



Modelling impacts of atmospheric deposition and temperature on long-term DOC trends

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1 **Modelling impacts of atmospheric deposition and temperature on long-term DOC**
2 **trends**

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16 **Keywords:** DOC, sulfur deposition, nitrogen deposition, warming, recovery, trend, dynamic
17 modelling

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. Effects of rising pH and declining ionic strength on
23 DOC solubility have been proposed as potential dominant mechanisms. However, since DOC
24 in 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. Such potential drivers
27 include fertilization by nitrogen (N) and global warming. We therefore ran the dynamic soil
28 chemistry model MADOC for a range of UK soils, for which time series data are available, to
29 consider the likely relative importance of decreased deposition of sulphate and chloride,
30 accumulation of reactive N, and higher temperatures, on soil DOC production in different
31 soils. Modelled patterns of DOC change generally agreed favourably with measurements
32 collated over 10-20 years, but differed markedly between sites. While the acidifying effect of
33 sulphur deposition appeared to be the predominant control on the observed soil water DOC
34 trends in all the soils considered other than a blanket peat, the model suggested that over the
35 long term, the effects of nitrogen deposition on N-limited soils may have been sufficient to
36 raise the “acid recovery DOC baseline” significantly. In contrast, reductions in non-marine
37 chloride deposition and effects of long term warming appeared to have been relatively
38 unimportant. The suggestion that future DOC concentrations might exceed preindustrial
39 levels as a consequence of nitrogen pollution has important implications for drinking water
40 catchment management and the setting and pursuit of appropriate restoration targets, but
41 findings still require validation from reliable centennial-scale proxy records, such as those
42 being developed using palaeolimnological techniques.

43

44 **1. Introduction**

45 Long-term monitoring of surface water quality has revealed increasing concentrations
46 of dissolved organic carbon (DOC) across large parts of the Northern Hemisphere,
47 particularly close to industrialised regions (Skjelkvale et al., 2001, Driscoll et al., 2003,
48 Evans et al., 2005, Monteith et al., 2007, Erlandsson et al., 2008). These observations have
49 raised concerns over increasing water treatment costs (Ritson et al., 2014b) and possible

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

60

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

72

73 Several studies suggest that there is also a link between N deposition and DOC
74 leaching (e.g. Pregitzer et al., Findlay, 2005, Bragazza et al., 2006). Nitrogen typically limits

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

86

87 One of the criticisms levelled at investigations into the drivers of DOC increases in
88 soils or waters is that studies founded on correlation (e.g. Skjelkvale et al., 2001, Vuorenmaa
89 et al., 2006, Monteith et al., 2007, Oulehle and Hruška, 2009, Sarkkola et al., 2009, Zhang et
90 al., 2010, Borken et al., 2011) do not in themselves provide proof of causation (Roulet and
91 Moore, 2006). In addition, study sites tend to be concentrated within geographically limited
92 areas and findings may, therefore, not necessarily be universally applicable. Furthermore,
93 although soils (particularly upper organic horizons) are recognised to often be the source of
94 most freshwater DOC (e.g. Brooks et al., 1999, Billett et al., 2006, Evans et al., 2007a,
95 Winterdahl et al., 2011), soil water monitoring data are scarce, and typically of shorter
96 duration than surface water data. There is increasing evidence that shallow soil water makes a
97 major contribution to trends in DOC in surface water (Hruška et al., 2014, Sawicka et al.,
98 2016) although the relationship between soil and surface water concentrations is complicated
99 by riparian and subsoil processes (Lofgren et al., 2010, Löfgren and Zetterberg, 2011).

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

106

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

120

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

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

139

140 **2. Methods**

141 *2.1 Field sites, measurements and chemical analyses*

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



150

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

153

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

163

164 The six study sites covered a gradient of S, N and Cl deposition from 44 to 86, 40 to
165 90, and 94 to 306 meq m⁻² yr⁻¹, respectively (long-term mean between 1993 and 2010
166 depending on the site), with a range of soil organic carbon (SOC) content (0.8 to 48.7 %),
167 C/N ratio (3 to 70 g g⁻¹), soil acidity (pH 3.6 to 7.0), and soil sensitivities to acid deposition
168 (e.g. base saturation (BS) 1.1 to 100 %, and Al saturation (Al sat.) 0 to 93.5 %). The sites
169 cover an altitudinal gradient from 115 m to 540 m above sea level. Mean annual temperature
170 (MAT) (for period 2002-2006) varied from 6.1 °C at Moor House up to 10.5 °C at
171 Ladybower; and mean annual precipitation (MAP) (for 2002-2006) from 1265 mm yr⁻¹ at
172 Ladybower to 2020 mm yr⁻¹ at Llyn Brienne. Additional information about the monitoring
173 networks is available in Vanguelova et al. (2007) and (Sier and Monteith, 2016).

174

175 At FLII sites soil water samples were collected every two weeks using tension
176 lysimeters (PRENART SuperQuartz soil water samplers, Plenart Equipment Aps, Denmark).
177 Twelve lysimeters were installed at each site, six located at 10 cm soil depth and the other six
178 at 50 cm soil depth. Soil water samples were collected and measured according to Level II
179 protocols described in detail in the ICP forests manual (ICP, 2006). Water samples were
180 filtered through a 0.45 µm membrane filter and analysed for pH; total aluminium (Al),
181 calcium (Ca), magnesium (Mg), potassium (K), sodium (Na) and iron (Fe) by ICP-OES
182 (Spectro-flame, Spectro Ltd.); ammonium N (NH₄-N) colorimetrically with sodium
183 salicylate and sodium dichloroisocyanurate; DOC by total carbon analyser (Shimadzu 5000,
184 Osaka, Japan) using catalytic or persulphate oxidation; and sulphate (SO₄), nitrate (NO₃) and
185 chloride (Cl) by Ion Chromatography (Dionex DX-500). Quality assurance and quality
186 control on dissolved ion concentrations in soil water are described by De Vries et al. (2001)
187 and in the ICP manual (2006). ECN soil waters were also sampled fortnightly by tension
188 lysimetry using the same Prenart SuperQuartz samplers. According to the Environmental

189 Change Network (ECN) protocols six samplers were placed at the base of each A and B
190 horizons, except for deep peats where fixed depths of 10 and 50 cm depths were used. Soil
191 water was analysed for pH, then filtered (<0.45 µm) and analysed for DOC by combustion
192 oxidation and IR (infra-red) gas detection; total metals (Al, Ca, Fe, K, Mg, Na) by ICP-OES;
193 Cl⁻, SO₄ by Dionex ion chromatography; and NO₃ colorimetrically with sodium salicylate
194 and sodium dichloroisocyanurate.

