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1 Fine-scale temporal characterization of trends in soil water dissolved 2 organic carbon and potential drivers.

3
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16 Abstract

17 Long-term monitoring of surface water quality has shown increasing concentrations of Dissolved
18 Organic Carbon (DOC) across a large part of the Northern Hemisphere. Several drivers have been
19 implicated including climate change, land management change, nitrogen and sulphur deposition and CO₂
20 enrichment. Analysis of stream water data, supported by evidence from laboratory studies, indicates that
21 an effect of declining sulphur deposition on catchment soil chemistry is likely to be the primary mechanism,
22 but there are relatively few long term soil water chemistry records in the UK with which to investigate this,
23 and other, hypotheses directly. In this paper, we assess temporal relationships between soil solution
24 chemistry and parameters that have been argued to regulate DOC production and, using a unique set of co-
25 located measurements of weather and bulk deposition and soil solution chemistry provided by the UK
26 Environmental Change Network and the Intensive Forest Monitoring Level II Network. We used statistical
27 non-linear trend analysis to investigate these relationships at 5 forested and 4 non-forested sites from
28 1993 to 2011. Most trends in soil solution DOC concentration were found to be non-linear. Significant
29 increases in DOC occurred mostly prior to 2005. The magnitude and sign of the trends was associated
30 qualitatively with changes in acid deposition, the presence/absence of a forest canopy, soil depth and soil
31 properties. The strongest increases in DOC were seen in acidic forest soils and were most clearly linked to
32 declining anthropogenic acid deposition, while DOC trends at some sites with westerly locations appeared
33 to have been influenced by shorter-term hydrological variation. The results indicate that widespread DOC
34 increases in surface waters observed elsewhere, are most likely dominated by enhanced mobilization of
35 DOC in surficial organic horizons, rather than changes in the soil water chemistry of deeper horizons. While

36 trends in DOC concentrations in surface horizons have flattened out in recent years, further increases may
37 be expected as soil chemistry continues to adjust to declining inputs of acidity.

38

39 **Keywords:** DOC, acidification, acid deposition, recovery, trend, additive model

40 **1. Introduction**

41 Reports of increasing concentrations of dissolved organic matter (DOM), as reflected by changes in
42 dissolved organic carbon (DOC), in surface waters over the past three decades (Freeman et al., 2001,
43 Skjelkvale et al., 2001, Evans et al., 2005, Hruska et al., 2009, Couture et al., 2012, Futter et al., 2014,
44 Monteith et al., 2014) have led to concerns both for public health (Ritson et al., 2014) and the fate of
45 terrestrial carbon stocks (Freeman et al., 2001). The DOM trend in upland drinking water sources has
46 exacerbated treatment costs, since most organic carbon has to be removed using expensive coagulation
47 procedures prior to the addition of disinfection agents such as chlorine. Failure to do so can result in
48 excessive production of potentially toxic disinfection bi-products (DPBs such as Trihalomethanes) (Ritson et
49 al., 2014). Separately, the increase in DOC raises various uncertainties with respect to carbon accounting
50 and the extent to which the carbon source/sink status of soils may be changing.

51

52 Climate and land use change have both been offered as explanations for rising DOM
53 concentrations and both might imply a long-term destabilisation of terrestrial carbon stocks (Freeman et
54 al., 2001). An alternative hypothesis, rapidly gaining acceptance, is that regional scale trends are linked to
55 biogeochemical recovery of soils from anthropogenic acidification (Evans et al., 2006, de Wit et al., 2007,
56 Monteith et al., 2007, Oulehle and Hruška, 2009, Erlandsson et al., 2011). The recovery hypothesis is
57 founded on three elements. The first is evidence that DOM in surface waters, that are not subject to
58 substantial point or diffuse sources of nutrients, tends to have a predominantly allochthonous source
59 (Thurman, 1985). The second is that factors associated with the production of organic matter, and the
60 hydrological forces of DOC transport from soils to waters, have not changed consistently across the area in
61 which the DOC concentrations have changed. The third is the biogeochemical theory that organic matter
62 mobility or solubility will increase in response to reductions in soil water acidity or ionic strength coupled
63 with the observation that there have been very large reductions in sulphur deposition in most regions
64 where DOC concentrations have increased substantially. Furthermore, indications of a recent reduction in
65 the rate of DOC increase in surface waters is consistent with the recovery hypothesis since rates of change
66 in acid deposition have also slowed in recent years (Monteith et al., 2014).

