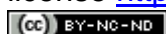


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1 **Modelling impacts of acidifying and eutrophying deposition on DOC trends**

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15 **Keywords:** DOC, acid deposition, eutrophying deposition, recovery, trend, dynamic
16 modelling

17

18

19 **Abstract**

20 It is increasingly recognised that widespread and substantial increases in Dissolved
21 organic carbon (DOC) concentrations in remote surface, and soil, waters in recent decades
22 are linked to declining acid deposition with effects of rising pH and declining ionic strength
23 on DOC solubility proposed as potential dominant mechanisms. However, since DOC in
24 these systems is derived mainly from recently-fixed carbon, and since organic matter

25 decomposition rates are considered sensitive to temperature, uncertainty persists over the
26 extent to which other drivers that could influence DOC production, including fertilization by
27 nitrogen (N) and global warming, may also contribute to these upward trends. We therefore
28 ran the dynamic soil chemistry model MADOC for a range of UK soils, for which time series
29 data are available, to consider the likely relative importance of decreased deposition of
30 sulphur and hydrochloric acid, accumulation of reactive N, and higher temperatures, on soil
31 DOC production and how this might differ between soils. Modelled patterns of DOC change
32 generally agreed favourably with measurements collated over 10-20 years, but differed
33 markedly between sites. While the acidifying effect of sulphur deposition appeared to be the
34 predominant control on the observed soil water DOC trends in all the soils considered other
35 than a blanket peat, the model suggested that over the long term, the effects of nitrogen
36 deposition on N-limited soils may have been sufficient to raise the “acid recovery DOC
37 baseline” significantly. In contrast, reductions in non-marine chloride deposition and effects
38 of long term warming appeared to have been relatively unimportant. The suggestion that
39 future DOC concentrations might exceed preindustrial levels as a consequence of
40 atmospheric eutrophication has important implications for drinking water catchment
41 management and the setting and pursuit of appropriate restoration targets, but findings still
42 require validation from reliable centennial-scale proxy records, such as those being developed
43 using palaeolimnological techniques.

44

45 **1. Introduction**

46 Long-term monitoring of surface water quality has revealed increasing concentrations
47 of dissolved organic carbon (DOC) across large parts of the Northern Hemisphere,
48 particularly close to industrialised regions (Skjelkvale et al., 2001, Driscoll et al., 2003,
49 Evans et al., 2005, Monteith et al., 2007, Erlandsson et al., 2008). These observations have

50 raised concerns over increasing water treatment costs (Ritson et al., 2014b) and possible
51 destabilisation of terrestrial carbon stocks (Freeman et al., 2001). A debate has ensued over
52 the possible causes of observed increases (Clark et al., 2010), that have included climate
53 change (Freeman et al., 2001), changes in land management and use (Yallop and Clutterbuck,
54 2009), nitrogen (N) deposition (Findlay, 2005), CO₂ enrichment (Freeman et al., 2004) and
55 declines in acid deposition (Evans et al., 2006, Monteith et al., 2007). Analyses of surface
56 water data (Evans et al., 2006, de Wit et al., 2007, Oulehle and Hruška, 2009, Erlandsson et
57 al., 2010, Monteith et al., 2014), supported by evidence from laboratory (Clark et al., 2006,
58 Clark et al., 2011) and field studies (Clark et al., 2005, Ekström et al., 2011, Evans et al.,
59 2012) have pointed to effects of declining sulphur deposition as the major cause, but do not
60 exclude the possibility that other drivers have also exerted influence on DOC trends.

61

62 Decreases in acid anion concentrations and increases in soil pH associated with a
63 reduction in acid deposition are thought to have increased the solubility of potentially-
64 dissolved organic matter by increasing negative charges on humic surfaces (Tipping and
65 Woof, 1991). There is also evidence that regional warming (e.g. Freeman et al., 2001, Pastor
66 et al., 2003) and changes in precipitation patterns (e.g. Keller et al., 2008, Pumpanen et al.,
67 2014) can affect DOC concentrations by influencing decomposition rates, vegetation type or
68 export paths. A further suggested mechanism is the effect of changed flow paths due to
69 changing precipitation patterns (e.g. Hongve et al., 2004, Erlandsson et al., 2008, Couture et
70 al., 2012). The relative degree to which these factors have contributed to DOC trends has
71 been debated extensively (e.g. Evans et al., 2006, Eimers et al., 2008, Futter and de Wit,
72 2008, Clark et al., 2010).

73

74 Several studies suggest that there is also a link between N deposition and DOC
75 leaching (e.g. Pregitzer et al., Findlay, 2005, Bragazza et al., 2006). Nitrogen typically limits
76 productivity in terrestrial ecosystems (Vitousek and Howarth, 1991), so increased net
77 ecosystem productivity due to N deposition might be expected to may increase the pool of
78 ecosystem C available for DOC production. This would, however, depend on prevailing
79 levels of ecosystem N saturation. In N-limited ecosystems addition of reactive N would be
80 expected to exert a fertilizing effect (LeBauer and Treseder, 2008). Conversely in N-saturated
81 environments additional N would be expected to contributes to acidification (Emmett et al.,
82 1998), that in turn could reduce decomposition (Janssens et al., 2010), and consequently a
83 reduction in DOC production and solubility. To predict how DOC levels are likely to change
84 in future it is therefore necessary to consider the integrated effects of acidifying and
85 eutrophying effects of air pollution and climate change on productivity, decomposition and
86 organic matter dissolution.

87

88 One of the criticisms levelled at investigations into the drivers of DOC increases in
89 soils or waters is that studies founded on correlation (e.g. Skjelkvale et al., 2001, Vuorenmaa
90 et al., 2006, Monteith et al., 2007, Oulehle and Hruška, 2009, Sarkkola et al., 2009, Zhang et
91 al., 2010, Borken et al., 2011) do not in themselves provide proof of causation (Roulet and
92 Moore, 2006). In addition, study sites tend to be concentrated within geographically limited
93 areas and findings may, therefore, not necessarily be universally applicable. Furthermore,
94 although soils (particularly upper organic horizons) are recognised to often be the source of
95 most freshwater DOC (e.g. Brooks et al., 1999, Billett et al., 2006, Evans et al., 2007a,
96 Winterdahl et al., 2011), soil water monitoring data are scarce, and typically of shorter
97 duration than surface water data. There is increasing evidence that shallow soil water makes a
98 major contribution to trends in DOC in surface water (Hruška et al., 2014, Sawicka et al.,

99 2016). Despite their limitations, however, long-term soil water monitoring data provide the
100 most effective resource for testing whether mechanisms that have been shown to operate in
101 experiments also operate at larger spatial and temporal scales. Therefore, we brought together
102 the United Kingdom's best long term soil solution records in order to provide a foundation
103 for testing our current process understanding and consider how anticipated change in climate
104 and deposition are likely to influence future behaviour of DOC.

105

106 To date, the majority of DOC process-based modelling studies have concentrated on
107 model developments and potential applications, or on simulating time series for direct
108 comparison with measurements (e.g. Futter et al., 2007, Futter et al., 2011, Jutras et al., 2011,
109 Xu et al., 2012, Zhang et al., 2013, Dick et al., 2014). Relatively few, in contrast have gone
110 on to consider the longer-term implications of model parameterisation, such as the most
111 likely pre-industrial "baseline" DOC levels that can help to inform catchment restoration and
112 management strategies. Exceptions include, Hruška et al. (2014), who linked a simple
113 empirical DOC function to the MAGIC acidification model to recreate DOC trends in an
114 acid-sensitive podzol site in the Czech Republic. This study was however based on modelling
115 DOC at organo-mineral sites only. Valinia et al. (2015), in turn, reconstructed reference
116 conditions of total organic carbon and long-term monitoring data to predict recent DOC
117 changes in Swedish lakes. Historic reconstructions like these provide a framework with
118 which to consider the likely relative importance of various potential anthropogenic pressures.

119

120 In the current study, DOC trends were simulated at long-term monitoring sites using
121 an annual time-step model, with the aim of exploring the likely relative importance of
122 different drivers and considering how DOC concentrations in soil water might be expected to
123 change in the future. Here we use the MADOC model (Rowe et al., 2014) which simulates

124 the long-term controls on DOC from terrestrial sites to streams, is responsive to a number of
125 drivers, and can be applied to catchments at any scale using a lumped-parameter approach.
126 The model is a representation of soil and vegetation carbon dynamics, acid-base dynamics
127 and organic matter dynamics. It has been shown to reproduce the effects of the key drivers of
128 DOC in terrestrial experimental sites and long-term surface water monitoring sites (Rowe et
129 al., 2014). We set out to first test the model directly against soil water monitoring data, and
130 then consider the likely relative effects of key contributory drivers in the model in influencing
131 soil water DOC at a range of sites with different characteristics over the longer term. We
132 therefore applied MADOC to six terrestrial long-term monitoring sites characterised by
133 different vegetation, soil type and acid deposition loading and considered: (1) the extent of
134 discrepancies between modelled trends, based on the hypothesised drivers (anthropogenic
135 sulphate, chloride, N deposition, temperature change), and measured trends and (2) the
136 changes that would have occurred with and without individual drivers to assess the
137 magnitude of impact of each on different ecosystems and on future DOC dynamics.

