere (e.g. Cole et al., 2007; Battin et al., 2007; Wehenmeyer et
47 al., 2011; Bianchi, 2011). During the last three decades, DOC concentrations have increased in
48 surface waters draining semi-natural ecosystems in many areas including the United Kingdom (Evans
49 et al., 2005; Worrall & Burt, 2007; Dawson et al., 2008; Chapman et al., 2010), Fennoscandia
50 (Hongve et al., 2004; De Wit et al., 2007; Sarkkola et al., 2009; Arvola et al., 2010), the Baltic States
51 (Pärn and Mander, 2012), Central Europe (Hejzlar et al., 2003; Oulehle & Hruska, 2009), the North-
52 eastern United States (Findlay, 2005; Stoddard et al., 2003; SanClements et al., 2012) and Eastern
53 Canada (e.g. Couture et al., 2011). In the United Kingdom, DOC concentrations have approximately
54 doubled since the 1980s in areas dominated by organic soils (Evans et al., 2005). In the water
55 industry, the high cost of DOC removal, and associated health risks through trihalomethane
56 formation (e.g. Chow et al., 2003), result in it being widely viewed as a pollutant. Changes in DOC
57 export to surface waters also affect aquatic energy supply and light regime (due to the
58 chromophoric properties of organic compounds), with potentially major consequences for the
59 functioning of aquatic ecosystems (Cole et al., 2001; Battin et al., 2009; Karlsson et al., 2010). When
60 first detected, DOC increases were thought to be a consequence of climate change (Freeman et al.,
61 2001; Hejzlar et al., 2003; Worrall & Burt, 2007; Hongve et al., 2004), and thus evidence of
62 ecosystem destabilisation, contributing to terrestrial carbon losses (Bellamy et al., 2005). Some
63 recent studies also suggest high climate-sensitivity of DOC leaching (e.g. Larssen et al., 2011; Fenner
64 & Freeman, 2011). Other studies have linked elevated DOC to land-management factors such as
65 moorland burning (Yallop et al., 2010) and drainage (e.g. Armstrong et al., 2010), or to the
66 eutrophying effects of nitrogen deposition (Findlay, 2005; Pregitzer et al., 2004). Again, these factors
67 all imply a response to ecosystem degradation. However, other research suggests that rising DOC is

68 instead linked to declining acid deposition (Evans et al., 2006a; Monteith et al., 2007). If correct, this
69 would have very different implications, as it implies that acid-sensitive waters are simply recovering
70 towards their high-DOC, pre-industrial state as sulphur deposition declines. Numerous studies have
71 since been published both supporting (e.g. De Wit et al., 2007; Oulehle & Hruska, 2009; Chapman et
72 al., 2010; Arvola et al., 2010; Clark et al., 2011; Ekström et al., 2011; SanClements et al., 2012) and
73 challenging (e.g. Roulet & Moore, 2006; Eimers et al., 2008; Worrall et al., 2008; Clair et al., 2008;
74 Sarkkola et al., 2009; Sarkkola et al., 2009; Zhang et al., 2010; Couture et al., 2011; Löfgren and
75 Zetterberg, 2011; Pärn & Mander, 2012) the hypothesis that rising trends in surface water DOC are
76 due to declining acid deposition. Although attempts have been made to reconcile conflicting
77 arguments by noting the different temporal scales over which climatic and depositional drivers
78 operate (Clark et al., 2010), there remains no overall scientific consensus on the mechanisms
79 controlling DOC leaching. This has, in turn, led to inconsistency and confusion in land-management
80 and water treatment policy in regions where DOC is increasing.

81 One of the major barriers to resolution of the debate regarding drivers of long-term DOC increase
82 has been the widespread reliance of nearly all of the published studies on long-term monitoring data
83 (Roulet & Moore, 2006). While monitoring has been crucial to the detection of DOC trends,
84 identification of causative relationships from correlative analysis of time series data is problematic,
85 especially since at many sites more than one of the proposed driving variables, namely atmospheric
86 deposition, climate and land-use, have changed over the time-periods for which data are available.
87 A further source of uncertainty in interpreting surface water DOC trends is the relative scarcity, and
88 typically shorter duration, of DOC monitoring data from soils. Soils, in particular shallow organic soil
89 horizons, are the main source of DOC found in most headwater catchments (e.g. Evans et al., 2007),
90 therefore it follows that an increasing trend in surface water DOC should be matched by an
91 increasing trend in soil water DOC concentrations. However, available long-term soil solution data
92 provide a mixed picture; while the majority of studies reporting DOC trends in organic horizons
93 suggest an increase similar to that observed in surface waters (Hruška et al., 2009; Vanguelova et al.,

94 2010; Borken et al., 2011; Stutter et al., 2011), more variable results have been reported for mineral
95 horizons, with evidence of increases at some sites (Hruška et al., 2009; Stutter et al., 2011) but
96 decreases at others (Löfgren et al., 2010; Wu et al., 2010; Borken et al., 2011; Löfgren and
97 Zetterberg, 2011; Stutter et al., 2011). This apparent discrepancy between mineral soil and surface
98 water DOC trends led Löfgren and Zetterberg (2011) to conclude that surface water DOC
99 concentrations must be determined by processes taking place in the riparian zone.