67

68 While statistical relationships between the rate of change in acid deposition and DOC
69 concentrations in water, modified by acid sensitivity (Monteith et al., 2007), hint strongly at a controlling
70 effect of atmospheric deposition on catchment soils, there is still no clear consensus regarding underlying
71 mechanisms. The organic soils of upper horizons and near-stream zones are considered to be the main

72 source of DOM in headwater catchments (e.g. Brooks et al., 1999, Billett et al., 2006, Evans et al., 2007,
73 Winterdahl et al., 2011), but considerably fewer long term soil chemistry monitoring records exist in
74 comparison with surface waters, and there are, therefore, relatively limited opportunities to test the
75 various DOC trend driver hypotheses at source. Where monitoring of soil solution has been conducted in
76 regions recovering from acidification, DOC concentrations in organic surficial layers have often been found
77 to be increasing at a similar rate to those observed in surface waters (Borken et al., 2011, Stutter et al.,
78 2011), but DOC trends in deeper horizons have both positive and negative gradients, with increases at
79 some sites (Borken et al., 2011, Stutter et al., 2011, Ukonmaanaho et al., 2014) and decreases at others
80 (Wu et al., 2010, Borken et al., 2011, Löfgren and Zetterberg, 2011, Stutter et al., 2011), possibly reflecting
81 the adsorption/desorption properties of more mineral-dominated layers and differences in redox state.
82 Differences in behaviour between surface waters and some soil waters may therefore result from
83 differences in soil properties, in addition to land use type (e.g. Vanguelova et al., 2010, Borken et al., 2011,
84 Stutter et al., 2011). Interactions with climatic factors also need to be taken into account since
85 investigations into the influence of temperature and hydrology on DOC have demonstrated the potential
86 for regional warming and changes in precipitation patterns to affect DOC production and export (Freeman
87 et al., 2001, Pastor et al., 2003, Freeman et al., 2004, Clark et al., 2005). As acid deposition declines to very
88 low levels, and significant changes in temperatures and precipitation are being forecast in response to the
89 continuing accumulation of greenhouse gasses in the atmosphere, it is increasingly important that
90 sensitivity to climatic parameters is quantified accurately.

91
92 Attempts to link DOC dynamics in both soils or surface waters and potential environmental drivers
93 have been based predominantly on the use of linear statistics. Yet recent analysis of the first two decades
94 of data from the UK Upland Waters Monitoring Network (Monteith et al., 2014) demonstrates that trends
95 in stream water chemistry have rarely been linear over this timescale. For example, sulphate
96 concentration, a surrogate for sulphur deposition that has been closely linked with recent DOC trends,
97 declined mostly in the latter half of the 1990s, while chloride concentration (primarily a surrogate for sea
98 salt deposition) fell from particularly high levels in the late 1980s to early 1990s and was relatively stable in
99 later years. Since the degree of long-term change in DOC can be orders of magnitude smaller than spatial
100 and seasonal variation (Clark et al., 2010), a substantial component of the potentially valuable diagnostic
101 temporal variation can be lost in the process of reducing time series data to monotonic linear trend
102 components (e.g. Sen Slope) when changes in both driving and response variables are visibly non-linear.
103 Neither parametric linear regression nor non-parametric Mann-Kendal procedures capture short-term,
104 local, variation in the mean in this type of time series data. Effective characterisation of patterns of inter-
105 annual scale variation could, therefore, provide new insights into potential cause-effect relationships that
106 would benefit process understanding.

107

108 Consequently, in this paper, we apply non-linear techniques to describe inter-annual scale
109 temporal dynamics in meteorological variables, soil water DOC and other chemical determinants. Data are
110 derived from two methodologically compatible environmental monitoring networks: the Intensive Forest
111 Monitoring Level II (FLII) and the Environmental Change Network (ECN). These are the only networks in the
112 UK that have systematically collated co-located soil and deposition chemistry and meteorological
113 measurements since the mid 1990s. They thus provide unique opportunities to explore linkages between
114 external drivers and the soil profile properties from different soils types, vegetation and land management,
115 and thus allow a clearer understanding of key processes governing DOC production.

116

117 **2. Methods**

118 **2.1. Field sites**

119 Data from five UK FLII and four terrestrial ECN sites across upland and lowland locations were used
120 for this study (Figure 1). FLII sites were established in 1995 (Vanguelova et al., 2007) and form part of the
121 European forest monitoring network (ICP Forests) that aims to improve understanding of the effects of air
122 pollution and other environmental factors on forest ecosystem structure, function and health. Monitoring
123 of ECN sites started officially in 1993 with the objectives of gathering long-term datasets to improve
124 understanding of the causes and consequences of environmental change across a range of semi-natural
125 and agricultural habitats in the UK (Morecroft et al., 2009, Sier et al., this issue).

126

127 The FLII sites were composed of stands of Oak (*Quercus robur*, *Quercus petraea*), Scots pine (*Pinus*
128 *sylvestris*) and Sitka spruce (*Picea sitchensis*) under standard forest management practices, including
129 thinning and brashing during their growth cycle. The plots varied in planting year between 1920 and 1974
130 and cover a range of forest production classes. The ECN terrestrial sites represented non-forest
131 environments, i.e. upland grassland or moorland vegetation, subject to seasonal grazing, mainly by sheep.
132 Site characteristics are provided in Table 1. The sites ranged in altitude from 20 m to 690 m above sea level.
133 Mean annual temperature (MAT) (for period 2002-2006) varied from 6.1 °C at Moor House up to 11.6 °C at
134 Thetford; and mean annual precipitation (MAP) (for the period 2002-2006) from 605 mm at Thetford to
135 3420 mm at Snowdon.