195

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

203

204 Soils at all FLII and ECN sites were surveyed between 1993 and 1995. In each plot,
205 the soil was described according to the FAO soil classification system and classified
206 according to the World Reference base for soil classification (WRB, 2014). FLII soil
207 sampling and analyses were carried out according to the UNECE ICP Manual for Soil
208 Sampling and Analysis (2006). ECN sites surveys were conducted using standard methods
209 (Sykes and Lane, 1996).

210

211 Meteorological data for Grizedale, Ladybower and Llyn Brianne were derived from
212 the nearest Met Office weather stations, within maximum 38km and mean distance of 24km
213 for all sites, available through the British Atmospheric Data Centre (Met Office - MIDAS

214 Land Surface). Each ECN site has a designated automatic weather station recording hourly
215 climatic data and manual equipment is installed at sites to provide quality control (Morecroft
216 et al., 2009).

217

218 **2.2 Simulation approach**

219 The MADOC model was developed to simulate long-term changes in carbon and N
220 cycling and soil acidity, and is described fully in Rowe et al. (2014). The model simulates
221 soil processes in a 1-D column, using three annual time-step mechanistic submodels as
222 summarised below (for more details see Supplementary Information). Production and
223 decomposition of organic matter is simulated by the N14C sub-model (Tipping et al., 2012).
224 The model simulates carbon inputs from vegetation productivity, which is determined by
225 temperature, precipitation and N supply. Nitrogen is supplied only from N fixation until the
226 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, which may be
232 flocculated/sorbed, or in solution, depending on solution conditions. The solubilisation and
233 dynamics of this pool are calculated using a simplified version of DyDOC (Michalzik et al.,
234 2003). In DyDOC Potentially-dissolved organic matter is partitioned into soluble and solid
235 phases, based on current pH and dilution as determined by net water flux. The solid phase is
236 retained as pDOM and may be solubilised subsequently or lost through mineralisation. The
237 soluble phase (DOC and DON) is leached from the topsoil and mainly enters the freshwater
238 system, although a proportion is sorbed in the subsoil where it is subject to further

239 mineralisation. Acid-base dynamics are simulated using VSD (Posch and Reinds, 2009). In
240 the VSD a constant proportion of DOC is assumed to potentially form acid anions, *i.e.* the
241 dissociation site density, P_{sites} . The actual dissociation of this potential capacity is determined
242 by solution conditions. Simulated soil solution chemistry depends on concentrations of
243 organic anions; nitrate (NO_3) and ammonia (NH_4) inputs as calculated by the N14C model;
244 deposition inputs of the main other acid anions (SO_4 and Cl) and base cations (Na, Ca, Mg
245 and K); and interactions with soil surfaces. Ionic exchange is described by equations that
246 define competition among cations for exchange sites and thus the partitioning of ions
247 between the solution and adsorbed phases.

248

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

259

260

261 **Table 1 Sites descriptions. Mean annual temperature (MAT) and precipitation (MAP) are averaged over period of 5 years 2002-2006. World Reference Base**
 262 **(WRB) classification was used to define soil types. Soil properties are given for 10cm depth (depth of the lysimeters placement).**

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]	SOC [%]	C/N	pH	Base Sat. [%]	Al Sat. [%]
Glensaugh	ECN	Podzol	Grassland/ Heathland	300	7.8	1530	263 (158 + 47 + 58)	34.5	28	3.9	5	0.07
Moor House	ECN	Histosol	Blanket bog	540	6.1	1930	209 (125 + 42 + 42)	40.6	32	3.8	11	2.5
Sourhope	ECN	Podzol	Grassland	495	7.7	1280	138 (83 + 21 + 35)	48.7	18	3.6	5	0.1
Grizedale	FLII	Podzol	Deciduous forest	115	9.6	1920	423 (317 + 34 + 72)	5.0	17	5.1	7	37.7
Ladybower	FLII	Podzol	Coniferous forest	265	10.5	1265	332 (216 + 46 + 70)	2.7	16	4.1	4	93.5
Llyn Brianne	FLII	Gleysol	Coniferous forest	450	10.1	2020	447 (340 + 31 + 76)	40.1	17	3.6	15	50.9