100 Results from the limited number of acidity manipulations from which DOC responses have been
101 reported are also somewhat equivocal. In the HUMEX catchment-scale acidification experiment in
102 Norway, surface water organic acid concentrations were observed to decrease (Lydersen et al.,
103 1996), as were organic soil solution DOC concentrations (Vogt et al., 1992), but changes in surface
104 water DOC were not detected (Lydersen et al., 1996; Hessen et al., 1997). A catchment-scale 'clean
105 rain' experiment at Risdalsheia, Norway, recorded increases in organic acids during recovery from
106 acidification, but no clear change in DOC (Wright, 1989), whilst a similar plot-scale study at Solling,
107 Germany recorded an increase in DOC, along with rising pH, in shallow soil solution (Corre and
108 Lamersdorf, 2004). Ten years after experimental liming of a Swedish forest plot, Nilsson et al. (2001)
109 recorded significantly higher DOC concentrations in the organic horizon and upper mineral soil
110 leachates, but less change at depth. Schindler et al. (1992) recorded DOC decreases in bog pools
111 after experimental acid additions to a bog in Ontario, as well as DOC reductions in a lake that was
112 directly acidified to pH < 5.0. More recently, DOC responses at a number of field nitrogen addition
113 experiments were evaluated, and found to be consistent with treatment-induced acidity changes,
114 rather than nutrient effects (Evans et al., 2008). Ekström et al. (2011) applied sulphuric acid to forest
115 plots in Sweden and observed reductions in organic horizon DOC concentrations, as well as
116 qualitative changes indicative of reduced aromaticity, molecular weight and colour of the leached
117 organic matter.

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

127 Materials and methods

128 Sites and experimental design

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

140 Two experiments were located in the Peak District. This peat-dominated upland area is located close
141 to major industrial centres, and has experienced amongst the highest historic levels of S and N

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

159 A second set of experiments were established on the Migneint, an extensive blanket peat in
160 relatively good condition located in North Wales. Again, two sets of manipulation plots were
161 established, on adjacent peats and peaty podzol sites (3° 48.8' W, 52° 59.6' N). This area has
162 received somewhat lower historic levels of S and N deposition, although significant acidification is
163 thought to have occurred (Evans et al., 2006b). Annual rainfall is 2.4 m, and present-day S deposition
164 is 15 kg S ha⁻¹ yr⁻¹. FRAME modelled estimates suggest that S deposition decreased by 66% between
165 1970 and 2007. Surface water monitoring data from the nearby Llyn Llagi AWMN site record an 89%
166 increase in annual mean DOC concentrations between 1989 and 2009 (Supplementary Figure S1b).
167 At the Afon Gwy AWMN site, 50 km to the south, DOC has increased by 51% over the same period

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

175

176

177 Experimental design and operation

178 At each of the four experimental sites, soil acidity was manipulated for more than three years by
179 regular addition of acid and alkaline treatment solutions. At each experiment, twelve 3x3 m plots
180 were assigned to control, acid and alkaline treatments in a randomised blocked design, giving four
181 replicates per treatment. All plots were established in August 2007, and treatments began in April
182 2008 following a period of pre-treatment measurements. Acid treatments comprised 4-weekly
183 additions of sulphuric acid (H_2SO_4), mixed with ambient rainwater collected at each site and applied
184 evenly across the plots using watering cans in 20 l of water, followed by a 10 l 'rinse' with ambient
185 rainwater to ensure that the treatment solution entered the soil, and to minimise any direct effects
186 on the vegetation. The initial annual treatment dose was $25 \text{ kg S ha}^{-1} \text{ yr}^{-1}$, while the additional water
187 addition (3.3 l m^{-2} per treatment application, or 43 mm yr^{-1}). was equivalent to 1.8% of average
188 annual rainfall at the Migneint, and 4.3% at the Peak District sites. In January 2009, after no
189 detrimental impacts on vegetation had been observed in the 2008 growing season, the treatment
190 was increased to $50 \text{ kg S ha}^{-1} \text{ yr}^{-1}$ (SO_4 concentration in solution 7.2 meq l^{-1}), and in September 2009
191 the dosage at the peat plots was increased to $100 \text{ kg S ha}^{-1} \text{ yr}^{-1}$ (SO_4 concentration in solution 14.4

192 meq l⁻¹). Dosages were increased to ensure a measurable pH change within the duration of the
193 experiment, with a higher dose found to be required at the peat plots due to SO₄ reduction. We
194 emphasise that the aim of the experiment was to evaluate DOC responses to a pH change, rather
195 than the response to a specific S application rate, and that acidification (and its reversal) represent
196 gradual responses to a cumulative deposition dose. Thus, the increases in dosage (having first
197 ensured that direct toxicity to vegetation was not occurring) represented an acceleration of the
198 experiment rather than a change in design. The maximum, 100 kg S ha⁻¹ yr⁻¹ treatment level applied
199 is of a similar order to ambient sulphur deposition in the Peak District during the 1970s, and thus
200 within a realistic environmental range for the ecosystems studied. Alkaline treatments comprised
201 additions of sodium hydroxide (NaOH) and magnesium chloride (MgCl₂), intended to obtain a molar
202 OH⁻ concentration equivalent to the H⁺ concentration in the acid treatments, and a Na/Mg ratio
203 similar to sea-salt. Alkaline dosages were increased in parallel to those in the acid treatments, and all
204 treatment rates remained constant during the last two full years, 2010 to 2011 (total base cation
205 concentrations in treatment solution 7.2 meq l⁻¹ and 14.4 meq l⁻¹ to podzol and peat sites
206 respectively).

207 Soil solution sampling and analysis

208 Measurements were made 4-weekly, immediately before the treatments were applied (i.e. 4 weeks
209 after the preceding treatment). This ensured that measured changes reflected a sustained alteration
210 to plot pH, rather than a transient response to treatment application. Soil-water samples were
211 collected using Rhizon[®] suction samplers (Van Walt Ltd.), comprising 10 cm long, 2.5 mm diameter
212 porous membranes attached to 20 ml syringes, which were used to apply suction and collect
213 samples. Four samplers were inserted diagonally into the surface organic horizon of each plot, at the
214 start of the study, and samples were collected by applying suction overnight, and bulking samples
215 the following morning to give one composite sample per plot. Samples were stored at 4°C and within
216 24 hours they were analysed for pH using an Orion 720A pH meter. The remaining sample was

217 filtered using pre-rinsed 0.45 μm cellulose acetate syringe filters, and DOC analysed with a
218 Thermalox 5001.03 (Analytical Sciences Limited) carbon analyser using the Non-Purgable Organic
219 Carbon (NPOC) method, whereby samples were acidified to pH 2.0 and purged with oxygen to drive
220 off any inorganic carbon prior to analysis for total carbon.