136

137 Soils at all FLII and ECN sites were surveyed between 1993 and 1995. In each plot the soil was
138 described according to the FAO soil classification system and classified according to the World Reference
139 base for soil classification (WRB, 2007). FLII were also classified using the Soil Classification for England and
140 Wales (Avery, 1980) and the Scottish Soil Classification system (Soil Survey of Scotland Staff 1981). FLII soil
141 sampling and analyses were carried out according to the UNECE ICP Manual for Soil Sampling and Analysis
142 (2006). ECN sites surveys were conducted according to The UK Environmental Change Network Protocols

143 for Standard Measurements at Terrestrial Sites (Sykes and Lane, 1996). Soil types were developed from a
144 range of parent materials and include gleysols, histosols, podzols, cambisols and arenosols. Soil chemical
145 characteristics also varied widely (Table 2): soil organic carbon (SOC) content ranged from 0.8 to 48.7 %;
146 C:N ratios from 3 to 70 and soil acidity from pH 3.6 to 7.0. Base Saturation (BS) and Al saturation (Al sat.),
147 indicative of soil sensitivities to acid deposition, ranged from 1.1 to 100 % and <0.1 to 93.5 % respectively.
148 Acid deposition spanned a gradient of 121 to 406 meq m⁻² yr⁻¹ (2002-2006 means).

149
150 While soil solution monitoring is conducted at all of the nine FLII sites and most of the 12 ECN
151 terrestrial sites, soils at the majority are too dry for collection of year round samples – a pre-requisite for
152 this analysis. Periods for which data were available differed between the two networks and, with respect to
153 the FLII sites, the period for which soil solution DOC data were available was shorter than that for other soil
154 solution solutes, and only corresponded with bulk deposition measurements during the period 2002 – 2006
155 (see supplementary information, table S1).

156 **2.2. Measurements and chemical analysis**

157 Soil water samples were collected at FLII sites every two weeks using tension lysimeters (PRENART
158 SuperQuartz soil water samplers, Plenart Equipment Aps, Denmark) between 1996 and 2011. Twelve
159 lysimeters were installed at each site, six located at 10 cm soil depth and the other six at 50 cm soil depth
160 (Figure 2). Soil water samples were collected and measured according to Level II protocols described in
161 detail in the ICP forests manual (ICP, 2006). Water samples were filtered through a 0.45 µm membrane
162 filter and analysed for pH; total aluminium (Al), calcium (Ca²⁺), magnesium (Mg²⁺), potassium (K⁺), sodium
163 (Na⁺) and iron (Fe) by ICP-OES (Spectro-flame, Spectro Ltd.); ammonium N (NH₄-N) colorimetrically; DOC by
164 total carbon analyser (Shimadzu 5000, Osaka, Japan) using catalytic or persulphate oxidation; and sulphate
165 (SO₄²⁻), nitrate (NO₃⁻) and Cl⁻ by Ion Chromatography (Dionex DX-500). Quality assurance and quality control
166 on dissolved ion concentrations in soil water are described by De Vries et al. (2001) and in the ICP manual
167 (2006). Soil acidity indexes at all sites and depths are shown in Table 2.

168
169 ECN soil waters were also sampled fortnightly by tension lysimetry using the same Prenart
170 SuperQuartz samplers between 1992 and 2010. In accordance with the Environmental Change Network
171 (ECN) protocols, six samplers were placed at the base of each A and B horizon, except for deep peats where
172 fixed depths of 10 and 50 cm depths were used (Figure 2). Soil water was analysed for pH, then filtered
173 (<0.45 µm) and analysed for DOC by combustion oxidation and IR (infra-red) gas detection; total metals (Al,
174 Ca²⁺, Fe, K⁺, Mg²⁺, Na⁺) by ICP-OES; Cl⁻, SO₄²⁻ by Dionex ion chromatography; and NO₃⁻ colorimetrically.

175
176 At each FLII site, samples from two bulk precipitation (installed in the open ground near the forest
177 plots) and 10 throughfall collectors (installed under the stands canopy) were collected every two weeks
178 from 1995 until 2006 and precipitation volumes determined by weighing. Water samples were filtered and

179 analysed for the same determinands and by the same methods as soil water samples. Bulk precipitation
180 samples from single bulk collectors at ECN sites were collected weekly and were analysed using the same
181 methods for the same determinands as soil water.

182
183 Automatic weather stations at FLII sites provided data at an hourly frequency but sufficiently
184 complete records were available only from Alice Holt and Thetford FLII sites (1995 to 2006 only). For the
185 remaining sites (i.e. Grizedale, Lady Bower and Llyn Brianne), and for Thetford for the period 2007-2010,
186 meteorological data were derived from the nearest Met Office weather stations available through the
187 British Atmospheric Data Centre (Met Office - MIDAS Land Surface). Each ECN site has a designated
188 automatic weather station recording hourly climatic data and manual equipment was installed at sites to
189 provide quality control (Morecroft et al., 2009). In the analysis presented here, the automatic weather
190 station data were used, except where data were missing, in which case data from manual measurements
191 were used.

192 **2.3. Data preparation**

193 Data for up to 18 years were collated for this analysis. A number of steps were required to
194 harmonise data between sites, and especially between the two monitoring programmes. For each sampling
195 day, FLII soil water data were provided as the volume-weighted average across the six samplers at each
196 depth and at each location at the site, resulting in one value per location per depth per point in time. The
197 ECN data were received as single values per lysimeter for each sampling date and, for consistency with the
198 FLII dataset, were then volume-weighted and averaged across lysimeters for the two depths. Pooling of
199 samples in this way was indeed sometimes necessary since, during dry periods, sample volumes from
200 individual samplers were too small to allow analysis (Stutter et al., 2011).