138

139 **2. Methods**

140 **2.1 *Field sites, measurements and chemical analysis***

141 Data from three United Kingdom Forest Level II (FLII) and three terrestrial
142 Environmental Change Network (ECN) sites were used for this study (Figure 1). FLII sites
143 were established in 1995 (Vanguelova et al., 2007) and form part of the European forest
144 monitoring network (ICP Forests) that aims to improve understanding of the effects of air
145 pollution and other environmental factors on forest ecosystem structure, function and health.
146 The monitoring at ECN sites started in 1993 with the objectives of gathering long-term
147 datasets to improve understanding of the causes and consequences of environmental change
148 across a range of semi-natural and agricultural habitats in the UK (ECN, 2014).



149

150 **Figure 1 Site locations. Triangles indicate Forest Level II monitoring sites (FRLII) and circles indicate**
 151 **Environmental Change Network (ECN) sites.**

152

153 The FLII sites were composed of stands of Oak (*Quercus robur* and *Q. petraea*) at Grizedale,
 154 Scots pine (*Pinus sylvestris*) at Ladybower and Sitka spruce (*Picea sitchensis*) at Llyn
 155 Brianne, under standard forest management practices including thinning and brashing during
 156 their growth cycle. The forest stands were planted between 1920 and 1974 and cover a range
 157 of forest yield classes. The soils were developed from a range of parent materials and include
 158 gleysols and podzols (Table 1). The ECN terrestrial sites represent non-forest environments,
 159 which are upland grassland (Sourhope) or heathland (Glensaugh) and blanket bog (Moor
 160 House) vegetation, subject to seasonal grazing, mainly by sheep. Soil types at the ECN sites
 161 include histosols and podzols (Table 1).

162

163 **Table 1 Sites descriptions. Mean annual median daily temperature (MAT) and precipitation (MAP) are averaged**
 164 **over period of 5 years 2002-2006. World Reference Base (WRB) classification used to define soil types.**

Site name	Network	Soil type (WRB)	Vegetation type	Altitude [m]	MAT [°C]	MAP [mm]	Acid deposition (Cl + NO ₃ + SO ₄) [meq m ⁻² y ⁻¹]
Glensaugh	ECN	Podzol	Grassland/ Heathland	300	7.8	1530	263
Moor House	ECN	Histosol	Blanket bog	540	6.1	1930	209
Sourhope	ECN	Podzol	Grassland	495	7.7	1280	138
Grizedale	FLII	Podzol	Deciduous forest	115	9.6	1920	423
Ladybower	FLII	Podzol	Coniferous forest	265	10.5	1265	332
Llyn Brianne	FLII	Gleysol	Coniferous forest	450	10.1	2020	447

165

166 The six study sites covered a gradient of S, N and Cl deposition from 44 to 86, 40 to
 167 90, and 94 to 306 meq m⁻² yr⁻¹, respectively (long-term mean between 1993 and 2010
 168 depending on the site), with a range of soil organic carbon (SOC) content (0.8 to 48.7 %), and
 169 C/N ratio (3 to 70 g g⁻¹), soil acidity (pH 3.6 to 7.0), soil sensitivities to acid deposition (e.g.
 170 base saturation (BS) 1.1 to 100 %, and Al saturation (Al sat.) 0 to 93.5 %). The sites cover an
 171 altitudinal gradient from 115 m to 540 m above sea level. Mean annual temperature (MAT)
 172 (for period 2002-2006) varied from 6.1 °C at Moor House up to 10.5 °C at Ladybower; and
 173 mean annual precipitation (MAP) (for 2002-2006) from 1265 mm yr⁻¹ at Ladybower to 2020
 174 mm yr⁻¹ at Llyn Brianne. Additional information about the monitoring networks is available
 175 in Vanguelova et al. (2007) and (Sier and Monteith, 2016).

176

177 At FLII sites soil water samples were collected every two weeks using tension
 178 lysimeters (PRENART SuperQuartz soil water samplers, Plenart Equipment Aps, Denmark).
 179 Twelve lysimeters were installed at each site, six located at 10 cm soil depth and the other six
 180 at 50 cm soil depth. Soil water samples were collected and measured according to Level II
 181 protocols described in detail in the ICP forests manual (ICP, 2006). Water samples were
 182 filtered through a 0.45 µm membrane filter and analysed for pH; total aluminium (Al),
 183 calcium (Ca), magnesium (Mg), potassium (K), sodium (Na) and iron (Fe) by ICP-OES
 184 (Spectro-flame, Spectro Ltd.); ammonium N (NH₄-N) colorimetrically with sodium

185 salicylate and sodium dichloroisocyanurate; DOC by total carbon analyser (Shimadzu 5000,
186 Osaka, Japan) using catalytic or persulphate oxidation; and sulphate (SO₄), nitrate (NO₃) and
187 chloride (Cl) by Ion Chromatography (Dionex DX-500). Quality assurance and quality
188 control on dissolved ion concentrations in soil water are described by De Vries et al. (2001)
189 and in the ICP manual (2006). ECN soil waters were also sampled fortnightly by tension
190 lysimetry using the same Prenart SuperQuartz samplers. According to the Environmental
191 Change Network (ECN) protocols six samplers were placed at the base of each A and B
192 horizons, except for deep peats where fixed depths of 10 and 50 cm depths were used. Soil
193 water was analysed for pH, then filtered (<0.45 µm) and analysed for DOC by combustion
194 oxidation and IR (infra-red) gas detection; total metals (Al, Ca, Fe, K, Mg, Na) by ICP-OES;
195 Cl⁻, SO₄ by Dionex ion chromatography; and NO₃ colorimetrically with with sodium
196 salicylate and sodium dichloroisocyanurate.

197

198 At each FLII sites, samples from two bulk precipitation (installed in the open ground
199 near the forest plots) and 10 throughfall collectors (installed under the stands canopy) were
200 collected every two weeks from 1995 until 2006 and precipitation volumes determined by
201 weighing. Water samples were filtered and analysed for the same determinants and by the
202 same methods as soil water samples. Bulk precipitation chemistry was measured at the ECN
203 sites. Samples were collected weekly and were analysed using the same methods for the same
204 determinants as in soil water.

205

206 Soils at all FLII and ECN sites were surveyed between 1993 and 1995. In each plot,
207 the soil was described according to the FAO soil classification system and classified
208 according to the World Reference base for soil classification (WRB, 2014). FLII soil
209 sampling and analyses were carried out according to the UNECE ICP Manual for Soil

210 Sampling and Analysis (2006). ECN sites surveys were conducted using standard methods
211 (Sykes and Lane, 1996).

212

213 Meteorological data for Grizedale, Ladybower and Llyn Brianne were derived from
214 the nearest Met Office weather stations available through the British Atmospheric Data
215 Centre (Met Office - MIDAS Land Surface). Each ECN site has a designated automatic
216 weather station recording hourly climatic data and manual equipment is installed at sites to
217 provide quality control (Morecroft et al., 2009).

218

219 **2.2 Simulation approach**

220 The MADOC model was developed to simulate long-term changes in carbon and N
221 cycling and soil acidity, and is described fully in Rowe et al. (2014). The model simulates
222 soil and dynamics in a 1-D column, using three annual time-step submodels as summarised
223 below. Production and decomposition of organic matter is simulated by N14C (Tipping et al.,
224 2012). The model simulates carbon inputs from vegetation productivity, which is determined
225 by temperature, precipitation and N supply. Nitrogen is supplied only from N fixation until
226 the beginning of the industrial period, after which impacts of anthropogenic N deposition are
227 simulated. Nitrogen uptake, immobilization, mineralisation and denitrification processes are
228 included. Decomposition and loss of soil organic matter (SOM) is simulated using conceptual
229 pools with fast, intermediate and slow turnover rates. Most SOM C is lost during turnover as
230 CO₂, with corresponding mineralisation of SOM N to mineral N forms; but a proportion of
231 the calculated turnover enters a 'potentially dissolved' pool. The solubilisation and dynamics
232 of this pool are calculated using a simplified version of DyDOC (Michalzik et al., 2003).
233 Potentially-dissolved organic matter is partitioned into soluble and solid phases, based on
234 current pH and dilution as determined by net water flux. The solid phase is retained as pDOM

235 and may be solubilised subsequently or lost through mineralisation. The soluble phase (DOC
236 and DON) is leached from the topsoil and mainly enters the freshwater system, although a
237 proportion is sorbed in the subsoil where it is subject to further mineralisation. Acid-base
238 dynamics are simulated using VSD (Posch and Reinds, 2009). A constant proportion of DOC
239 is assumed to potentially form acid anions, *i.e.* the dissociation site density, P_{sites} . Simulated
240 soil solution chemistry depends on concentrations of organic anions; nitrate (NO_3) and
241 ammonia (NH_4) inputs as calculated by the N14C model; deposition inputs of the main other
242 acid anions (SO_4 and Cl) and base cations (Na, Ca, Mg and K); and interactions with soil
243 surfaces. Ionic exchange is described by equations that define competition among cations for
244 exchange sites and thus the partitioning of ions between the solution and adsorbed phases.