221 Data analysis

222 After testing the data for normal distribution and equal variance, pH and DOC data were analysed
223 for the pre-treatment period (August 2007 to April 2008) and for each full year of manipulation data
224 (i.e. 2009, 2010 and 2011) using linear mixed effects models (lme) analysed by ANOVA using R
225 version 2.12.1 as $\text{lme}(\text{DOC} \sim \text{treatment} * \text{date}, \text{random} = \sim 1 | \text{plot})$ for each of the four experimental
226 sites and for each time period. This approach was used to enable the raw data to be analysed
227 accounting for replication at the level of the experimental unit, or plot ($n = 12$). The four sites were
228 then combined within a linear mixed effects model as (schematically) $\text{lme}(\text{DOC} \sim \text{site}_{\text{soil}} + \text{treatment},$
229 $\text{random} = \sim 1 | \text{fullplot})$, again analysed for the four time periods, with location indicating the four
230 site/soil combinations. This analysis provides estimates of treatment differences and also, in
231 principle, soil differences. However, the test for soil differences ($F_{1,1}$) is very weak and does not lead
232 to the rejection of the hypothesis of no difference between peat and podzol (i.e. $p > 0.05$) for either
233 pH or DOC for any period. The site effect (Peak District vs Migneint) is treated as random in the
234 model.

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

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

$$245 \quad RDOC_{std\ t} = \frac{DOCT_{treatment\ x} \times DOC_{pre\ control}}{DOCT_{control\ x} \times DOC_{pre\ treatment}} \quad (1)$$

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

254 Relationships between DOC and acidity change at each experiment were evaluated by plotting
 255 $RDOC_{std}$ against RH_{std} , and fitting a hyperbolic function of the form:

$$256 \quad RDOC_{std} = \frac{1}{(RH_{std})^b} \quad (2)$$

257 Where the parameter b is fitted to the data. This function was used because i) results showed
 258 apparently non-linear relationships between $RDOC_{std}$ and RH_{std} ; ii) it passes through the point
 259 $RDOC_{std} = 1$, $RH_{std} = 1$ (i.e. no experimentally induced change in DOC where there was no change in
 260 acidity); and iii) it is reversible, i.e. an increase in H concentration from X to Y, followed by a decrease
 261 from Y to X, will return DOC concentration to its initial value, regardless of the value of b (this would
 262 not be the case, for example, if a linear fit were applied). The exponent b was fitted to the data using
 263 the Microsoft Excel Solver function to minimise the sum of squared errors, multiplied by a weighting
 264 factor equal to $1/(RDOC_{std})^2$. This weighting factor was found to result in an improved fit to the larger

265 treatment-induced changes in $RDOC_{std}$ associated with the most acidic samples from the acid
266 treatment plots.

267 Estimation of long-term change in organic soil DOC concentrations

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

284 Second, to provide estimates of the magnitude of DOC change potentially associated with recovery
285 from acidification in comparable soils at a UK scale, we analysed data from the UK Countryside
286 Survey (CS, Emmett et al., 2010), in which the pH of 'topsoil' (0-15 cm) samples was measured in
287 1978, and again in 2007, in both cases using a slurry with a 1:2.5 soil:water ratio by weight. An
288 analysis of parallel measurements of mean soil water and soil-water slurry pH at a set of 18 UK
289 monitoring sites (F. Oulehle, unpublished data) showed a 1:1 relationship between the two pH

290 measurements ($R^2 = 0.75$), suggesting that one pH measure could reasonably be used as a proxy for
291 the other. We estimated changes in soil water DOC concentrations in unforested semi-natural
292 habitats that characteristically occur on acidic peat or organo-mineral soils (i.e. those considered
293 reasonably comparable to the experimental sites in terms of vegetation, soil type and acidity), using
294 data from the CS Bog, Dwarf Shrub Heath, Acid Grass and Bracken broad habitat categories. All
295 habitats showed an increase in mean pH between the two surveys, and these mean values were
296 used to calculate RH_{std} as above, and to predict mean percentage increase in DOC concentration by
297 habitat class using the $RDOC_{std} - RH_{std}$ relationships obtained from the experiments, using data from
298 the most appropriate soil type. Thus, predictions for Acid Grass and Bracken were based on the
299 combined podzol data, and predictions for Bog on the combined peat data. Dwarf Shrub Heath
300 occurs on both peats and podzols, and predictions for this habitat were therefore based on the full
301 set of experimental data.

302 Results

303 Four-weekly experimental additions of acidic (sulphuric acid) and alkaline (sodium hydroxide)
304 solutions led to changes in soil water pH at all four sites (Figure 1a-d). The magnitude of re-
305 acidification due to acid addition ranged from a pH reduction of 0.06 units at the Migneint peat to
306 0.20 units at the Peak District peat (based on 2010-11 means). Alkali additions led to only a marginal
307 pH increase at the Migneint peat (0.03 units), while increases ranged from 0.07 to 0.29 units at the
308 other sites. DOC responses to pH manipulations were consistent for both soils at both sites (Figure
309 1e-h). In all experiments, 2010-11 mean DOC was lower in the acid treatments than in the controls,
310 and it was higher in all alkaline treatments except for the Migneint peat, where the absence of a
311 DOC change coincided with the very small treatment-induced pH change. Analysis of variance
312 revealed significant ($p < 0.05$) treatment effects on pH at all sites except the Migneint peat by 2010,
313 and for all four sites by 2011. For DOC, significant differences were observed between treatments
314 for the two Peak District sites in 2010, and additionally for the Migneint podzol site in 2011 (Table 1).