201
202 Monthly deposition chemistry concentrations were calculated as a volume-weighted averages from
203 the bi-weekly sampling events at the FLII sites and weekly sampling events at the ECN sites.

204
205 Soil water chemistry variables considered for statistical analysis included absolute concentrations
206 of Cl^- , non-marine SO_4^{2-} (nmSO_4^{2-}), NO_3^- , NH_4^+ , total Al and Na^+ . They also included the sum of
207 concentrations of divalent base cations (Ca^{2+} and Mg^{2+}) to represent catchment sensitivity to acidification
208 (Monteith et al., 2007). In all subsequent analyses acid anion and base cation concentrations were
209 expressed in $\mu\text{eq L}^{-1}$ (Trudgill, 1995). Zero values in the dataset in the measured chemistry variables were
210 replaced with half of the limit of detection (i.e. 0.05 mg L^{-1} for DOC, $1.041 \mu\text{eq L}^{-1}$ for SO_4^{2-} , $1.41 \mu\text{eq L}^{-1}$ for
211 Cl^- , $0.435 \mu\text{eq L}^{-1}$ for Na^+ , $0.025 \mu\text{eq L}^{-1}$ for Ca^{2+} , $0.41 \mu\text{eq L}^{-1}$ for Mg^{2+} , $0.081 \mu\text{eq L}^{-1}$ for NO_3^- , $0.356 \mu\text{eq L}^{-1}$ for
212 NH_4^+ , 0.007 mg L^{-1} for Al).

213

214 Soil water $nmSO_4^{2-}$ concentration, which refers to the fraction of SO_4^{2-} derived from anthropogenic
215 sources only was determined following Evans et al. (2001):

216

$$217 \quad nmSO_4^{2-} = Total\ SO_4^{2-} - 0.104 [Cl^-] [\mu eq\ L^{-1}] \text{ (Eq. 1).}$$

218

219 For this purpose all Cl^- in soil water was assumed to be from a marine source (Evans et al., 2001).

220 While it now appears likely that several sites would have been impacted by hydrochloric acid deposition in
221 the past, it is thought that levels of this pollutant (derived from coal-burning) are likely to have fallen to
222 very low levels in the last 20 years (Evans et al., 2011). For these reasons, $nmSO_4^{2-}$ concentrations in bulk
223 deposition were calculated using the ratio with Na^+ rather than Cl^- :

224

$$225 \quad nmSO_4^{2-} = Total\ SO_4^{2-} - (0.104/0.86) [Na^+] [\mu eq\ L^{-1}] \text{ (Eq. 2).}$$

226

227 Further deposition chemistry variables included: Cl^- , Na^+ , NO_3^- , NH_4^+ , $Ca^{2+}+Mg^{2+}$, and pH. The bulk
228 deposition concentrations of non-marine Cl^- were also estimated from established sea-salt $Cl^-:Na^+$ ratios
229 using:

230

$$231 \quad nmCl^- = Total\ Cl^- - (1/0.86) [Na^+] [\mu eq\ L^{-1}] \text{ (Eq. 3).}$$

232 **2.4. Trends analysis**

233 In order to determine the significance of short-term changes, and determine the timing of key
234 shifts and flows in the data, non-linear smoothers were fitted to the soil water, deposition chemistry and
235 climate data adapting the Generalized Additive Mixed Models (GAMMs) method described in detail in
236 Monteith et al. (2014) and Curtis and Simpson (2014). By fitting the following model to each series, the
237 method allowed separation of the seasonal signal and the longer-term trend into two independent,
238 additive components of the model (Figure 3), and accounted for commonly occurring autocorrelation in
239 environmental time series (Chandler and Scott, 2011). The fitted models took the following form:

240

$$241 \quad y_i = \beta_0 + s_1(Date_i) + s_2(DayOfYear_i) + \varepsilon_i, \quad \varepsilon = N(0, \sigma^2 \Lambda) \text{ (Eq.4),}$$

242

243 where y_i is observed data; β_0 is the intercept or constant term; s_1 and s_2 are smooth functions of time in
244 days since the start of the series and the day of the year respectively; $s_1(Date_i)$ represents the trend in the
245 response and describes how the level of the response varies through time; $s_2(DayOfYear_i)$ represents
246 the seasonal, within year signal in the data); ε_i and ε are model residuals assumed to be zero mean,
247 normal random variables with variance $\sigma^2 \Lambda$, and Λ is a correlation matrix describing the dependence
248 structure in the residuals.

249

250 Models were fitted using GAMMs with a continuous-time AR(1) correlation via restricted maximum
251 likelihood estimation (REML) (Wood, 2004, Wood, 2006, Wood, 2011) using the 'mgcv' package (Wood,
252 2012) for R statistical software (version 3.0.2, R Core Development team, 2013).