245

246 Since more organic acid anions enter the soil solution when acidity decreases, there is
247 a negative feedback between pH and DOC concentration, and the MADOC model was
248 previously prone to instability when there were abrupt changes in pollutant deposition. The
249 calculation method was improved using a simple second-order integration algorithm, in
250 which the model was first run forward to determine what the organic anion concentration
251 would be assuming no change in pH. The change in pH that this change in anion
252 concentration would result was then calculated. The actual change in soil water pH was
253 assumed to be half of this change, and the actual organic anion concentration was
254 recalculated accordingly. This modification did not change equilibrium values for model
255 outputs, but resulted in considerably faster and more reliable convergence.

256

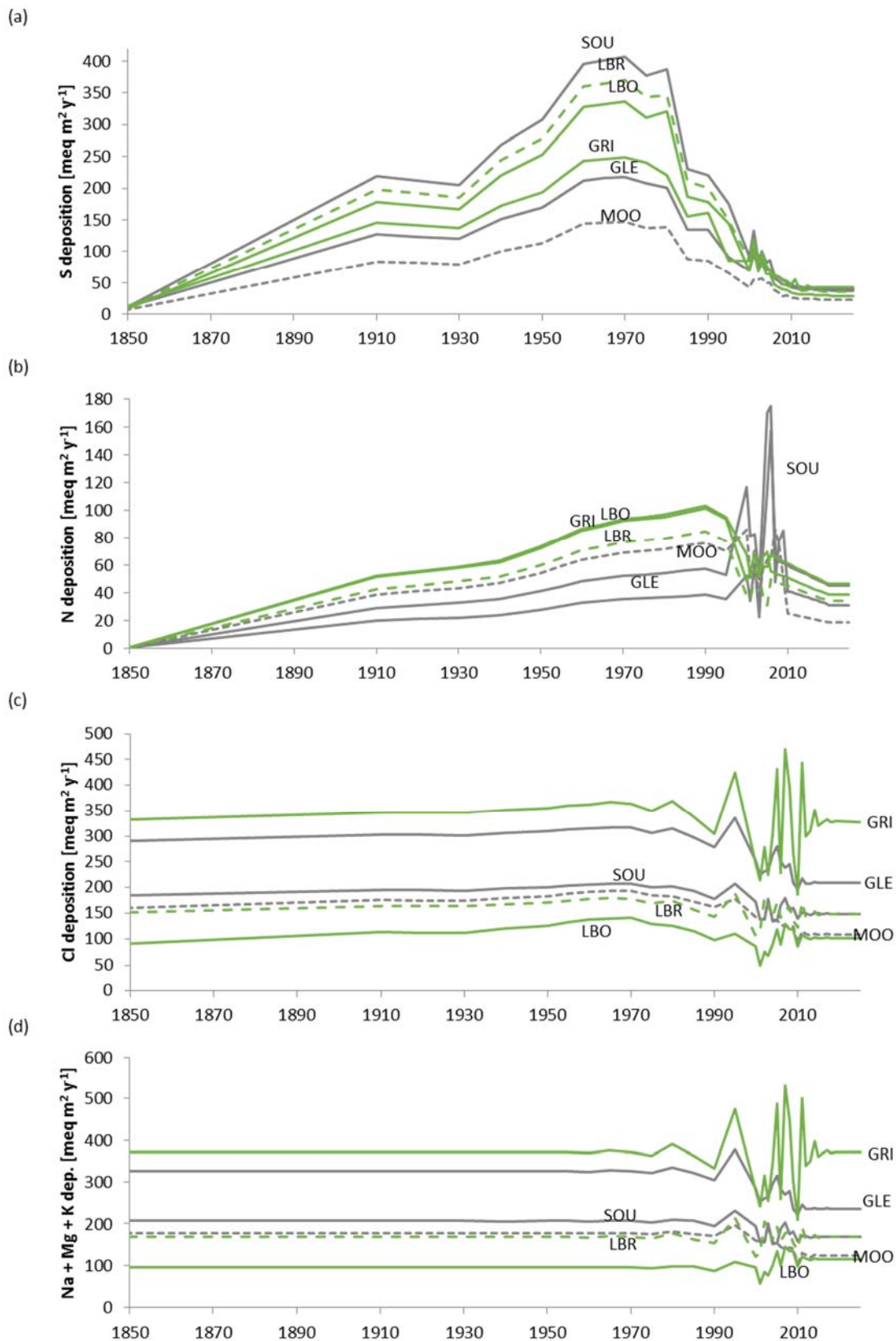
257 **2.3 Model setup and calibration**

258 **2.3.1 Data preparation**

259 Deposition input trajectories (Figure 2) were developed using a combination of
260 modelled, measured and calibrated data. Measured NO₃ and NH₄ deposition was used for the
261 years where it was available (1993-2010 for ECN sites and 1996-2006 for FLII sites). For the
262 previous (from 1850) and subsequent years (including forecasts), modelled sequences from
263 FRAME model were used (Dore et al., 2009). The pre-industrial level of N input, comprising
264 natural deposition plus N₂ fixation (DeLuca et al., 2008), was set at 0.3 g m⁻² yr⁻¹ (Tipping et
265 al., 2012). Anthropogenic N deposition during the 1850 - 1910 period was assumed to
266 increase linearly from zero to the rate calculated by the deposition model for 1910 (Rowe et
267 al., 2014).

268

269 The 'present day' was defined as year 2010 and present-day deposition was adjusted
270 for each site to the mean non-marine sulphate (nmSO₄) in soil water in 2010. Peatlands often
271 retain a proportion of S inputs in reduced organic forms and sulphides (Adamson et al.,
272 2001), and the sulphate retention coefficient (fS_{ret}) for the peatland site included in the study
273 was set to 0.6 on the basis of input-output fluxes. The soils of the remaining (non-peat) sites
274 were assumed not to retain significant amounts of S, and thus fS_{ret} was set to zero. Transport
275 of SO₄ through the soil profile was otherwise assumed to be conservative, and present-day
276 nmSO₄ deposition at the site was calculated as that required to produce the observed soil
277 output flux. The long-term nmSO₄ deposition sequence was then calculated by scaling the
278 sequence observed at the Eskdalemuir monitoring site for the years 1973 – 2007 (Fowler et
279 al. (2005) to the site value. Historic S deposition trajectories (1850-1973) were obtained by
280 scaling estimates obtained using the FRAME model (Dore et al., 2009) to the calculated
281 value for 1973. In order to calculate the total deposition load the dry deposition S trend was
282 assumed to be uniform across the UK and proportional to bulk deposition, as in Fowler et al.
283 (2005).



284

285 Figure 2 Trajectories of deposition rates for: (a) total nitrogen [meq N m⁻² y⁻¹], (b) total sulphate [meq S m⁻² y⁻¹],
 286 (c) total chloride [meq Cl m⁻² y⁻¹], and (d) sum of total base cations [meq Na + Ca + Mg + K m⁻² y⁻¹] for the
 287 studied sites. Green colour indicates forested sites and grey colour indicates non-forested sites. Solid line indicates
 288 podzol sites, dotted line indicates peat and dashed line indicates gleysol.

289

290 To account for anthropogenic Cl deposition, sites were allocated to one of four non-
291 marine Cl (nmCl) regional deposition patterns in geographical zones after Evans et al. (2011).
292 Present day nmCl deposition was assumed to be negligible and linear regression was used to
293 reconstruct preceding annual mean values of nmCl deposition up to year 1986 (the earliest
294 year represented in Evans et al., (2011)). The trajectory of nmCl before year 1986 was
295 assumed to have the same shape as anthropogenic S deposition.