263

264

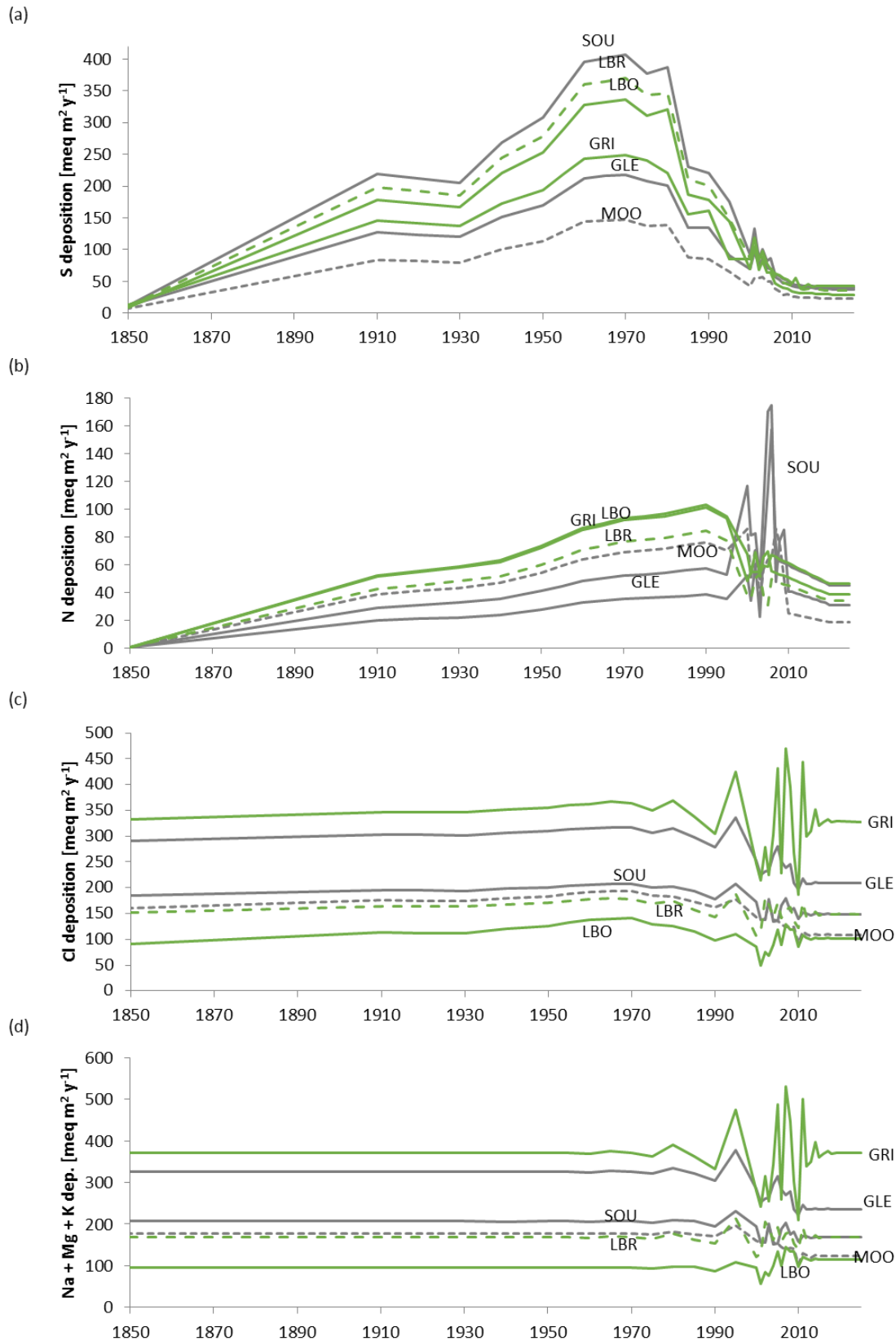
2.3 Model setup and calibration

2.3.1 Data preparation

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

The 'present day' was defined as year 2010 and present-day deposition was adjusted for each site to the mean non-marine sulphate (nmSO₄) in soil water in 2010 by minimising the error in solution SO₄ using Nelder-Mead algorithm (Nelder and Mead, 1965). Peatlands often retain a proportion of S inputs in reduced organic forms and sulphides (Adamson et al., 2001), and the sulphate retention coefficient (fS_{ret}) for the peatland site included in the study was set to 0.6 on the basis of input-output fluxes. The soils of the remaining (non-peat) sites were assumed not to retain significant amounts of S, and thus fS_{ret} was set to zero. Transport of SO₄ through the soil profile was otherwise assumed to be conservative, and present-day nmSO₄ deposition at the site was calculated as that required to produce the observed soil output flux. The long-term nmSO₄ deposition sequence was then calculated by scaling the sequence observed at the Eskdalemuir monitoring site for the years 1973 – 2007 (Fowler et al. (2005) to each site specific value. Historic S deposition trajectories (1850-1973) were obtained by scaling estimates obtained using the FRAME model (Dore et al., 2009) to the

290 calculated value for 1973 according to the equation: $Deposition\ Site_{year\ t} =$
291 $Deposition\ Esk_{year\ t} \cdot \frac{Deposition\ Site_{2010}}{Deposition\ Esk_{2010}}$, where $Deposition\ Site_{2010}$ is calculated by MADOC
292 based on SO₄ concentration in soil water (as above). In order to calculate the total deposition
293 load the dry deposition S trend was assumed to be uniform across the UK and proportional to
294 bulk deposition, as in Fowler et al. (2005).



295

296 **Figure 2** Trajectories of deposition rates for: (a) total nitrogen [meq N m² y⁻¹], (b) total sulphate [meq S m² y⁻¹], (c)
 297 total chloride [meq Cl m² y⁻¹], and (d) charge sum of total base cations [meq Na + Ca + Mg + K m² y⁻¹] for the
 298 studied sites. Green colour indicates forested sites and grey colour indicates non-forested sites. Solid line indicates
 299 podzol sites, dotted line indicates peat and dashed line indicates gleysol.

300

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

307

308 Trends in sea-salt ion deposition, namely the marine fractions of total Cl, Mg, Ca, K
309 and marine SO₄, deposition trajectories, were calculated on the basis of the ratios in which
310 these ions are known to occur with Na in sea salt. Firstly, all Na was assumed to be of marine
311 origin, and ‘present day’ marine inputs of Na⁺ were calibrated to soil water concentrations
312 using the implemented solver based on Nelder-Mead algorithm (Nelder and Mead, 1965).
313 Next, Cl deposition was calculated using the marine proportions factor of 1.163 (Evans et al.,
314 2001). If the Cl concentration in soil water was overestimated then Cl deposition was
315 adjusted to correspond to soil water concentrations. This decreased Na deposition (according
316 to sea-salt ratio) and where necessary assumed Na weathering was increased to match soil
317 water Na concentrations. Deposition of other sea-salt cations was then calculated on the basis
318 of the ratios in which these ions are known to occur with Na⁺ in sea water (eq eq⁻¹): 0.244 for
319 Mg²⁺, 0.047 for Ca²⁺, 0.022 for K⁺ and 0.121 for SO₄²⁻, following Evans et al. (2001).