253
254 A log transformation was applied to each deposition and soil water variable (except pH), and
255 precipitation, to achieve constant variance and to omit the need to use a generalized linear mixed model
256 (GLMM) with Gamma errors interpretation (Curtis and Simpson, 2014). Where negative values were
257 present in nmSO_4^{2-} series, a constant of 100 was added to each observation to allow log transformation and
258 subsequently subtracted during back transformation. Confidence intervals were calculated and back
259 transformed to allow presentation on the real scale of magnitude of the studied variables.

260
261 Periods of significantly increasing or decreasing concentrations or weather metrics were
262 determined by computing the first derivatives of s_1 using the method of finite differences. Fitted values of
263 the trend (s_1) were obtained from each model for a grid of equally spaced time points over the period of
264 observation. This grid was then shifted in time by a very small amount and fitted values of the trend
265 determined from the model again. The differences between the two sets of fitted values, divided by the
266 difference in time, yielded the first derivatives of the trend. Standard errors for the first derivatives were
267 also computed and a 95% point-wise confidence interval on the derivative determined. Where the
268 confidence interval on the first derivative did not include or cover zero (which is zero slope, zero rate of
269 change) the trend was significantly different from zero at the 95% level. These periods are illustrated on
270 the Figures 4 and 5 showing the fitted trends by a thicker line.

271 3. Results

272 Figures 4a and 4b provide fitted trends for selected indicators of bulk deposition and soil solution
273 chemistry, including DOC, measured at ECN (grassland) sites and FLII (forested) sites respectively.
274 Throughout this section, references to specific solutes, including "DOC", imply solute concentrations unless
275 otherwise stated. Mean concentrations for these solutes for the records analysed are presented in Table 3.

276 3.1. Trends in bulk deposition chemistry

277 The initial and mean concentrations respectively of nmSO_4^{2-} in bulk deposition were mostly much
278 higher in the throughfall collectors in the FLII forested sites than the ECN grassland bulk collectors (Figure
279 4, Table 3). All sites showed a relatively monotonic decline in nmSO_4^{2-} in bulk deposition. Concentrations at
280 three out of four grassland sites, Glensaugh, Moor House and Snowdon, declined significantly (as indicated
281 by thickened lines) throughout the available monitoring records. Concentrations at the forested sites, and
282 the ECN site Sourhope, declined significantly up to around the year 2000. Changes in nmSO_4^{2-} in bulk
283 deposition at these sites were not statistically significant over the period 2000-2005, but concentrations at
284 four (Lady Bower, Thetford, Alice Holt and Grizedale) then showed a brief second significant downturn to

285 the end of the record in 2007. In common with initial concentrations, overall rates of change in bulk
286 deposition of nmSO_4^{2-} at forested sites were substantially greater than those for the ECN sites but were
287 similar relative to mean levels; on average, mean nmSO_4^{2-} in the last year of the record was about 60%
288 lower than in the first year.

289
290 Concentrations of NO_3^- , NH_4^+ and divalent base cations in deposition were also invariably much
291 higher at forested sites, where they also fell substantially, significantly and largely synchronously with the
292 reduction in nmSO_4^{2-} . Nitrate also fell significantly and synchronously with nmSO_4^{2-} at the grassland sites
293 Glensaugh and Sourhope, but otherwise changes in N species and divalent base cations at the grassland
294 sites were mostly difficult to detect and not statistically significant. Concentrations of non-marine chloride
295 (nmCl^-) were generally very low in comparison with the other acid anions (i.e. nmSO_4^{2-} and NO_3^-) but were
296 initially relatively high at three of the forested sites, Alice Holt, Lady Bower and Thetford, prior to declining
297 to levels close to zero, (i.e. Na:Cl ratios approached those found in sea-salt) by the end of these records.
298 Reductions in nmCl^- at Lady Bower and Thetford were again significant up to around 2000 only, but slopes
299 in the modelled means remained downward over the remainder of the records.

300
301 Bulk deposition pH increased significantly over extended periods at almost all sites although the
302 signal was sufficiently noisy at Glensaugh for the gradual increase in the mean not to be deemed
303 statistically significant at any point in the record. While the timing of periods of significant change in pH
304 varied between sites, rates of pH change at Lady Bower and Thetford increased significantly throughout
305 the available records. Periods of significant increase at most forested sites included the first few years of
306 the 21st century, despite the absence of concomitant significant declines in concentrations of nmSO_4^{2-} ,
307 nmCl^- or NO_3^- . Nevertheless, the net effect of continued, albeit individually statistically insignificant, gradual
308 reductions in acid anions, coupled with similar insignificant increases in base cations, appears to have been
309 sufficient to perpetuate upward trends in pH during this time.