296

297 Trends in sea-salt ion deposition, namely the marine fractions of total Cl, Mg, Ca, K
298 and marine SO₄, deposition trajectories, were calculated on the basis of the ratios in which
299 these ions are known to occur with Na in sea water. Firstly, all Na was assumed to be of
300 marine origin, and ‘present day’ marine inputs of Na⁺ were calibrated to soil water
301 concentrations using solver. Next, Cl deposition was calculated using the marine proportions
302 factor of 1.163 (Evans et al., 2001). If the Cl concentration in soil water was overestimated
303 then Na deposition would be adjusted to match the calculated Cl deposition, and the
304 subtracted in this process Na was assumed to come from weathering. Deposition of other sea-
305 salt cations was then calculated on the basis of the ratios in which these ions are known to
306 occur with Na⁺ in sea water (eq eq⁻¹): 0.244 for Mg²⁺, 0.047 for Ca²⁺, 0.022 for K⁺ and 0.121
307 for SO₄²⁻, following Evans et al. (2001).

308

309 The mean annual temperature (MAT) trajectory for each site was modelled using a
310 HadCRUT4 (Morice et al., 2012b) mean annual average temperatures for the northern
311 hemisphere from the beginning of the previous century until present (Morice et al., 2012a)
312 fitted to the present-day values.

313

314 Inputs for the MADOC model are listed in Table 2 and Table 3. The annual
315 precipitation surplus, i.e. the water flux flowing down through the soil profile, was assumed
316 to equal annual effective rainfall. Organic acids were assumed to be triprotic, and mean
317 values from a study by Oulehle et al. (2013) were used to set dissociation constants for the
318 three protons. The partial pressure of CO₂ in solution in soil was assumed to be 0.037 atm,
319 i.e. 100 times atmospheric concentration (Rowe et al., 2014). Net base cation uptake was
320 assumed to be zero, except for forested sites where a constant uptake rate was assumed from
321 the initiation of each plantation (Table 4). Weathering of N, Cl and S was assumed to be zero.
322 The temperature range (i.e. the difference between growing season and non-growing season
323 mean temperature) was set to 7oC for all sites. The temperature coefficient Q₁₀ was
324 assumed to be 2.0, i.e. decomposition measured in terms of soil respiration (i.e. CO₂ loss)
325 doubles for a 10oC increase in temperature (Kätterer et al., 1998, Davidson and Janssens,
326 2006, Xu et al., 2014). Values for MADOC inputs which are difficult to ascertain
327 empirically were then obtained by calibrating the model to observations, as described below.
328 Values for other input parameters for the N14C sub-model were as described by Tipping et
329 al. (2012).

330 **Table 2 Site-specific inputs for the MADOC model.**

Input	Description	Glensaugh	Moor House	Sourhope	Grizedale	Ladybower	Llyn Brianne
k_{AlOx}	aluminium equilibrium constant	0.001 ^a	0.001 ^a	0.001 ^a	80.0 ^a	0.01 ^a	0.001 ^a
k_{minpd}	Proportion of potential DOC mineralized, yr ⁻¹	0.094 ^a	0.076 ^a	0.049 ^a	0.276 ^a	0.037 ^a	0.133 ^a
k_{inpdC}	Proportion of C turnover entering potentially-dissolved pool	0.172 ^a	0.240 ^a	0.227 ^a	0.145 ^a	0.086 ^a	0.171 ^a
P_{sites}	Dissociable protons per mol DOC, eq(-) mol ⁻¹	0.134 ^a	0.130 ^a	0.110 ^a	0.09 ^a	0.110 ^a	0.15 ^a
W_{Na}	weathering rate for Na, meq m ⁻³ yr ⁻¹	0.614 ^a	0.805 ^a	0.725 ^a	0 ^a	0 ^a	0.31 ^a
W_{BC}	topsoil weathering rate for base cations (Ca ²⁺ + Mg ²⁺ + K ⁺) meq m ⁻³ yr ⁻¹	0.197 ^a	0.398 ^a	0.701 ^a	0.891 ^a	0.715 ^a	0 ^a
T_{org}	thickness of organic soil horizon, m	0.10	0.1	0.1	0.02	0.025	0.1
T_{min}	thickness of mineral soil horizon, m	-	-	-	0.08	0.075	-
$PPTN$	annual precipitation, m	1.532	1.933	1.28	1.92	1.264	2.02
W_d	precipitation surplus or drainage flux, m yr ⁻¹	1.33	1.73	1.07	1.23	0.37	0.92
BD	soil field bulk density, kg dry mass L ⁻¹	0.22	0.07	0.24	0.243	0.492	0.434
θ	average annual volumetric water content, m ³ m ⁻³	0.74	0.77	0.79	0.64	0.52	0.77
P_{nit}	nitrate proportion of (nitrate + ammonium)	0.74	0.29	0.262	0.92	0.99	0.88
MAT	mean annual temperature, °C	7.6	6.1	7.7	9.6	10.5	10.1
$Planttype$	1=Broadleaf, 2=Conifer, 3=Herbs, 4=Shrub	4	4	3	1	2	3
CEC	cation exchange capacity, meq kg ⁻¹	234.36	498.82	152.28	129.18	65.13	165.36
f_{Sret}	proportion of S deposition retained	0 ^a	0.603 ^a	0 ^a	0 ^a	0 ^a	0 ^a
K_{AlBc}	selectivity constant for Al-Bc exchange	6.3 ^b	8.7 ^b	6.3 ^b	6.3 ^b	6.3 ^b	6.3 ^b
k_{inpdN}	Proportion of N turnover entering potentially-dissolved pool	0.066 ^a	0.09 ^a	0.114 ^a	0.104 ^a	0.03 ^a	0 ^a

331 ^a fitted; ^b (Hall et al., 2003);

332 **Table 3 Fixed inputs for the MADOC model.**

Input	Description	Value
α_{org}	DOC sorption constant in organic soil, $\text{m}^3 \text{g}^{-1} \text{L mol}^{-1}$	6.34×10^6 ^a
α_{min}	DOC sorption constant in mineral soil, $\text{m}^3 \text{g}^{-1} \text{L mol}^{-1}$	6.88×10^6 ^a
$pKpar(1)$	1 st dissociation constant for triprotic organic acids	3.5 ^c
$pKpar(2)$	2 nd dissociation constant for triprotic organic acids	4.4 ^c
$pKpar(3)$	3 rd dissociation constant for triprotic organic acids	5.5 ^c
K_{HBc}	selectivity constant for H-Bc exchange	199.5 ^b
exp_{Al}	aluminium equilibrium exponent	1.85 ^d
Q_{10}	Rate of decomposition change driven by 10°C temperature increase	2.0 ^e

333 ^a fitted; ^b Hall et al. (2003); ^c(Oulehle et al., 2013), ^dUBA (2004), ^e (Kätterer et al., 1998)

334

335

336 **Table 4 Site-specific base cation uptake [$\text{meq m}^{-2} \text{y}^{-1}$] for forested sites included as a flat rate from approximate**
 337 **plantation start.**

Site	Plantation start	Uptake [$\text{meq m}^{-2} \text{y}^{-1}$]		
		Ca ²⁺	Mg ²⁺	K ⁺
Grizedale	1900	19.5	3.5	8.5
Ladybower	1952	17.7	5.3	4.0
Llyn Brianne	1965	25.3	6.5	7.9

338

339

340 2.3.2 Calibration of model parameters

341 The model was calibrated to the measurements made at each site individually. The
 342 methodology for the calibration procedure was based on that described by Rowe et al. (2014).
 343 The calibration was based on minimizing the sum of absolute differences between
 344 observations and predictions using the Nelder-Mead simplex method (Nelder and Mead,
 345 1965). For simultaneous calibrations to more than one type of indicator, indicators were
 346 given equal weighting by dividing each error term by the mean measured value. Simulations
 347 began 12,000 years before present, to allow organic matter pools simulated by the N14C sub-
 348 model to stabilize. Parameter values were fitted in the following sequence: 1) Na⁺ and BC
 349 weathering rates (W_{Na} , W_{BC}) were calibrated for each site to best predict the concentrations in
 350 soil water; 2) the proportion of N entering the potentially dissolved pool (k_{inpdN}) was
 351 calibrated for each site to minimize error in the average C/N ratio in soil above the

352 lysimeters; 3) the proportion of C entering the potentially dissolved pool (k_{impdC}) and the
353 mineralization rate (k_{minpd}) were calibrated to best predict DOC concentration; 4) the site
354 density of potentially dissociated organic acid functional groups on DOC (P_{sites}) (constrained
355 to the range between 0.09 – 0.15 eq mol⁻¹) (Oulehle et al., 2013) was calibrated for each site
356 and soil type to minimize error in soil water pH.