315 Inherent natural background differences in DOC concentrations during the pre-treatment period
316 slightly obscured treatment responses at some sites, notably the Peak District peat where pre-
317 treatment DOC was apparently higher in the 'acid' plots, a pattern which had completely reversed by
318 2010 (Figure 1d). The effect of treatment on pH for the combined dataset was highly significant ($p <$
319 0.001) in all three treatment years, and separate analysis of the acid and alkaline treatments also
320 revealed significant pH responses to each treatment across the four-site dataset in each treatment
321 year. The effect of treatment on DOC for the combined dataset was also significant ($p \leq 0.002$) in all
322 three treatment years, while the individual acid treatments showed a significant DOC response in
323 2010 and 2011, and the alkaline treatments from 2009 to 2011 (Table 1).

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

336 At the Migneint podzol site, a large group of apparent outliers were observed for the alkaline
337 treatment, in which DOC differed little from the controls despite treatment-induced reductions in
338 acidity (circled area of Figure 2d). This site had the highest pre-treatment pH of those studied, and
339 showed the largest pH increase in response to alkaline treatment (Figure 1). For samples from this

340 treatment, we noted a significant, positive relationship in the residual of predicted versus observed
341 DOC concentrations (based on the best-fit relationship shown in Figure 2d), and mean measured pH
342 ($R^2 = 0.20$, $p = 0.006$). Above pH 4.63, all residuals were positive. In other words, the relationship
343 between $RDOC_{std}$ and RH_{std} observed for the remainder of the data at this site, and at all other sites,
344 appeared to break down at the highest recorded pH values; possible reasons for this are discussed
345 below. To assess the influence of these samples on results, we re-analysed the Migneint podzol
346 dataset based on the acid treatment data only, and also re-analysed the combined Migneint, podzol
347 and full datasets with the Migneint podzol alkaline treatment data excluded (Table 2; dashed best fit
348 lines in Figures 2, 3 and S2). In all cases, excluding these data strengthened the relationship between
349 $RDOC_{std}$ and RH_{std} for the remaining data, and gave higher (and convergent) values of the coefficient
350 b.

351 The observed relationships between $RDOC_{std}$ and RH_{std} from the experiments were used to estimate
352 the amount of DOC change that could be accounted for by changing acidity for i) nearby stream
353 monitoring sites, and ii) UK-wide soil pH chemistry data from the Countryside Survey (Emmett et al.,
354 2010). For the streams, as described above, changes in 90th percentile stream H and DOC
355 concentrations were assumed to reflect changes in acid, high-DOC runoff from surface organic
356 horizons, comparable to the data from the experimental sites. Results suggest that reductions in
357 organic soil acidity could account for 48% of the observed high flow DOC increase at the Peak District
358 monitoring stream (based on combined Peak District dataset), and 51-94% of the (smaller) high flow
359 DOC increases at the Welsh site (Figure 4; lower estimate based on full Migneint dataset, higher
360 estimate on Migneint dataset with podzol alkaline treatment data omitted). Scaling predictions up to
361 a national level, based on Countryside Survey data, we estimate that soil pH increases observed
362 since 1978 could have generated average DOC increases of 46% to 126% in habitat types similar to
363 our experimental sites (Figure 5).

364

365 Discussion

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

388 The apparently decreasing sensitivity of DOC concentration to further pH increases at the Migneint
389 podzol site is consistent with this physico-chemical control on DOC leaching, and may explain the

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

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

411 Normalising the treatment data as RH_{std} and RDOC_{std} revealed that, to a large extent, DOC leaching
412 responses to acidity change were fundamentally similar among sites and over time. There is some
413 evidence, based on the larger fitted 'b' coefficient values in the hyperbolic $\text{RDOC}_{\text{std}}\text{-RH}_{\text{std}}$
414 relationships for individual sites, that the Peak District soils are more sensitive to acidity change than

415 those of the Migneint. This would be consistent with laboratory experiments on peat cores collected
416 from the same areas (Clark et al., 2011), and with the greater observed DOC increases in Peak
417 District surface waters compared to those in Wales generally (Figure 5, S1). On the other hand, the
418 'b' value obtained from the acid plots alone at the Migneint podzol site (-0.871) is similar to that
419 obtained from the full Peak District dataset (-0.794), suggesting that more acidic soils (i.e. those with
420 $\text{pH} < 4.6$) may behave similarly in different locations, and therefore that a reasonably generic overall
421 relationship may exist between acidity change and DOC change in organic soils across larger spatial
422 scales. Taking the fitted b value of -0.540 for the entire experimental dataset, we estimate that a 0.3
423 unit increase in pH (equivalent to a halving of hydrogen ion concentrations) would lead to a 45%
424 increase in DOC concentrations. Excluding data from the Migneint podzol alkaline treatment ($b = -$
425 0.753) gives a predicted DOC increase of 68%. On the same basis, the pH increase required to double
426 DOC concentrations would be 0.56 units based on the full dataset, or 0.40 units with the Migneint
427 podzol alkaline treatment data excluded.

428 Applying our experimental results to observations of long-term pH change in UK soils and surface
429 waters (Figures 4-5) suggests that reductions in acid deposition, and subsequently observed pH
430 increases, may be sufficient to explain a large proportion of the observed increase in surface water
431 DOC concentrations. The range of predicted DOC increases for the acidic upland habitat classes of
432 the Countryside Survey (46-126%) is of the same order as observed (mean 91%) DOC increases in UK
433 surface waters (Evans et al., 2005), albeit over a longer time period (1978-2007 versus 1988-2007).
434 Since the Countryside Survey encompasses the entire UK, including remote areas such as Northwest
435 Scotland that were not subject to significant acidification, it is likely that pH changes in more
436 deposition-impacted areas (including our study sites) significantly exceeded the national means
437 reported, and that acidity reductions thus generated larger DOC increases in these regions. The
438 comparatively small predicted DOC increase for bogs appears to reflect the extent to which pH
439 change in peats has been buffered by other processes such as sulphate (SO_4) reduction (as in the
440 Migneint peat experiment), and the relatively high proportion of the total UK bog area located in

441 less pollution-impacted north-western areas. On the other hand, there is some recent evidence that
442 acidification of peatlands in the UK was at least partly caused by deposition of hydrochloric acid
443 which, unlike sulphuric acid, remains mobile under the reducing conditions associated with
444 waterlogged peats (Evans et al., 2011). Clark et al (2011) showed that laboratory additions of
445 chloride, even as neutral sea-salt, could have a similar effect on peat porewater pH and DOC
446 concentrations to sulphuric acid. This would potentially enhance the magnitude of pH (and therefore
447 DOC) change in areas of high SO_4 retention such as the Migneint peat plots.