320

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

325

326 Inputs for the MADOC model are listed in Table 2 and Table 3. The annual drainage
327 flux, i.e. the water flux flowing down through the soil profile, was assumed to equal annual
328 effective rainfall. Organic acids were assumed to be triprotic, and mean values from a study
329 by Oulehle et al. (2013) were used to set dissociation constants for the three protons. The
330 partial pressure of CO₂ in solution in soil was assumed to be 0.037 atm, i.e. 100 times
331 atmospheric concentration (Rowe et al., 2014). Net base cation uptake was assumed to be
332 zero, except for forested sites where a constant uptake rate was assumed from the initiation of
333 each plantation (Table 4). Weathering of N, Cl and S was assumed to be zero. The
334 temperature range (i.e. the difference between growing season and non-growing season mean
335 temperature) was set to 7°C for all sites. The temperature coefficient Q^{10} was assumed to be
336 2.0, i.e. decomposition measured in terms of soil respiration (i.e. CO₂ loss) doubles for a
337 10oC increase in temperature (Kätterer et al., 1998, Davidson and Janssens, 2006, Xu et al.,
338 2014). Values for MADOC inputs which are difficult to ascertain empirically were then
339 obtained by calibrating the model to observations, as described below. Values for other input
340 parameters for the N14C sub-model were as described by Tipping et al. (2012).

341 **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	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
$theta$	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

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

343 **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

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

345

346

347 **Table 4 Site-specific base cation uptake [$\text{meq m}^{-2} \text{y}^{-1}$] for forested sites included as a flat rate from approximate**
 348 **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

349

350

351 2.3.2 Calibration of model parameters

352 The model was calibrated to the measurements made at each site individually. The
 353 methodology for the calibration procedure was based on that described by Rowe et al. (2014).
 354 The calibration was based on minimizing the sum of absolute differences between
 355 observations and predictions using the Nelder-Mead simplex method (Nelder and Mead,
 356 1965). For simultaneous calibrations to more than one type of indicator, indicators were
 357 given equal weighting by dividing each error term by the mean measured value. Simulations
 358 began 12,000 years before present, to allow organic matter pools simulated by the N14C sub-
 359 model to stabilize. Parameter values were fitted in the following sequence: 1) Na⁺ and BC
 360 weathering rates (W_{Na} , W_{BC}) were calibrated for each site to best predict the concentrations in
 361 soil water; 2) the proportion of N entering the potentially-dissolved pool (k_{inpdN}) was
 362 calibrated for each site to minimize error in the average C/N ratio in soil above the

363 lysimeters; 3) the proportion of C entering the potentially-dissolved pool (k_{inpdC}) and the
364 mineralization rate (k_{minpd}) were calibrated to best predict DOC concentration; 4) the site
365 density of potentially-dissociated organic acid functional groups on DOC (P_{sites}) (constrained
366 to the range between 0.09 – 0.15 eq mol⁻¹) (Oulehle et al., 2013) was calibrated for each site
367 and soil type to minimize error in soil water pH. Calibration of k_{inpdN} resulted in low or zero
368 values in some cases, illustrating low net N loss at these sites. This low net loss could also be
369 explained by relatively high N fixation or low denitrification, but each of these processes is
370 poorly constrained, so the k_{inpdN} was the only parameter selected for adjustment.

371

372 *2.3.3 Model performance*

373 The accuracy of DOC predictions was assessed using the absolute error as a
374 proportion of the mean. The statistic should be interpreted as follows: if the calculated value
375 is less than 0.2 the error is less than 20% (i.e. good and comparable to analytical uncertainties
376 [accuracy and precision]). If it is more than 200% the model performs poorly. The patterns
377 and behaviours that were reproduced by the model were also inspected visually.

378

379 *2.3.4 Pollution and climate scenarios*

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

385

386

387

388 **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
4	Anthropogenic S effect only
5	Anthropogenic Cl effect only
6	Anthropogenic N effect only

389 ^a deposition and temperature trajectories as described in section 2.3 - Model setup and calibration; ^b all
 390 deposition and temperature values set to value from 1850 year (presented in section 2.3 - Model setup and
 391 calibration) and assumed constant throughout the simulation period.

392

393

394 **3. Results**

395 **3.1 Major ions in soil solution**

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

398

399 **Table 6 Model performance assessment using the absolute error as a proportion of the mean efficiency criterion for**
 400 **selected soil water indicators concentrations.**