357

358 *2.3.3 Model performance*

359 The accuracy of DOC predictions was assessed using the Nash-Sutcliffe (NS)
360 efficiency criterion (Nash and Sutcliffe, 1970). Values of NS are between $-\infty$ and 1, where 1
361 is a perfect fit, and any positive value suggests the model is a better predictor than the mean
362 of the observations. The NS statistic provides only an overall assessment of whether
363 predictions match observations (e.g. Schaepli and Gupta, 2007, Jain and Sudheer, 2008,
364 Jackson-Blake et al., 2015) so we also visually inspected the patterns and behaviours that
365 were reproduced by the model.

366

367 *2.3.4 Pollution and climate scenarios*

368 The scenarios for the historic DOC simulations are listed in Table 5. These were
369 designed to assess the relative impact of four plausible causes of DOC increases. The model
370 was run with (1) combined effect of warming, anthropogenic S, anthropogenic Cl, and N, (2)
371 no anthropogenic forces, (3) anthropogenic warming only, (4) anthropogenic S effect only,
372 (5) anthropogenic Cl effect only, (6) anthropogenic N effect only.

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377 **Table 5 Description of scenarios used for analysing alternative DOC trends.**

Scenario	Description
1	Combined effect of the selected drivers (S, N, Cl and warming) ^a
2	No anthropogenic force ^b
3	Anthropogenic warming only ^c
4	Anthropogenic S effect only ^d
5	Anthropogenic Cl effect only ^e
6	Anthropogenic N effect only ^f

378 ^a deposition and temperature trajectories as described in section 2.3 - Model setup and calibration; ^b all
 379 deposition and temperature values set to value from 1850 year (presented in section 2.3 - Model setup and
 380 calibration) and assumed constant throughout the simulation period; ^{c, d, e, f} combinations of one of the selected
 381 potential DOC trends drivers 'on' and the remaining 'off'.
 382

383

384 **3. Results**

385 **3.1 Major ions in soil solution**

386 Overall, MADOC predictions corresponded reasonably well with observed
 387 concentrations of major ions (Table 6). Observed declines in soil water SO₄ were reproduced
 388

389 **Table 6 Model performance assessment using Nash-Sutcliffe efficiency criterion for selected soil water indicators**
 390 **concentrations.**

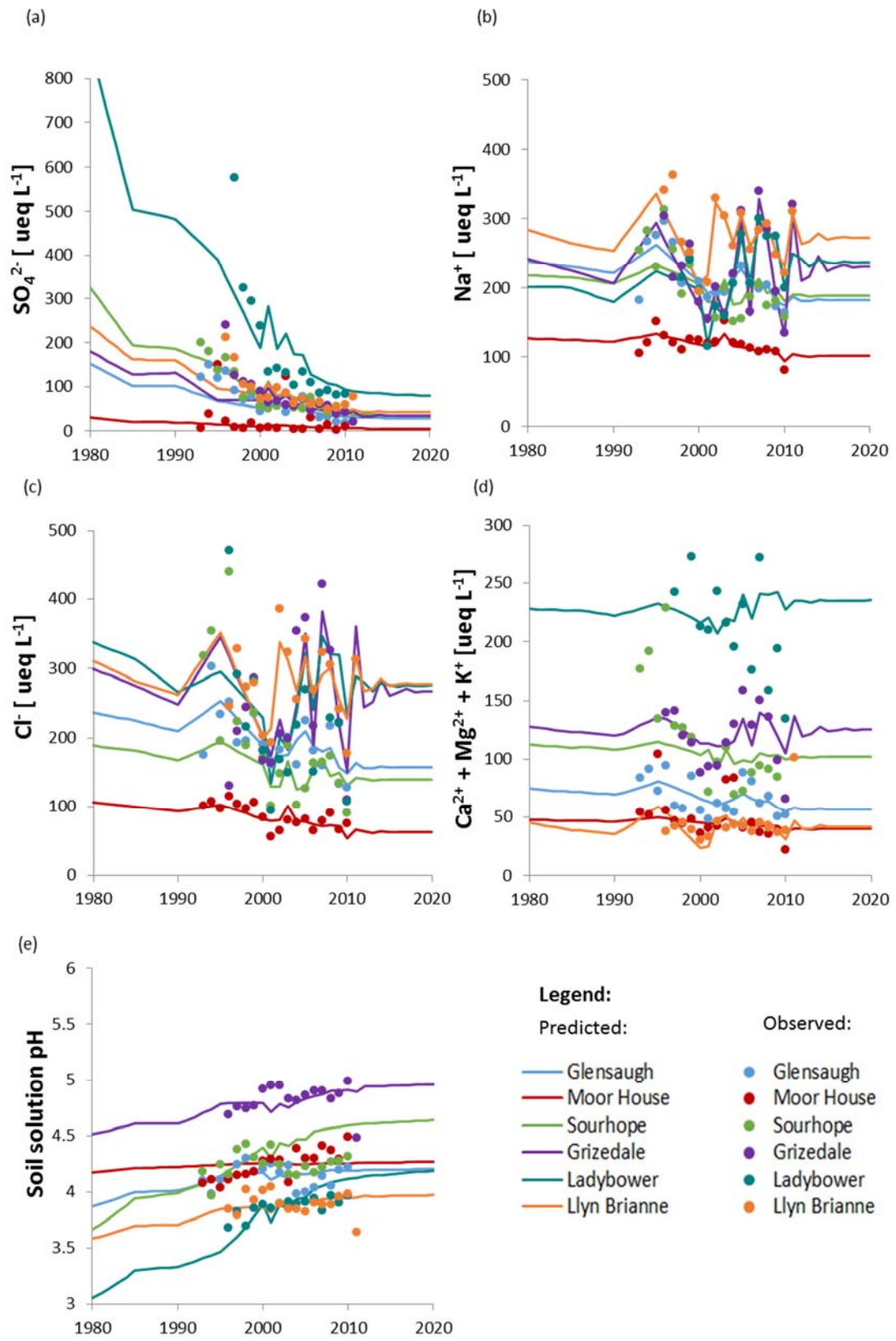
Site/Variable	SO ₄	Cl	Na	Ca+Mg+K	pH	DOC
Glensaugh	0.27	0.53	0.65	0.40	-0.09	0.17
Moor House	-0.09	0.39	0.58	0.12	0.04	-0.04
Sourhope	0.77	0.16	0.55	0.15	-3.29	0.05
Lady Bower	0.44	0.41	-0.10	-0.05	-1.40	-0.22
Llyn Brianne	0.18	0.65	0.77	0.02	-0.47	0.17
Grizedale	0.01	0.38	0.89	0.13	-0.33	0.13

391

392

393 by MADOC (Figure 3a), although at the beginning of the monitoring period SO₄
 394 concentrations were underestimated relative to observations at most sites, suggesting that
 395 anthropogenic S deposition was higher at this time than the extrapolated Eskdalemuir bulk
 396 deposition sequence would indicate. The model also reproduced the downward trends in Cl
 397 concentrations at Glensaugh and Moor House (Figure 3c). Base cation measurements were

398 also mainly predicted accurately (Figure 3d), although the model failed to reproduce the very
399 high base cation concentrations at Sourhope in the early years, again presumably reflecting a
400 discrepancy between the S deposition data used to drive MADOC and higher true S
401 deposition rates. The rate of long-term recovery from acidification was captured well at Llyn
402 Brianne, Grizedale and Glensaugh, slightly over-predicted at Sourhope and Ladybower, and
403 underpredicted at Moor House, where the model largely failed to reproduce the observed
404 recovery of pH. The Nash-Sutcliffe criterion for pH mostly took negative values however, as
405 a result of the relatively large inter-annual variation in observations (Table 6). This implies
406 that the mean of the observations would give better predictions than model simulations.



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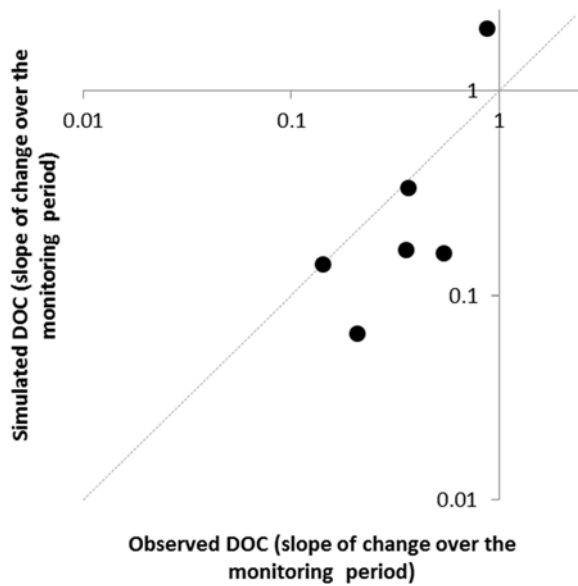
Figure 3 Observed (dots) and predicted (lines) values of selected indicators for the studied sites.