448 To our knowledge, relationships between DOC trends and acidity have only previously been inferred
449 from long-term monitoring data (e.g. Monteith et al., 2007), laboratory experiments (Clark et al.,
450 2011), indirect interpretation of results from field N addition experiments (Evans et al., 2008), and
451 from the acidification experiment by Ekström et al. (2011). As noted earlier, monitoring data are
452 susceptible to differing interpretations under conditions where multiple environmental changes are
453 occurring simultaneously, whereas experiments are limited by the need to obtain measurable
454 ecosystem responses during comparatively short manipulation periods, and the accompanying risks
455 of experimental artefacts. By combining monitoring, laboratory and field experimental data, the
456 limitations of each method are to some extent overcome, and the consistent results obtained
457 provide overall support for the hypothesis that DOC increases are attributable to declining acid
458 deposition. The general consistency of our findings (over time at individual sites, for both acid and
459 alkaline treatments, and between four sites with differing soils, vegetation, ambient deposition and
460 acidity), as well as the rapidity of DOC response to pH change, appear best explained by a direct,
461 physico-chemical mechanistic influence of acidity on organic matter solubility. This interpretation is
462 supported by earlier laboratory experiments (e.g. Vance & David, 1989; Tipping and Woof, 1989;
463 Lofts et al., 2001), which derived relationships between DOC and acidity in soil cores, across wide pH
464 ranges. Our data demonstrate that such relationships also operate under vegetated, field conditions,
465 and across the pH range (approximately 3.8 to 4.6) within which much of the observed change in UK

466 upland soil acidity during the last 30 years has taken place (e.g. Emmett et al., 2010; Kirk et al.,
467 2010).

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

492 which could help to explain why overall DOC responses to the acid treatment (in which acidity and
493 ionic strength would have had been reinforcing) appeared somewhat stronger than DOC responses
494 to the alkaline treatments (in which the two effects would have would have been opposing) (Figures
495 2-3). If this were the case, the empirical relationships obtained from the experiments may under-
496 estimate the magnitude of DOC change due to reduced acid deposition.

497 In this study, we have focused on quantitative changes in DOC concentration, but qualitative
498 changes in dissolved organic matter composition may also have important consequences, for
499 example in relation to water colour and drinking water treatment. Other studies have demonstrated
500 compositional changes in DOM alongside rising DOC trends in long-term surface water datasets (e.g.
501 De Wit et al., 2007; Dawson et al., 2009) and in response to field and laboratory experimental acidity
502 manipulations (Clark et al., 2011; Ekström et al., 2011), with which results from our experimental
503 study appear consistent (Oulehle et al., in prep.). The inference from the Migneint podzol site that
504 DOC-pH relationships may break down at higher pH values, or that limitations to DOC supply may
505 begin to outweigh controls on solubility, requires further investigation. Similarly, our study focused
506 only on organic soil horizons, whereas controls on organic matter solubility within mineral soils,
507 associated with adsorption and binding to mineral surfaces, and interactions with metal ions such as
508 aluminium and iron, may lead to more complex responses (e.g. Zech et al., 1994; Kalbitz et al., 2000;
509 Lofts et al., 2001; Löfgren et al., 2010; Mikkuta & Kaiser, 2011). These interactions may help to
510 explain the more heterogeneous, and in some cases divergent, DOC trends observed in monitoring
511 data from mineral soils, noted earlier. In particular, competition for anion adsorption sites between
512 SO_4 and DOC appears to explain decreasing DOC trends in more weathered, iron-rich mineral
513 horizons (e.g. Borken et al., 2011; Wu et al., 2010), a conclusion supported by results from the
514 Solling field experiment in Germany, where $(\text{NH}_4)_2\text{SO}_4$ additions led to large DOC reductions in the
515 mineral soil (Evans et al., 2008). In the more organic soils of the UK uplands, on the other hand, SO_4
516 adsorption capacity is relatively low, and competition between SO_4 and DOC for adsorption sites
517 appears limited (Hughes et al., 2012). In these soils, the effects of acid deposition on DOC leaching

518 may even be amplified by passage through mineral horizons, due to the strong negative effect of Al
519 mobilisation on DOC solubility (Kennedy et al., 1996; Lofts et al., 2001; Chapman et al., 2010).
520 Because Al solubility declines above pH 4.6-4.9 (Nordstrom & Ball, 1987), its effect on DOC solubility
521 in mineral soils may diminish over a similar pH range to the decrease in direct pH effects on DOC
522 solubility in the organic horizon, as inferred from the Migneint podzol data. Although UK soil solution
523 time series data remain insufficient to draw firm conclusions on organic versus mineral horizon
524 trends, our results do not suggest that there is necessarily a disconnection between DOC changes in
525 organic soils and DOC changes in surface waters.

526 Finally, while our data support a physico-chemical control on DOC mobility, it seems likely that this
527 may be reinforced, over longer periods, by the effects of biologically-mediated responses to pH
528 change. Many aspects of soil biological activity, including microbial abundance and activity,
529 decomposition rates and enzyme activity have all been shown to be constrained by low pH (e.g.
530 Baath et al., 1980; Fierer and Jackson, 2006; Sinsabaugh, 2011; Oulehle et al., 2011), therefore a
531 change in DOC production due to pH change might be expected. During the experiment, we made
532 regular measurements of a number of indicators of soil biological activity, including soil enzyme
533 activities and soil CO₂ respiration, but were unable to detect any treatment effects (T. Jones,
534 unpublished data). At this stage, therefore, we have to attribute observed DOC responses to
535 physico-chemical factors, but do not rule out a more gradual biological response. Longer-term
536 experimental manipulation studies and monitoring of DOC production processes will be required to
537 elucidate this further.