310

311 **3.2. Trends in soil water chemistry**

312 The lower panels of Figures 4a and 4b represent the smoothed trends in selected indicators of soil
313 water chemistry measured at two depths at the ECN grassland and FLII forested sites respectively. Periods
314 of significant decreases in soil water SO_4^{2-} were observed at the majority of sites, and mostly coincided with
315 periods of significant declines in nmSO_4^{2-} deposition. Reductions in SO_4^{2-} occurred in both shallow and deep
316 samplers, but in most cases patterns of change in the shallow, and generally more organic, layers more
317 closely mimicked change in bulk deposition concentrations. Sharp initial declines in the shallow samplers of
318 several sites often ceased to be significant by around 2002-2003, indicating a slight lag relative to the
319 termination of significant reductions in deposition. At Glensaugh, where reductions in SO_4^{2-} in bulk
320 deposition were significant across the full monitoring period, shallow soil water SO_4^{2-} declined significantly

321 over two extended periods, i.e. prior to 2000 and after 2007. Despite large reductions in nmSO_4^{2-} in bulk
322 deposition, SO_4^{2-} in shallow samplers in the Moor House peat, the Snowdon cambisol and the Thetford
323 arenosol did not change significantly. However, mean concentrations still showed overall downward
324 tendencies, so the absence of clear trend at these sites may at least partly reflect greater short term
325 variability relative to other sites. An overall decline in shallow soil water SO_4^{2-} at Alice Holt was interrupted
326 by a temporary pulse centred around year 2006, coinciding both with the termination of a major drought
327 and significant insect infestation of the canopy (Pitman et al., 2010).

328
329 At the onset of monitoring, SO_4^{2-} concentrations in deep samplers were mostly similar to those in
330 shallow collectors, with the exception of Alice Holt where the former were much higher. A hysteretic effect
331 can then be seen over the period of the sharpest decline in nmSO_4^{2-} deposition, resulting from a more
332 immediate response in surficial layers to changes in deposition relative to the deeper soils where changes
333 were mostly much more linear over the full monitoring period. The tendency for more linear reductions in
334 SO_4^{2-} is most marked in the B horizons of the podzols monitored at both grassland (Glensaugh and
335 Sourhope) and forested sites (Lady Bower and Grizedale), in addition to the gleysol B horizons of Llyn
336 Brianne and Alice Holt. In contrast, there is no obvious trend in SO_4^{2-} in the deep samplers of the younger
337 and less well developed cambisol soils at Snowdon. Sulphate concentrations in the Thetford arenosol were
338 unusually noisy and showed less indication of sustained change in either soil layer although significant
339 reductions were observed from 2005 to the end of the record.

340
341 In contrast to their marked downward trends in deposition, NO_3^- and NH_4^+ concentrations in soil
342 water displayed high variation in temporal patterns between sites. Ammonium concentrations were
343 invariably very low, indicating rapid nitrification of deposited reduced N in the surface layers of all sites,
344 and these have therefore not been included in Figure 4. Concentrations of NO_3^- in soil solution at several
345 forested sites were exceptionally high, relative to the grassland sites, for at least part of the monitoring
346 records. Mean concentrations and temporal variation in NO_3^- were invariably very similar in both horizons
347 at individual sites, demonstrating a dominance of mineralisation processes in the organic surficial layers
348 and relatively little interaction with mineral horizon exchange sites. Nitrate concentrations in the shallow
349 samplers at Lady Bower and Thetford declined substantially (from high initial concentrations) and
350 significantly over extended periods, possibly reflecting the very large reductions in bulk deposition
351 concentrations of N species at these two sites. A large and rapid reduction in soil water NO_3^- at Grizedale
352 also mirrored the pattern of reductions in N species in deposition at this site, but elsewhere NO_3^- in soil
353 solution did not track trends in N in bulk deposition. Concentrations at Llyn Brianne increased sharply from
354 around 2008.

355
356 Chloride concentrations in the shallow Lady Bower soils declined synchronously with the
357 substantial reduction in nmCl^- deposition. Elsewhere, sustained significant Cl^- trends were detected in both

358 the shallow and deep soil samplers for the most long running time series, Sourhope, Glensaugh and Moor
359 House, despite very low levels of nmCl^- in bulk deposition throughout these records, and mostly
360 insignificant trends in Na^+ in bulk deposition (thereby ruling out a dynamic response to changes in sea-salt
361 inputs as the key influence). While Cl^- is generally considered a relatively conservative anion with respect to
362 its passage through catchments, the parallel downward trends seen in both horizons of the ECN sites are
363 broadly consistent with a process of long term gradual release of organically bound Cl^- from surficial
364 horizons (see Section 4.2). However, there was no clear trend in the forested sites other than Lady Bower.
365

366 Trends in the sum of concentrations of divalent base cations (i.e. $\text{Ca}^{2+} + \text{Mg}^{2+}$) varied amongst sites
367 and the soil depths but were largely downward. At the grassland sites there was little indication of any
368 downward trend in the comparable metric in bulk deposition, and soil solution trends were therefore most
369 likely dominated by reduced displacement from soil exchange sites as a consequence reductions in acid
370 deposition. At Lady Bower, where $\text{Ca}^{2+} + \text{Mg}^{2+}$ in shallow samplers declined significantly throughout the
371 record, trends were generally less directional and mostly insignificant. Outside this period there was
372 relatively little evidence for significant directional change for the majority of sites, although concentrations
373 at Alice Holt broadly mimic those for soil water SO_4^{2-} , including with respect to the pulse centred on 2005.
374

375 Soil water pH at the majority of sites increased over the full records at both depths at most sites,
376 but again changes were most pronounced in the earlier years of the time series. Despite common recovery
377 from acidification, the analysis also detected brief periods of significant reduction in soil water pH, most
378 markedly towards the end of the Llyn Brianne record – corresponding to a surge in nitrate concentration
379 (see Discussion). The strongly buffered Thetford arenosol (Table 2) unsurprisingly showed little evidence of
380 change in soil water pH across the soil profile.