410

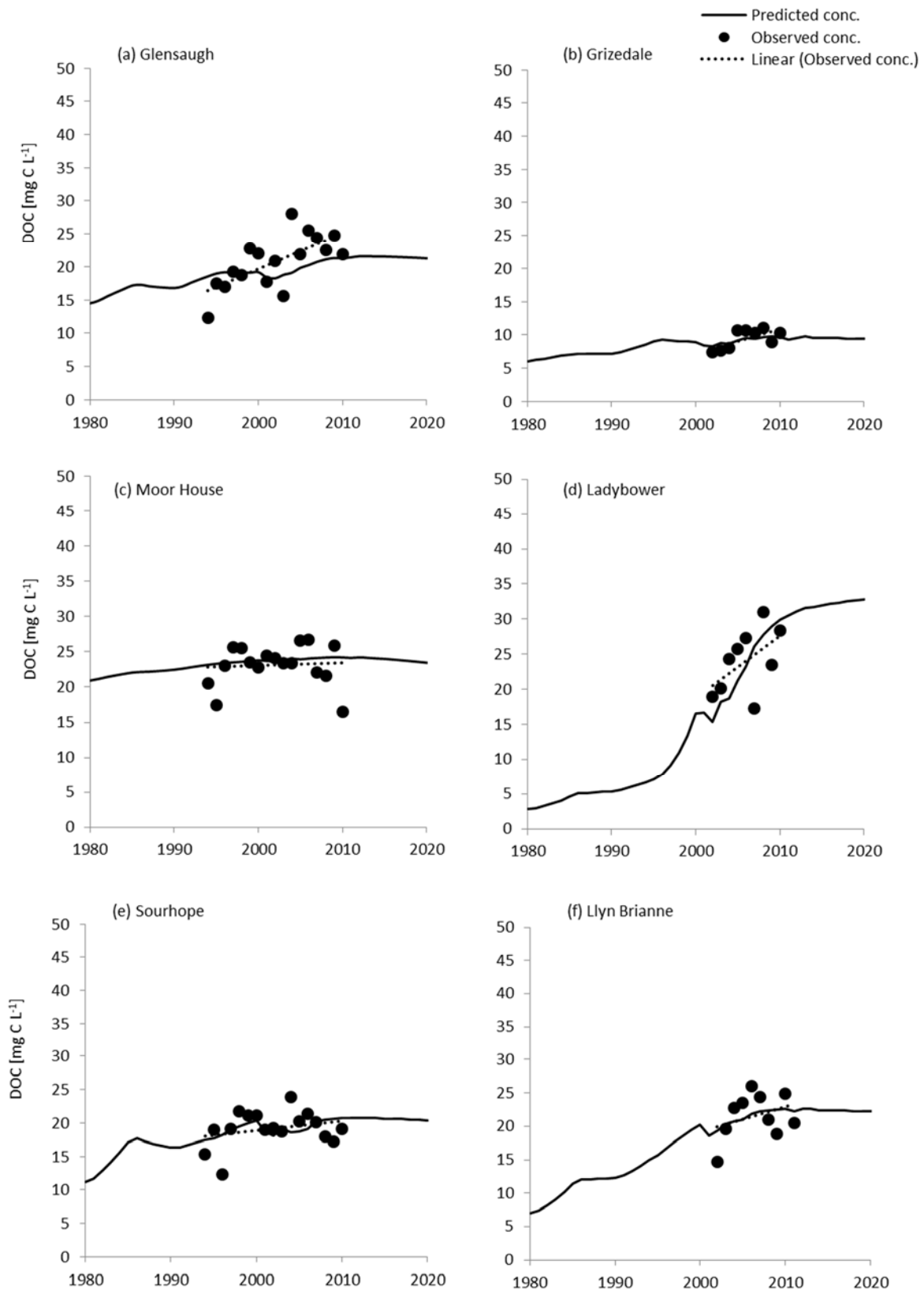
411 **3.2 Dissolved organic carbon**

412 The MADOC model reproduced observed long-term changes in DOC concentrations
413 reasonably well for all sites (Figure 4). In five cases the model captured the overall upward
414 trends in the observations more effectively than a line with zero slope, while also simulating
415 the absence of trend in the DOC data for Moor House (Figure 5). The model was not
416 designed to reproduce between-year fluctuations in mean DOC (or other variables) associated
417 with factors such as climate variability (e.g. Clark et al., 2011), so inevitably the predictions
418 fluctuate less than the observations. This is the main reason for the low values of the NS
419 statistic. However, the model reproduced the temporal pattern and rates of DOC change
420 across the sites with most sites showing an upward trend in DOC.

421



422 **Figure 4 Comparisons of observed with predicted rate of change for the monitoring period for each site DOC**
423 **concentrations; Equivalence (1:1) lines are also shown. The values are presented on the log-log-scale.**
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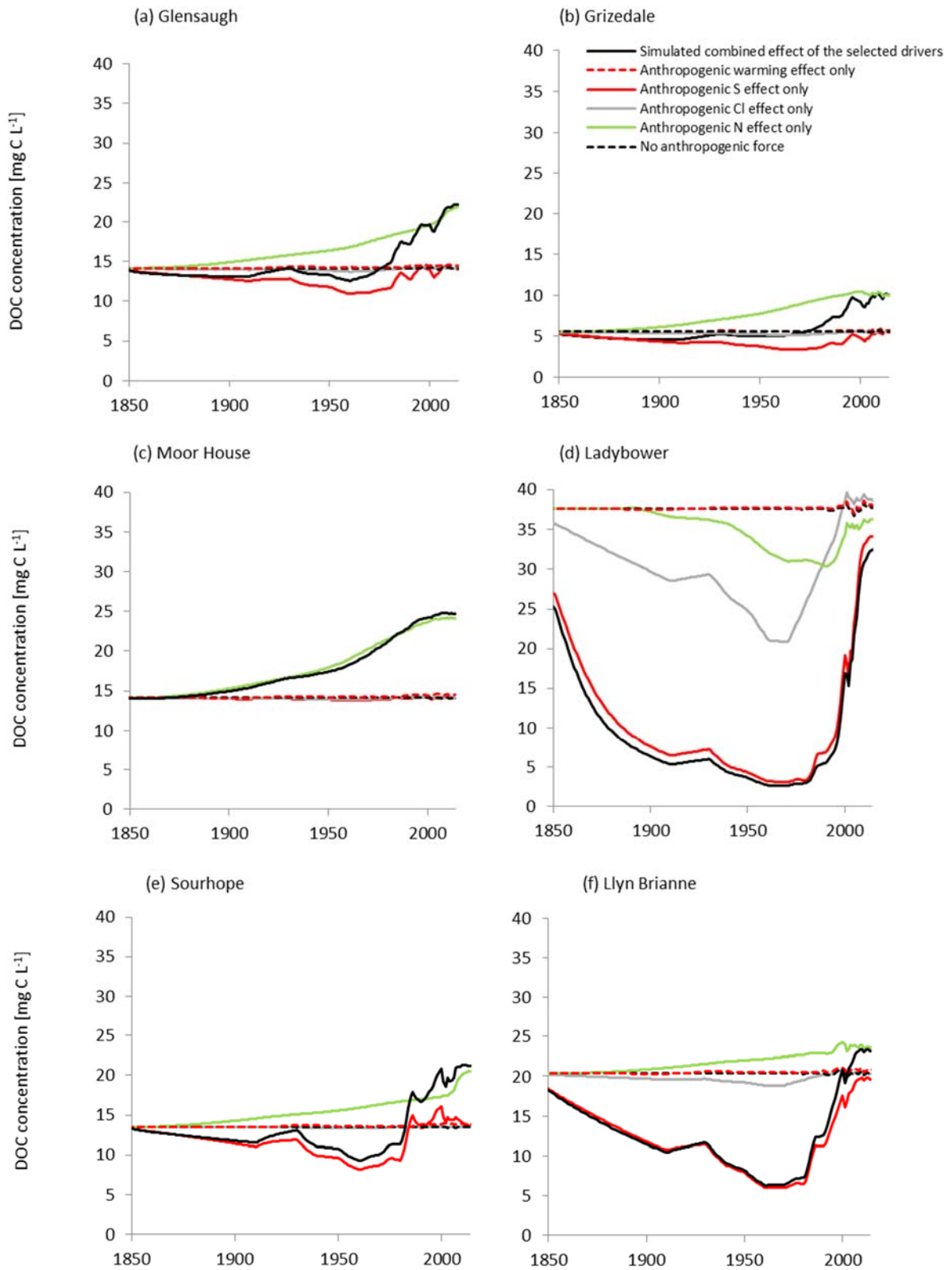
429

Figure 5 Figure 65 Observed (dots), predicted (solid line) and fitted linear trend (dotted line) values for DOC concentration for the studied sites.