538 Overall, based on our results, we conclude that decreasing acid deposition represents a highly
539 plausible driver of the surface water DOC increases observed across many areas. While we would
540 caution against extrapolating results too far from the moorland areas of the UK in which the
541 experiments were undertaken, we note that the soil types they represent, histosols and podzols,
542 occupy substantial areas of Northern and Central Europe, and of Northeast North America, namely

543 those regions in which rising trends in DOC have been recorded. We recognise that our results do
544 not preclude the influence of climatic factors such as discharge, temperature and solar radiation,
545 and indeed there is little doubt that these affect episodic, seasonal, and inter-annual variations, as
546 has been demonstrated in many previous studies (e.g. Erlandsson et al., 2008; Sarkkola et al., 2009;
547 Zhang et al., 2010; Clark et al., 2010). In areas not subject to historic acid deposition these drivers
548 may dominate DOC variability, and where they exhibit long-term changes, factors such as climate
549 may also have led to observed changes in DOC (e.g. Schindler et al., 1997; Striegl et al., 2005) or may
550 be expected to do so in the future (Larssen et al., 2011). Similarly, land-use factors may contribute to
551 spatial DOC variations and, in cases where land-use has changed, to long-term trends. On the other
552 hand, few if any of these drivers have exhibited consistent long-term changes over the last 20-30
553 years, across the full area over which DOC has increased. Based on our results, we do not believe
554 that it is necessary to invoke these additional factors in order to explain the general magnitude and
555 spatial extent of rising DOC trends that have been observed to date (almost exclusively) in areas
556 historically affected by acid deposition (Monteith et al., 2007). The often-cited view that there has
557 been no universal driver of rising DOC trends (e.g. Roulet & Moore, 2007; Zhang et al., 2010; Preston
558 et al., 2011), despite their consistency across large areas, must therefore be open to question.

559 The observed sensitivity of DOC leaching to pH also raises wider questions about the importance of
560 acidity to other aspects of the carbon cycle. Previous studies have suggested that acidity changes
561 may have contributed to observed soil carbon changes in the UK (Evans et al., 2007; Emmett et al.,
562 2010). Experimental liming studies have shown increased soil respiration, enhanced microbial
563 activity and long-term changes in the distribution of soil C, concurrent with pH and DOC increases
564 (Nilsson et al., 2001; Andersson and Nilsson 2001), while methanogenesis may also be sensitive to
565 pH change (Ye et al., 2012). Recent measurements suggest that decreased acid deposition loadings
566 may have caused a 40% loss of organic horizon carbon at a Czech forest monitoring plot (Oulehle et
567 al., 2011). Acidity dynamics are rarely incorporated in carbon models, or considered as a driver of
568 change in carbon fluxes, yet many of the measurements from which process understanding and

569 models have been developed and tested have taken place in Europe and North America against a
570 background of dramatically changing sulphur deposition. Further work is required to establish the
571 impacts of changing soil acidity on the wider carbon cycle, and to ensure that observed changes in
572 terrestrial carbon cycling, particularly those based on measurements in industrialised regions, are
573 not erroneously attributed to other drivers.

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- 787
- 788

789 FIGURE CAPTIONS

790

791 Figure 1. Mean and standard error of soil solution pH and DOC at each experimental site for control,
792 acid and alkaline treatment plots (n=4 per treatment and experimental site). Data are shown for the
793 pre-treatment period (August 2007 to April 2008) and for the last three full years of manipulation.
794 Significant treatment effects by site and time period denoted by * $p < 0.05$, ** $p < 0.01$, *** $p <$
795 0.001 (Table 1)

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

806 Figure 3. Ratio of treatment to control standardised DOC ($RDOC_{std}$) versus ratio of treatment to
807 control standardised hydrogen ion concentration (RH_{std}) for all samples collected in 2009-2011 from
808 all experimental sites and (acid and alkaline) treatments. Trendline shown is of the form $RDOC_{std} =$
809 $1/(RH_{std}^b)$, with b fitted to each dataset by weighted least squares regression (see Methods, Table 2).
810 Open circles represent samples from alkaline treatments, filled circles samples from acid treatments.
811 Solid trendlines show fit to full dataset, dashed trendlines show fit to data after excluding data from
812 the Migneint podzol alkaline treatment.

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

818 Figure 5. Observed changes in hydrogen ion concentrations, and predicted changes in DOC, between
819 1978 and 2007, for the four acidic moorland habitat classes in the UK Countryside Survey. Predicted
820 changes are based on $RDOC_{std}$ vs RH_{std} regressions. Dwarf shrub heath predictions are based on the
821 full dataset, and bog predictions on the combined peat data, both with the Migneint podzol alkaline
822 treatment excluded from regressions. Predictions for the alkaline acid grass and bracken habitats are
823 based on the combined podzol data. Because the pH of these habitats rose above 4.6 by 2007,
824 predicted DOC changes are shown both with (light grey) and without (dark grey) the Migneint podzol
825 alkaline treatment included in the regressions (See Table 2).

826

827 Table 1. Analysis of variance for pH and DOC for pre-treatment, 2009, 2010 and 2011
 828 measurements. One-way analysis of variance against treatment carried out for individual sites, and
 829 two-way analysis of variance for the combined dataset against site and treatment (including a
 830 separate assessment for acid and alkaline treatments across the four sites). Significant effects ($p <$
 831 0.05) highlighted in bold.