381
382 Two grassland and two forested sites showed significant long term reductions in total aluminium
383 concentrations in deep samplers (i.e. Glensaugh, Sourhope, Lady Bower and Llyn Brianne). Similar, albeit
384 slightly weaker, trends were observed in the shallow samplers of these sites, with the exception of Llyn
385 Brianne where an increase in Al again appeared to coincide with an increase in shallow soil nitrate. Shallow
386 soil Al concentrations also increased steadily and significantly at Grizedale.
387

388 **3.3. Trends in soil water DOC**

389 With the exception of Alice Holt, DOC concentrations were markedly higher in shallow samplers
390 than in deep samplers throughout the records (Figure 4, Table 4), demonstrating both a dominance of DOC
391 production in the surficial soils and varying degrees of adsorption in deeper mineral soils. There was no
392 strong linear relationship between mean DOC and %SOC across all sites in either shallow or deep samplers.
393 While mean DOC concentrations in the shallow samplers of the four sites with particularly organic upper

394 horizons, i.e. %SOC > 30 (i.e. Moor House, Sourhope, Glensaugh and Llyn Brianne were invariably high (i.e.
395 above 20 mg L⁻¹), and were mostly 12 mg L⁻¹ or less in the deeper samplers in B horizons (where %SOC was
396 invariably <8), Ah and Bw horizons of the Thetford Arenosol, both with very low %SOC, exhibited the
397 highest DOC of all sites.

398
399 At all three grassland sites with DOC records extending back to 1993 (Moor House, Glensaugh and
400 Sourhope), DOC increased significantly during periods up to 2000, but in shallow soil samplers only, while
401 significant increases beyond this time were confined to a brief period at Glensaugh only. The main changes
402 in shallow soil DOC at Glensaugh and Sourhope broadly coincided, therefore, with the periods of steepest
403 reductions in SO₄²⁻ in the same samplers and the period of strongest reductions in nmSO₄²⁻ and other acid
404 anions in deposition observed at Sourhope and all five forested sites. DOC trends in the deep samplers of
405 these grassland sites showed contrasting behaviours. Concentrations in the peaty gleyed podzol B horizon
406 of Sourhope showed a continuously significant downward trend, while those for the Glensaugh podzol B
407 horizon indicated a very slight upward step (although concentrations were very low throughout). Deep
408 peat concentrations at Moor House, oscillated at concentrations between 15 – 20 mg L⁻¹ and were more
409 variable than in the shallow samplers.

410
411 Unfortunately, soil water DOC records for the forested sites were too short to determine whether
412 the pre-2000 increases seen at the grassland sites were more widespread. However, shallow samplers in all
413 five FLII sites, in common with Glensaugh, experienced significant increases in DOC between around 2002
414 and 2005, while these were sustained throughout the 2002 to 2011 monitoring period at Alice Holt and
415 Thetford. Dissolved Organic Carbon in the B horizons at Llyn Brianne and Lady Bower (two of the three
416 coniferous sites) also increased significantly throughout that period, while that for Thetford and Grizedale
417 showed significant brief increases centred on 2005, in common with the deep samplers at Glensaugh and
418 Moor House. In contrast, DOC in the B horizon deep samplers at Alice Holt decreased significantly and
419 relatively linearly over most of the full monitoring period analysed, in common with that for Snowdon and
420 Sourhope. Trends in DOC at the two depths at Alice Holt were diametrically opposed and of the same
421 magnitude so that the zone of higher concentrations moved from shallow to deep samplers over the
422 monitoring period. In contrast, DOC concentration declines in the freely drained Snowdon soil at the two
423 depths roughly mimicked each other. Snowdon was the only site to exhibit a significant decrease in DOC in
424 shallow horizons.

425

426 **3.4. Trends in precipitation and temperature**

427
428 Smoothed trends in monthly total precipitation and average air temperatures observed at or near
429 each site are presented in Figure 5. All sites showed similar air temperature profiles with a general

430 indication of slight (but insignificant) increases over the first 10 years of these records, followed by
431 significant downturns at the majority of sites from around 2006. There was no evidence for any periods of
432 significant temperature increases that were common between two or more sites.

433
434 Precipitation at Sourhope increased linearly and significantly throughout the analysed period, and
435 increased particularly sharply at Llyn Brianne from around 2006. Other sites, displayed mostly similar non-
436 linear profiles with most showing a general tendency for long-term increases although change throughout
437 most of the monitoring period was deemed insignificant.