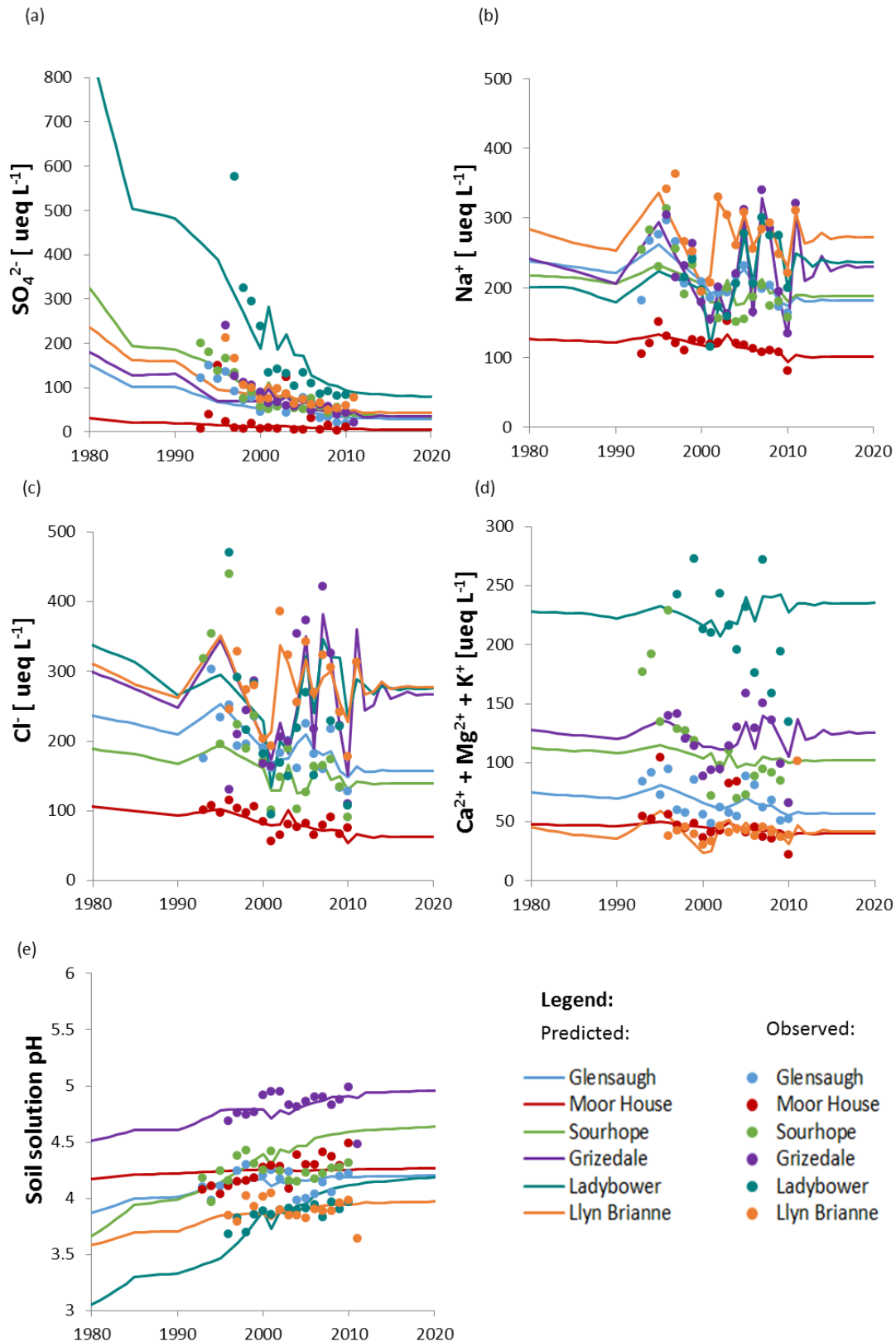
Site/Variable	SO ₄	Cl	Na	Ca+Mg+K	pH	DOC
Glensaugh	0.27	0.11	0.03	0.16	0.02	0.12
Moor House	0.26	0.10	0.04	0.09	0.03	0.08
Sourhope	0.18	0.12	0.11	0.16	0.04	0.08
Lady Bower	0.23	0.20	0.004	0.16	0.02	0.17
Llyn Brianne	0.13	0.06	0.02	0.15	0.01	0.14
Grizedale	0.22	0.12	0.04	0.11	0.01	0.12

401

402

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

408 also mainly predicted accurately (Figure 3d), although the model failed to reproduce the very
409 high base cation concentrations at Sourhope in the early years, again presumably reflecting a
410 discrepancy between the S deposition data used to drive MADOC and higher true S
411 deposition rates. The rate of long-term recovery from acidification was captured well at Llyn
412 Brianne, Grizedale and Glensaugh, slightly over-predicted at Sourhope and Ladybower, and
413 underpredicted at Moor House, where the model failed to reproduce the observed recovery of
414 pH.



415

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

417

418

419

3.2 Dissolved organic carbon

420

The MADOC model reproduced observed long-term changes in DOC concentrations

421

reasonably well for all sites (Figure 4). In five cases the model captured the overall upward

422

trends in the observations more effectively than a line with zero slope, while also simulating

423

the absence of trend in the DOC data for Moor House (Figure 5). The model was not

424

designed to reproduce between-year fluctuations in mean DOC (or other variables) associated

425

with factors such as climate variability (e.g. Clark et al., 2011), so inevitably the predictions

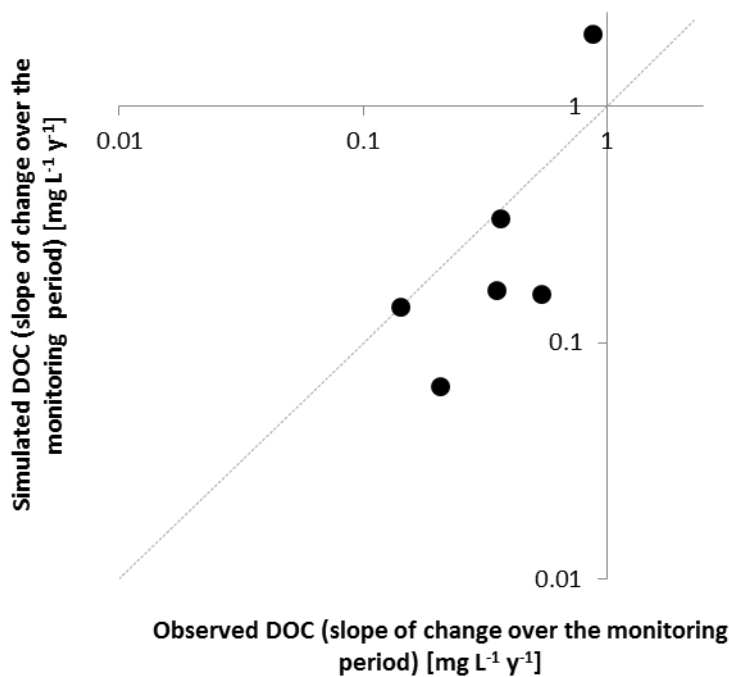
426

fluctuate less than the observations. However, the model reproduced the temporal pattern and

427

rates of DOC change across the sites with most sites showing an upward trend in DOC.