3.3 *Alternative historical reconstructions of DOC trends*

430
431 To explore the influence of the main anthropogenic drivers of change within the
432 model, i.e. individual impacts of S, N and Cl deposition and temperature trajectories (Table
433 5), the calibrated model was applied to each site to simulate long-term DOC trends, first with
434 all four parameters varying according to the historic reconstruction scenarios , and then with
435 all but one fixed. Since a fertilising effect of N deposition for N-limited soils is an implicit
436 assumption in the full model runs, and since the modelled DOC mean for the site is calibrated
437 against measurements on a site specific basis, close fits to observations were only likely to be
438 achieved using the full model or N deposition-only scenarios. Reconstructions under (i.e. non
439 N-deposition) sequences will inevitably under-predict theoretical pre-industrial and current
440 DOC concentrations, where the assumption is that only one driver (e.g. S deposition) is
441 operating. The reconstructions in Figure 6, therefore, need to be interpreted in terms of
442 expected long term change in DOC relative to a common pre-industrial baseline in the case of
443 these different scenarios, and do not provide an indication of theoretical absolute differences
444 between scenarios in hypothetical pre-industrial levels.

445
446 With all drivers included, the simulated DOC concentrations for the non-forested
447 podzols (Glensaugh and Sourhope) showed slight decreases until around 1970, before
448 increasing rapidly to levels exceeding pre-industrial reference values (Figure 6a,e). Similarly,
449 at the forested sites (Ladybower, Llyn Brianne and Grizedale) modelled DOC concentrations
450 decreased over the 100 year period following the onset of acidification (Figure 6b,d,f) and
451 increased markedly in the last quarter of the 20th century. Despite a decrease in soil water pH
452 over the 20th century, prior to recovery (not shown), modelled DOC at the peatland site
453 (Moor House) started to increase in early 1900s, reaching a peak after 2000 coincident with
454 the peak in N deposition (Figure 6c).



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Figure 6 Historic reconstructions of DOC trends under scenarios including actual trends in S, CI and N deposition and in mean annual temperature (black line), and including each of these trends in isolation: only temperature (dashed red line); only S (solid red line); only CI (grey line) and only N (green line).

459

460 For the S deposition only scenario, modelled DOC variations tracked those in pH with
461 long-term decreases until mid-1990s and recovery onwards, for all sites except Moor House,
462 where negligible change was simulated. The magnitude of simulated DOC change was
463 greatest under conifer forest at Ladybower and Llyn Brianne, reflecting a relatively large soil
464 acidification and recovery response compared to other sites. These scenarios suggest that if
465 recovery from acidification due to S pollution was the only driver of change, present-day
466 DOC concentrations would be close to pre-industrial reference levels. The scenario in which
467 nmCl deposition (another potential acidifying factor) was the only driver of change suggests
468 that nmCl made a negligible contribution to DOC change at most sites, although at
469 Ladybower nmCl deposition alone could have significantly reduced DOC leaching. The
470 simulated impact of this driver was minor compared to that of S deposition.

471

472 If N deposition had been the only driver to change with time, the historical
473 reconstruction simulations suggest that there would have been a steady increase in soil water
474 DOC concentrations at all sites other than Ladybower (Figure 6a-c,d,f). In contrast, the other
475 conifer site (Ladybower) showed a decrease in simulated DOC leaching in response to
476 increasing N deposition (Figure 6d). Extremely high NO_3 leaching (over $250 \mu\text{eq L}^{-1}$ median
477 annual concentration) at this site relative to the others ($< 25 \mu\text{eq L}^{-1}$, Table 7), implies that N
478 makes a significant contribution to soil water acidity. For all other sites, N deposition would
479 have left current DOC concentrations greatly above pre-industrial levels. For the warming-
480 only scenario, very little variation in DOC concentrations was simulated at any of the sites.

481

482

483

484 **Table 7 Measured annual (2002-2006) median NO₃ concentrations [$\mu\text{eq L}^{-1}$] in pore water of the topsoil of the studied**
485 **sites.**

Site	Median pore water NO ₃ concentrations [$\mu\text{eq L}^{-1}$]
Glensaugh	2.89
Moor House	0.58
Sourhope	5.22
Grizedale	12.48
Ladybower	254.8
Llyn Brianne	23.38

486

487

488 **4. Discussion**

489 **4.1 *Efficacy of the model in predicting concentrations of soil water***

490 ***indicators***

491 The MADOC model reproduced observations during the monitoring period of major
492 ion concentrations, pH and DOC well at most sites. Although model accuracy as indicated by
493 the NS criterion was limited, this was mainly due to the large inter-annual variation in the
494 observations. However, the reproduction of SO₄ and Cl trends indicates that the model
495 captures adequately the processes governing longer term behaviour of these ions and their
496 annual budgets. The soil water concentrations of sulphate reflected a marked and general
497 decrease in S deposition, a pattern which was also shown in bulk deposition and soil water
498 monitoring data from UK ECN and FLII sites (Sawicka et al., 2016). Including estimates of
499 dry deposition of S in the deposition input sequences improved the model simulation of soil
500 water SO₄ trends for all sites. The underestimation of annual SO₄ concentrations at the
501 beginning of the monitoring period at four sites, and consequent underestimation of effects on
502 pH and DOC concentrations, was presumably because S deposition was underestimated using
503 only nationally wide estimates for dry deposition. The ecosystem type itself strongly
504 influences the deposition process. For example, conifer forest at Ladybower would have had
505 higher levels of scavenged pollutant in comparison to deciduous Grizedale or the non-

506 forested sites (Fowler et al., 1989, Miller et al., 1991) and would also, therefore, have
507 experienced sharper reductions in the deposition load . Given the absence of local dry
508 deposition monitoring at the ECN or FLII sites, the method used generally performed well.

509

510 Simulations of Cl concentrations in soil water corresponded well with the monitoring
511 data, and inclusion of the non-marine component estimated from Evans et al. (2011) helped
512 to capture the declining trend in soil water concentrations over the monitoring period. Non-
513 marine Cl has often been overlooked as a driver of ecosystem change, and at polluted sites
514 such as Ladybower the reduction of nmCl deposition could account for up to 40% of
515 chemical recovery from acidification.

516

517 Base cation concentrations and trends were reproduced at most sites, although the
518 model did not fully reproduce observed trends at one conifer site (Ladybower) and one
519 grassland site (Sourhope). Historical variation in non-marine inputs of base cations is
520 currently poorly understood, and including base cation deposition trends might improve
521 predictions of soil water concentrations.

522

523 Although the accuracy of pH predictions as indicated by NS was poor, this was
524 largely due to inter-annual variation in the observed data. Increases in soil water pH with
525 recovery from acidification were reproduced at all sites, albeit with an over-estimation of the
526 rate of pH change under grassland (Sourhope) and conifer (Ladybower) and an under-
527 estimation in peatland (Moor House). The rapid simulated pH recovery in the podzols of
528 Sourhope and Ladybower suggests that increased DOC dissolution with greater pH, which
529 would have buffered the simulated pH increase (Rowe et al., 2014), may be under-
530 represented in the model. The relatively rapid observed increase in pH over the monitoring

531 period at Moor House may be due to an underestimate of nmCl deposition in the late 20th
532 century, and/or to the release of retained reduced S following drought events during the
533 period of intense S pollution.

534

535 ***4.2 Efficacy of the model in predicting DOC concentrations***

536 Despite considerable uncertainties in the driving data, the MADOC model reproduced
537 reasonably well the observed rates of DOC change across different sites (Figure 4). The slow
538 simulated increase in DOC at Glensaugh relative to observations was likely due to
539 underestimation of S inputs in the early part of the monitoring period (see above). Improved
540 estimates of S and base cation deposition sequences would likely improve the accuracy with
541 which DOC observations and trends could be simulated.

542

543 Simulated DOC concentrations depended on several factors and processes combined
544 in the model. Soil solution pH was a key factor influencing the dissolution of N, but
545 simulated DOC concentrations were also strongly affected by soil organic matter turnover.
546 Simulated DOC increases over the monitoring period were mostly attributable to the
547 dependence of potentially dissolved organic matter on pH and therefore on changes in acid
548 deposition and recovery (SanClements et al., 2012, Monteith et al., 2014). However,
549 increased plant productivity due to N fertilisation, and to a lesser extent increased turnover of
550 SOM due to higher temperatures, also affected simulated DOC concentrations at most sites
551 (Figure 6). The importance of SOM turnover in determining DOC concentrations is
552 illustrated by observations that much DOC is of recent origin at least in temperate and boreal
553 systems (Evans et al., 2007a, Raymond et al., 2007, Tipping et al., 2010), although this may
554 not be true for recently drained peats, particularly in the tropics (Evans et al., 2014).