832

	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	$F_{1,27} = 1.34$	$p = 0.257$	$F_{1,27} = 9.52$	$p = 0.005$	$F_{1,27} = 8.70$	$p = 0.007$	$F_{1,27} = 16.69$	$p < 0.001$	

833

834

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

Site	Full dataset				Dataset excluding Migneint podzol alkaline treatment data			
	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
<u>Allsitescombined</u>	<u>-0.540</u>	<u>0.34</u>	<u><0.001</u>	<u>299</u>	<u>-0.753</u>	<u>0.47</u>	<u><0.001</u>	<u>271</u>

840

Figure 1

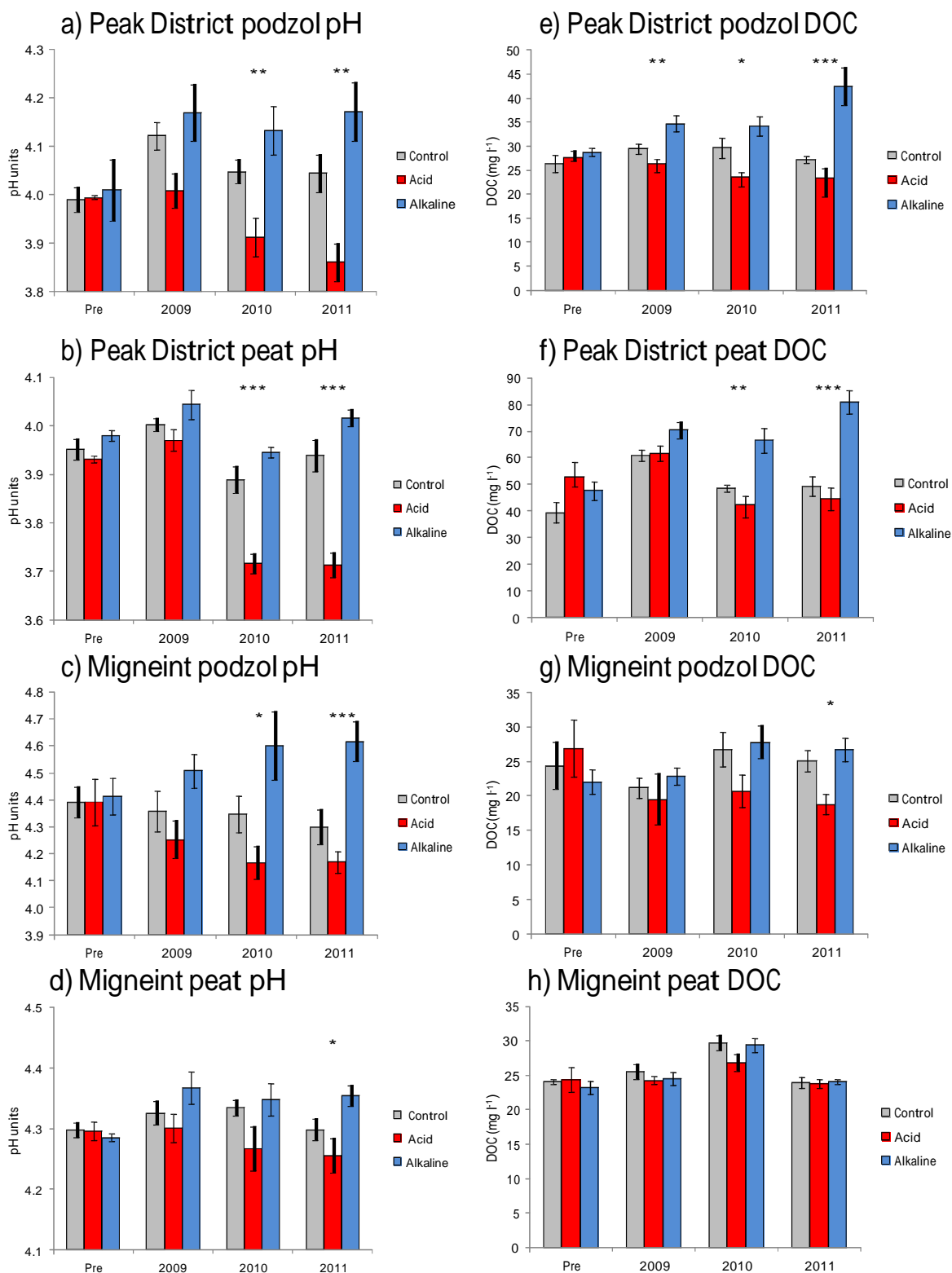


Figure 2

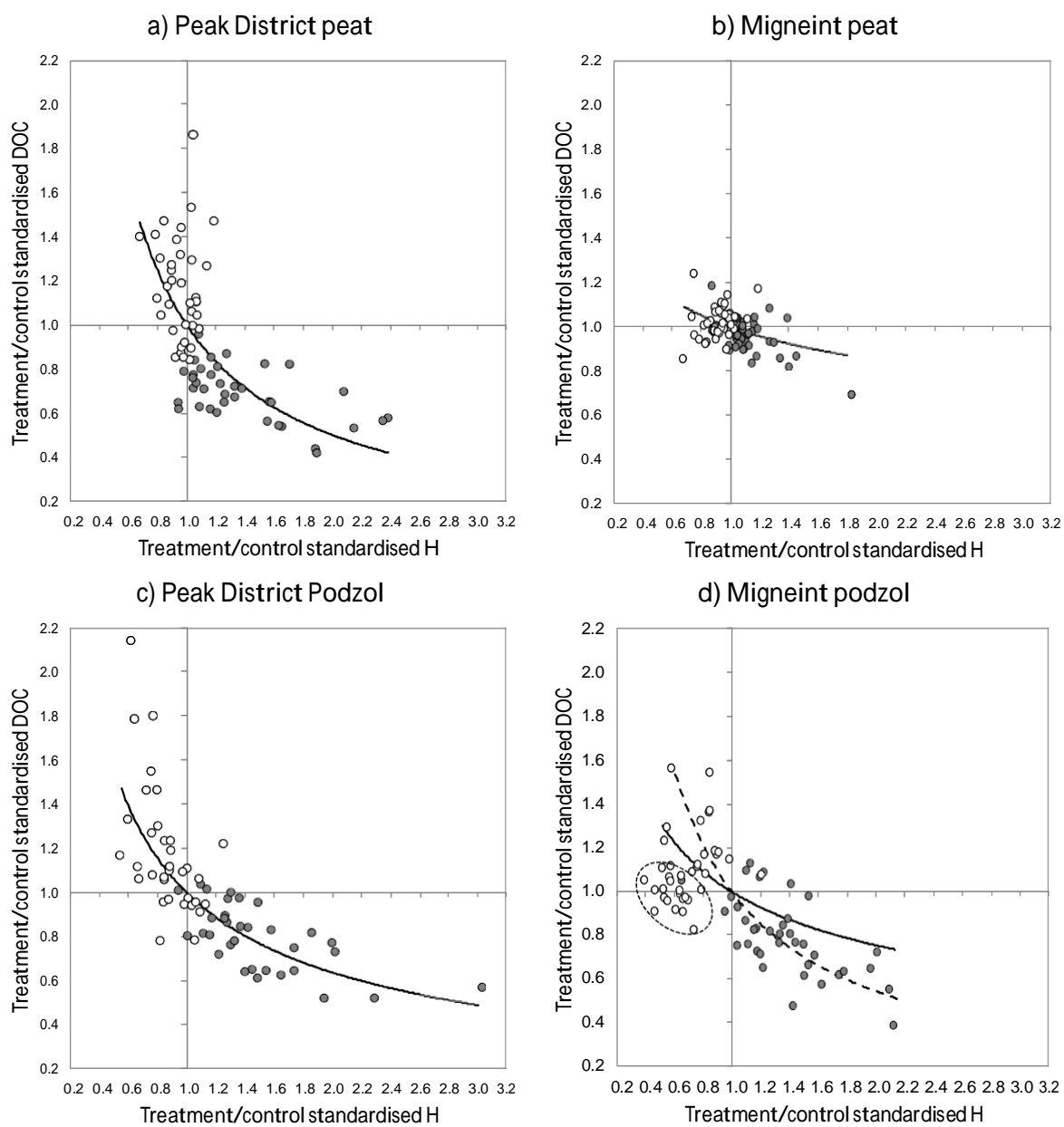


Figure 3

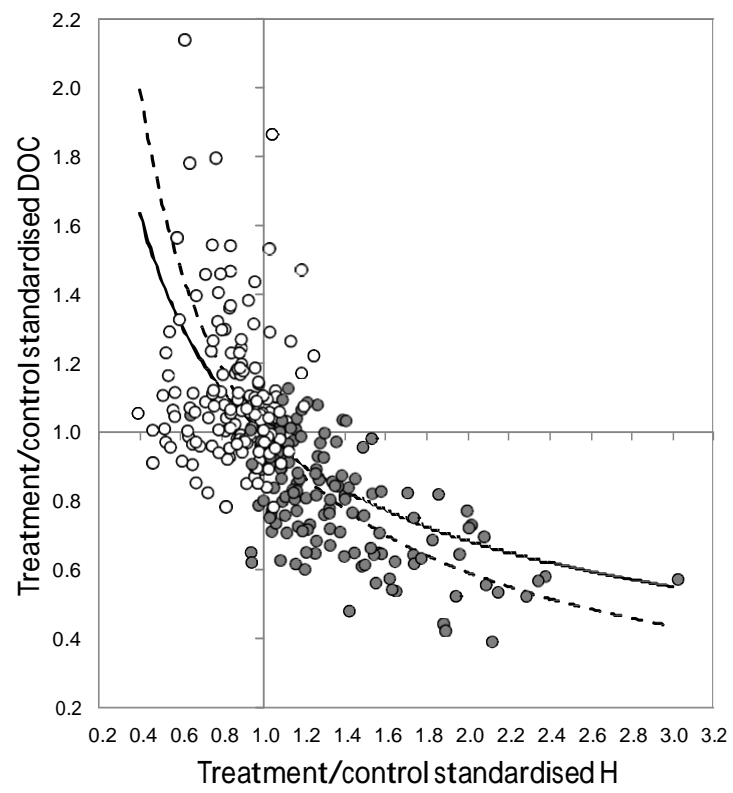
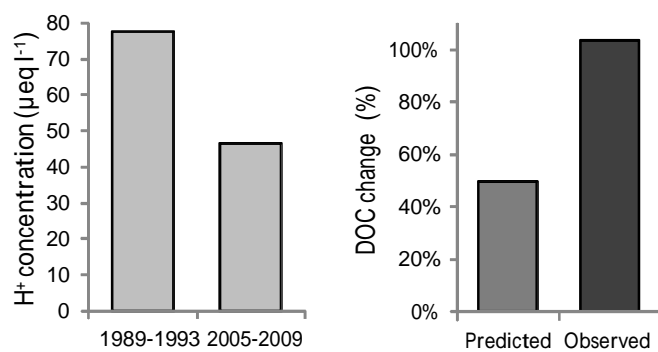


Figure 4

a) River Etherow, Peak District



b) Afon Gwy, Wales

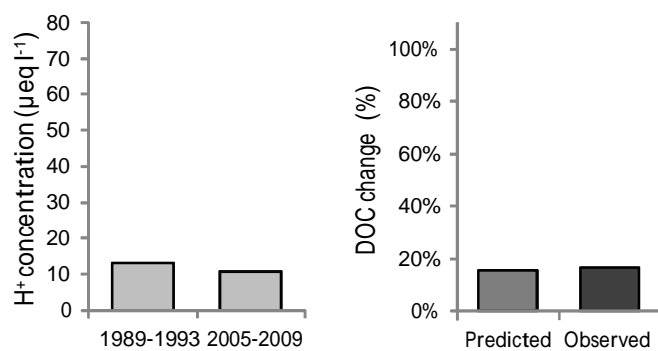


Figure 5