428



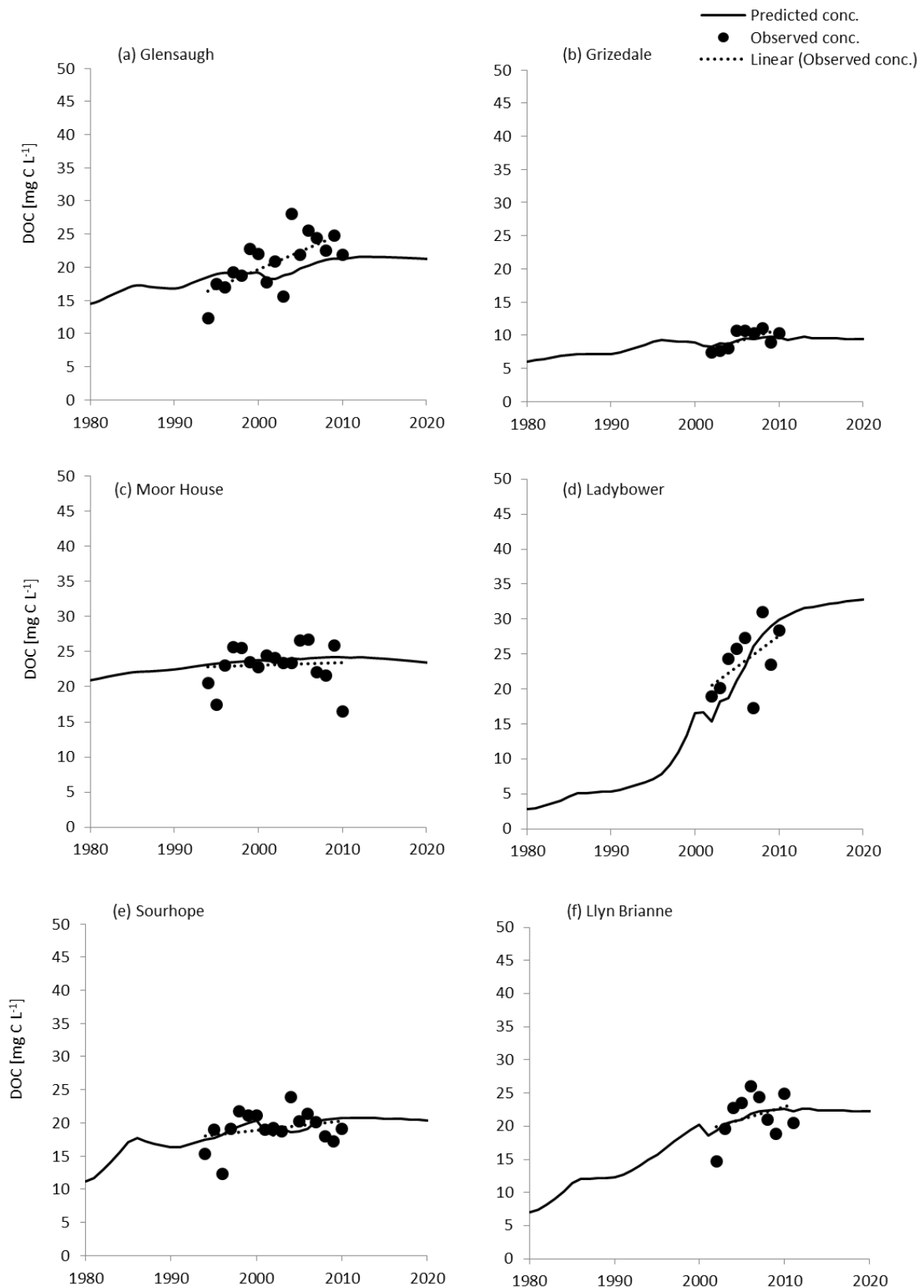
429

430

431

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

433



434

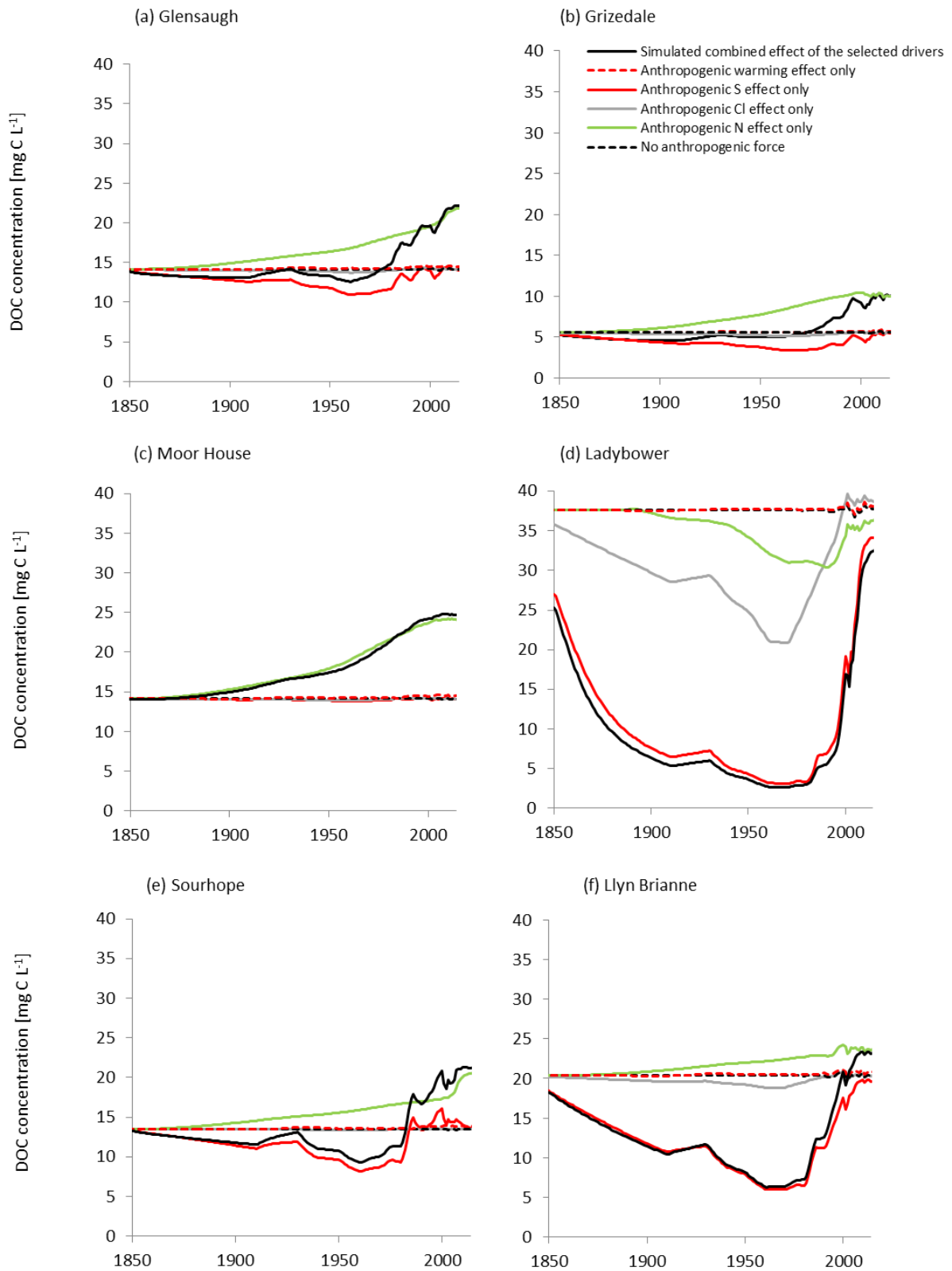
435 **Figure 5** Observed DOC concentrations (dots), fitted linear trend to the observed values (dotted line) and predicted
 436 DOC concentrations values by MADOC (solid line) for the studied sites.

437

3.3 *Alternative historical reconstructions of DOC trends*

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

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



463
464
465
466

Figure 6 Historic reconstructions of DOC trends under scenarios including actual trends in S, Cl 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 Cl (grey line) and only N (green line).

467

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

479

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

489

490

491

492 **Table 7 Measured annual (2002-2006) median NO₃ concentrations [$\mu\text{eq L}^{-1}$] in pore water of the topsoil of the studied**
 493 **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

494

495

496 **4. Discussion**

497 **4.1 Efficacy of the model in predicting concentrations of soil water**
 498 **indicators**

499 The MADOC model reproduced observations during the monitoring period of major
 500 ion concentrations, pH and DOC well at most sites. The reproduction of SO₄ and Cl trends
 501 indicates that the model captures adequately the processes governing longer term behaviour
 502 of these ions and their annual budgets. The soil water concentrations of sulphate reflected a
 503 marked and general decrease in S deposition, a pattern which was also shown in bulk
 504 deposition and soil water monitoring data from UK ECN and FLII sites (Sawicka et al.,
 505 2016). The underestimation of annual SO₄ concentrations at the beginning of the monitoring
 506 period at four sites, and consequent underestimation of effects on pH and DOC
 507 concentrations, was presumably because S deposition was underestimated using only
 508 nationally wide estimates for dry deposition. The ecosystem type itself strongly influences
 509 the deposition process. For example, conifer forest at Ladybower would have had higher
 510 levels of scavenged pollutant in comparison to deciduous Grizedale or the non-forested sites
 511 (Fowler et al., 1989, Miller et al., 1991) and would also, therefore, have experienced sharper