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4.3 *DOC sensitivity to the elementary drivers.*

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In general, the agreement between modelled and observed trends was primarily due to the substantial reduction in modelled S deposition and, consequent increase in modelled pH. Modelled effects of N deposition at most sites were confined to the pre-monitoring period and are therefore unlikely to explain recent DOC increases at Ladybower, Grizedale, Llyn Brianne and Sourhope. The simulations therefore suggest that historical changes in soil acidity likely have had a considerably larger effect on DOC concentrations over time than changes in the other potential drivers, and that continuing reductions in sulphur deposition on organo-mineral soils may drive further increases in DOC (Monteith et al., 2015). However this may not be the sole driver of DOC change in all cases, as N deposition alone was able to mimic the recent upward trend at Glensaugh. Nitrogen deposition was the only driver capable of producing a long-term DOC increase in the Moor House peats, although monitoring records do not go back far enough to validate such a trend.

Simulated scenarios with individual drivers demonstrate that the relative effects on DOC fluxes of changes in pH and in productivity are likely to be sensitive to the history of the site in terms of acid and N deposition and on the acid buffering capacity of the soil. At forested sites such as Ladybower with weakly-buffered organo-mineral soils and historically high S interception rates due to canopy effects the model suggests that DOC is likely to be highly sensitive to acidification and recovery, either directly through changing soil acidity (e.g. Vanguelova et al., 2010, Clark et al., 2011, Evans et al., 2012) or via lowered ionic strength (Hruska et al., 2009) and this is borne out between the relatively good agreement between modelled and measured DOC for this site (Figure 5d). By contrast, DOC trends in peatland at Moor House were hardly affected by S deposition, as a consequence of the

581 immobilisation of most S to reduced (and therefore non-acidifying) forms and peats being
582 less sensitive to changes in acidity than organo-mineral soils (Clark et al., 2005, Clark et al.,
583 2011). The model implies that, effects of N on plant productivity and therefore on the
584 turnover of soil organic matter at Moor House, may have been an important driver of DOC
585 historically, in which case current levels may be substantially higher than they were prior to
586 the industrial period.

587

588 The reduction in acidity associated with a decline in non-marine Cl deposition has
589 previously been suggested to be a potential driver of slight long-term DOC increases at Moor
590 House (Evans et al., 2011). The MADOC model, in which soil water Cl depends solely on the
591 deposition inputs, reproduced downward trends in annual soil water Cl levels particularly
592 well at the non-forested sites. At historically heavily-polluted sites such as Ladybower, nmCl
593 likely contributed significantly to pH decreases during acidification, and hence recovery from
594 nmCl pollution had a strong influence on subsequent DOC trends. This observation is
595 supported by analysis of long-term monitoring data from ECN and FLII sites (Sawicka et al.,
596 2016). For most sites, however, simulations with and without nmCl forcing were only
597 marginally different, suggesting that nmCl input made only a small contribution to DOC
598 increases. Sawicka et al. (2016) suggested that, rather than industrially derived Cl, it could be
599 that longer term retention and release of Cl from organic complexes (Bastviken et al., 2006)
600 has driven decreases in soil water Cl. Deposition of nmCl can contribute to DOC trends, but
601 at most sites its impact is probably negligible.

602

603 The model simulations indicated that the DOC response to the observed historic trend
604 in global temperature may be also negligible. Decomposition rates increase exponentially
605 with temperature, with a Q_{10} here assumed to be 2.0, i.e. decomposition measured in terms of

606 soil respiration (i.e. CO₂ loss) doubles for a 10°C increase in temperature (Kätterer et al.,
607 1998, Davidson and Janssens, 2006, Xu et al., 2014). At such a rate, the simulated increase in
608 DOC due to the 0.66°C increase over the last three decades of the 20th century would have
609 only amounted to a change of 10-20%, suggesting temperature was not a major driver of
610 DOC increase in recent decades *cf.* (Clark et al., 2005, Evans et al., 2006). However, effects
611 of temperature on DOC (via increased plant productivity and increased decomposition rates)
612 are likely to become more significant in future. This is consistent with a comprehensive study
613 of climate change impact on DOC in Irish catchments (Naden et al., 2010), which showed
614 that under IPCC future temperature change scenarios DOC concentrations may increase
615 between 20 and 89%.

616

617 The MADOC model simulations demonstrate that, according to our current system
618 understanding, current soil water (and hence surface water) DOC concentrations may have
619 been influenced by the long term effects of N deposition and accumulation. On this basis, the
620 pattern of increasing DOC association with recovery from acidification may have obscured a
621 more gradual long-term increase in DOC linked to rising productivity and litter production,
622 with the exception of N-saturated sites such as Ladybower where high NO₃ leaching is likely
623 to have contributed to acidification. Nitrogen fertilising impact will depend on the amount of
624 N input and the degree of limitation by other factors. Low to moderate N deposition to N-
625 limited forests typically stimulates plant growth (Quinn et al., 2010) through positive effects
626 on photosynthesis, and this is supported by modelling and experimental results suggesting
627 increased rates of biomass C sequestration in response to N additions (Holland et al., 1997, de
628 Vries et al., 2009). At N deposition rates above 10 kg N ha⁻¹ y⁻¹ the growth response of trees
629 to N may become saturated (Fleischer et al., 2013, de Vries et al., 2014) such that litterfall
630 may be unchanged or even decreased under severe N saturation conditions (Aber et al., 1998)

631 due to nutrient imbalances and increased susceptibility to insect attack (Flückiger and Braun,
632 1998, Kennedy, 2003).

633

634 With regard to DOC, the effects of N deposition may also vary, from increased DOC
635 production where additional N stimulates NPP, to decreased production if excess N causes
636 ecological damage or reduced solubility if high NO₃ leaching causes acidification.

637 Application of the MAGIC dynamic model predicts that in the long-term, despite the
638 recovery of the coniferous sites, there will be re-acidification of sites such as Ladybower if N
639 deposition continues at current rates (Evans et al., 2007b). The ongoing N-enrichment of
640 unforested ecosystems also has the potential to trigger shifts in vegetation communities
641 (Aerts and Berendse, 1988), potentially from plant species adapted to low-N conditions (such
642 as Sphagnum moss and dwarf shrubs, towards more productive species which may alter the
643 proportion of DOC produced relative to NPP and litter quality (Armstrong et al., 2012, Ritson
644 et al., 2014a). There is no evidence that such changes in vegetation have occurred at the sites
645 we have studied during the period of which we have, however it is possible in future that N-
646 induced plant species changes could provide a negative feedback on the NPP-DOC link over
647 longer time periods (e.g. Chambers et al., 2013).

648

649 In addition, it is possible that the link between N deposition and NPP will weaken if
650 the ecosystem reaches N saturation, as other limitations to plant growth may then start to
651 dominate, such as temperature, drought, waterlogging (in peaty soils) and deficiency of other
652 nutrients such as phosphorus.

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5. Conclusions

The MADOC model was able to reproduce changes in soil water DOC concentrations observed for a range of upland organic soil types, although performance was strongly dependent on deposition sequences, implying that good deposition estimates are essential for site-scale modelling. The application of MADOC to terrestrial monitoring data provides insight into the extent to which drivers other than sulphur deposition might contribute to DOC trends. According to the process understanding and parameterisation we have incorporated in the model, S deposition is likely to have exerted a considerably larger influence on DOC than other potential drivers. Temperature changes appeared to have had little impact. The relative importance of S and N loading depended on soil sensitivity to acidification, and on N limitation. In all N-limited podzols and gleysols investigated, modelled DOC increases over the monitoring period were dominated by the effects of recovery from acidification (higher DOC solubility), but effects of N enrichment driving higher DOC production may have been important in the longer term. At the most N saturated forest site, it is likely that nitrate leaching will actually have contributed to acidification and DOC leaching reduced, whereas at a peatland site where S deposition was retained through sulphate reduction, N enrichment was the only driver capable of driving a potential (but not-recorded) DOC change.

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Our modelling study emphasises the possibility that although recent soil and surface water trends in DOC concentrations trend are in keeping with a return toward pre-industrial levels, concentrations for a range of soil types may now be higher than historical levels as a consequence of the effect of N fertilisation raising the baseline. However, even the longest reliable soil water DOC records only extend back for two decades or so and this is not sufficient to fully disentangle possible acidification recovery and eutrophication effects.

681 Hence further evidence may be best derived through the further refinement of
682 paleolimnological reconstruction approaches that may allow changes in DOC in surface
683 waters to be inferred over centennial time scales, and continued monitoring over an extended
684 period of sulphur deposition rates that now appear to be approaching pre-industrial levels in
685 some areas.

686

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692 sites.

693

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