 512 reductions in the deposition load. Given the absence of local dry deposition monitoring at the
 513 ECN or FLII sites, the method used generally performed well.

514

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

521

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

527

528 Increases in soil water pH with recovery from acidification were reproduced at all
529 sites, albeit with an over-estimation of the rate of pH change under grassland (Sourhope) and
530 conifer (Ladybower) and an under-estimation in peatland (Moor House). The rapid simulated
531 pH recovery in the podzols of Sourhope and Ladybower suggests that increased DOC
532 dissolution with greater pH, which would have buffered the simulated pH increase (Rowe et
533 al., 2014), may be under-represented in the model. The relatively rapid observed increase in
534 pH over the monitoring period at Moor House may be due to an underestimate of nmCl
535 deposition in the late 20th century, and/or to the release of retained reduced S following
536 drought events during the period of intense S pollution.

537

538 **4.2 *Efficacy of the model in predicting DOC concentrations***

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

545

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

557

558

559 ***4.3 DOC sensitivity to the elementary drivers.***

560 In general, the agreement between modelled and observed trends was primarily due to
561 the substantial reduction in modelled S deposition and consequent increase in modelled pH.
562 Modelled effects of N deposition at most sites were confined to the pre-monitoring period
563 and are therefore unlikely to explain recent DOC increases at Ladybower, Grizedale, Llyn

564 Brianne and Sourhope. The simulations therefore suggest that historical changes in soil
565 acidity likely have had a considerably larger effect on DOC concentrations over time than
566 changes in the other potential drivers, and that continuing reductions in sulphur deposition on
567 organo-mineral soils may drive further increases in DOC (Monteith et al., 2015). However
568 this may not be the sole driver of DOC change in all cases, as N deposition alone was able to
569 mimic the recent upward trend at Glensaugh. Nitrogen deposition was the only driver capable
570 of producing a long-term DOC increase in the Moor House peats, although monitoring
571 records do not go back far enough to validate such a trend.

572

573 Simulated scenarios with individual drivers demonstrate that the relative effects on
574 DOC fluxes of changes in pH and in productivity are likely to be sensitive to the history of
575 the site in terms of acid and N deposition and on the acid buffering capacity of the soil. At
576 forested sites such as Ladybower with weakly-buffered organo-mineral soils and historically
577 high S interception rates due to canopy effects the model suggests that DOC is likely to be
578 highly sensitive to acidification and recovery, either directly through changing soil acidity
579 (e.g. Vanguelova et al., 2010, Clark et al., 2011, Evans et al., 2012) or via lowered ionic
580 strength (Hruska et al., 2009) and this is borne out between the relatively good agreement
581 between modelled and measured DOC for this site (Figure 5d). By contrast, DOC trends in
582 peatland at Moor House were hardly affected by S deposition, as a consequence of the
583 immobilisation of most S to reduced (and therefore non-acidifying) forms and peats being
584 less sensitive to changes in acidity than organo-mineral soils (Clark et al., 2005, Clark et al.,
585 2011). The model implies that, effects of N on plant productivity and therefore on the
586 turnover of soil organic matter at Moor House, may have been an important driver of DOC
587 historically, in which case current levels may be substantially higher than they were prior to
588 the industrial period.

589

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

604

605 The model simulations indicated that the DOC response to the observed historic trend
606 in global temperature may be also negligible. Decomposition rates increase exponentially
607 with temperature, with a Q_{10} here assumed to be 2.0, i.e. decomposition measured in terms of
608 soil respiration (i.e. CO_2 loss) doubles for a $10^\circ C$ increase in temperature (Kätterer et al.,
609 1998, Davidson and Janssens, 2006, Xu et al., 2014). At such a rate, the simulated increase in
610 DOC due to the $0.66^\circ C$ increase over the last three decades of the 20th century would have
611 only amounted to a change of 10-20%, suggesting temperature was not a major driver of
612 DOC increase in recent decades (*cf.* Clark et al., 2005, Evans et al., 2006). However, effects
613 of temperature on DOC (via increased plant productivity and increased decomposition rates)

614 are likely to become more significant in future (Futter et al., 2009). This is also consistent
615 with a comprehensive study of climate change impact on DOC in Irish catchments (Naden et
616 al., 2010), which showed that under IPCC future temperature change scenarios DOC
617 concentrations may increase between 20 and 89%.

618

619 The MADOC model simulations demonstrate that, according to our current system
620 understanding, current soil water (and hence surface water) DOC concentrations may have
621 been influenced by the long term effects of N deposition and accumulation. On this basis, the
622 pattern of increasing DOC association with recovery from acidification may have obscured a
623 more gradual long-term increase in DOC linked to rising productivity and litter production,
624 with the exception of N-saturated sites such as Ladybower where high NO₃ leaching is likely
625 to have contributed to acidification. Nitrogen fertilising impact will depend on the amount of
626 N input and the degree of limitation by other factors. Low to moderate N deposition to N-
627 limited forests typically stimulates plant growth (Quinn et al., 2010) through positive effects
628 on photosynthesis, and this is supported by modelling and experimental results suggesting
629 increased rates of biomass C sequestration in response to N additions (Holland et al., 1997, de
630 Vries et al., 2009). At N deposition rates above 10 kg N ha⁻¹ y⁻¹ the growth response of trees
631 to N may become saturated (Fleischer et al., 2013, de Vries et al., 2014) such that litterfall
632 may be unchanged or even decreased under severe N saturation conditions (Aber et al., 1998)
633 due to nutrient imbalances and increased susceptibility to insect attack (Flückiger and Braun,
634 1998, Kennedy, 2003).

635

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

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

653

654 **5. Conclusions**

655 The MADOC model was able to reproduce changes in soil water DOC concentrations
656 observed for a range of upland organic soil types, although performance was strongly
657 dependent on deposition sequences, implying that good deposition estimates are essential for
658 site-scale modelling. The application of MADOC to terrestrial monitoring data provides
659 insight into the extent to which drivers other than sulphur deposition might contribute to
660 DOC trends. According to the process understanding and parameterisation we have
661 incorporated in the model, S deposition is likely to have exerted a considerably larger
662 influence on DOC than other potential drivers in most sites. Temperature changes appeared to
663 have had little impact. The relative importance of S and N loading depended on soil

664 sensitivity to acidification, and on N limitation. In all N-limited podzols and gleysols
665 investigated, modelled DOC increases over the monitoring period were dominated by the
666 effects of recovery from acidification (higher DOC solubility), but effects of N enrichment
667 driving higher DOC production may have been important in the longer term. At the most N
668 saturated forest site, it is likely that nitrate leaching will actually have contributed to
669 acidification and reduced DOC leaching, whereas at a peatland site where S deposition was
670 retained through sulphate reduction, N enrichment was the only driver capable of driving a
671 potential DOC change before the monitoring period.

672

673 Our modelling study emphasises the possibility that although recent soil and surface
674 water trends in DOC concentrations are keeping up with a return toward pre-industrial levels,
675 concentrations for a range of soil types may now be higher than historical levels as a
676 consequence of the effect of N fertilisation raising the baseline. However, even the longest
677 reliable soil water DOC records only extend back for two decades or so and this is not
678 sufficient to fully disentangle possible acidification recovery and eutrophication effects.
679 Hence further evidence may be best derived through the further refinement of
680 paleolimnological reconstruction approaches that may allow changes in DOC in surface
681 waters to be inferred over centennial time scales, and continued monitoring over an extended
682 period of sulphur deposition rates that now appear to be approaching pre-industrial levels in
683 some areas.

684

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691

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