438

439 **4. Discussion**

440 **4.1. Influence of location and land use in influencing bulk deposition concentrations and trends**

441 Since the onset of the industrial revolution, acid deposition, originating largely from the
442 combustion of fossil fuels, has resulted in widespread acidification of soils and waters across many parts of
443 the UK and other industrialised regions (Schindler, 1988). Until recently, this deposition was dominated by
444 sulphur species, i.e. wet and dry deposition of sulphuric acid and dry deposition of sulphur dioxide.
445 However, sulphur emissions peaked in the 1980s and have since fallen rapidly, and particularly during the
446 1990s, as a series of measures were introduced, including the phasing out of more polluting plant, a move
447 from gas to oil, and the commissioning of flue gas desulphurisation (FGD) technology (RoTAP, 2012). Over
448 the 20th century, atmospheric deposition of N species made a secondary contribution to the acidity of
449 deposition, both directly, through the deposition of nitrate, and indirectly through mineralisation or
450 biological uptake of reduced N (Visgilio et al., 2007). Nitrogen deposition has not responded to the same
451 extent as S deposition to recent reductions in industrial emissions (Fowler et al., 2007). The data presented
452 in this paper demonstrate a gradual re-balancing of the relative contributions of S and N to the acidity of
453 bulk deposition in the UK as S deposition has fallen more rapidly. Downward trends in both NO_3^- and NH_4^+
454 in bulk deposition are also widely detectable across the ECN, although patterns in atmospheric ammonia
455 (NH_3) concentrations are more variable (Monteith et al., this issue). Hydrochloric acid, derived from the
456 combustion of coal with a high chlorine content, was recently shown to also have made a significant
457 contribution to acid deposition in parts of the UK, although this fuel source is believed to have been largely
458 phased out by the end of the 20th century. Evans et al. (2011) estimated that reductions in non-marine Cl^-
459 between 1986 and 2007 were on average around half of those for nmSO_4^{2-} suggesting that reductions in
460 anthropogenic Cl^- deposition could account for a significant proportion of ecosystem recovery from
461 acidification.

462
463 Our analysis demonstrates that responses in bulk deposition chemistry to reductions in the
464 emission of S, N and Cl species were most marked at the forest sites, where initial concentrations of
465 nmSO_4^{2-} , NO_3^- , NH_4^+ , divalent cations and, to a lesser extent nmCl^- , in bulk deposition were invariably

466 considerably higher than at the grassland sites. Differences in rates of change between FLII and ECN sites
467 likely reflect both geographical distribution and the role of forest canopies in enhancing deposition. In an
468 assessment of regional variation in trends of acid deposition across the UK Acid Deposition Network for the
469 period 1986-2002 (Fowler et al, 2005), rates of decline in nmSO_4^{2-} were shown to be greatest in the close-
470 to-source areas of southern and eastern England (classified as Zone 1- see Figure 1) and weakened in a
471 north-westerly direction with the least affected region (northwest Scotland) classified as Zone 4 (Figure 1,
472 Fowler et al., 2005). Of the sites assessed in this paper, three forest sites, Alice Holt, Thetford and Lady
473 Bower, but no grassland sites, fell within Zone 1 of this classification. These three sites exhibited both the
474 highest mean concentrations of major ions of all sites and the most marked reductions. Nevertheless, a
475 comparison of mean chemistry of sites that fall within Zone 2 (i.e., Moor House, Sourhope, Glensaugh,
476 Grizedale and Llyn Brianne) show that concentrations and trends in major ions in the former three
477 grassland sites were consistently lower than those at the latter two forest sites. The role of forests relative
478 to other vegetation types in ecosystem acidification and recovery has been widely recognised with respect
479 to both soils (Stuanes et al., 1992, Hruska et al., 2002, Vanguelova et al., 2010, Nisbet and Evans, 2014) and
480 surface waters (Fölster and Wilander, 2002, Oulehle et al., 2013, Malcolm et al., 2014, Nisbet and Evans,
481 2014). Forests have a much higher capacity to scavenge air pollutants than grasslands (Fowler et al., 1989,
482 Miller et al., 1991, Harriman et al., 2003) resulting in considerably higher fluxes of acidifying ions being
483 deposited in throughfall collectors, and hence also to soils, relative to bulk collectors in open ground (Ivens
484 et al., 1990).

485

486 Our assessment of trends in deposition is confined to solute concentrations in bulk collectors. At
487 the grassland sites the chemical composition of bulk deposition samples will have been dominated by
488 solutes in precipitation, i.e. wet deposition, although a proportion of dry deposition to the collector funnel
489 will also have been captured. Dry deposition velocities tend to be enhanced in forests as a consequence of
490 the high aerodynamic roughness of the vegetation (Fowler et al., 1999), and while throughfall collector
491 samples will have provided a more integrated measure of wet, dry and occult deposition to the canopy, it
492 has been demonstrated that dry deposition may still be significantly underestimated using this approach
493 (Rustad et al., 1994). Since dry deposition at a national scale has decreased more than wet deposition
494 (Fowler et al., 2005) it is likely that trends in total anthropogenic deposition at forest sites were even more
495 marked than implied by the trends in bulk deposition concentrations reported here. Nevertheless, trends
496 in nmSO_4^{2-} , NO_3^- , NH_4^+ , and divalent cations showed a distinctive spatially coherent temporal pattern at all
497 forest sites and, to a lesser extent, the grassland site Sourhope, with sharp declines in all species prior to
498 2000. Although rates of change in the concentration of individual ions often ceased to be significant after
499 2000, the combined effect of further gradual change appears to have been sufficient for precipitation pH to
500 continue to increase throughout much of the remaining records. The more continuously statistically
501 significant change in nmSO_4^{2-} in deposition identified for Moor House, Glensaugh and Sourhope, relative to

502 change at the forested sites might in part represent a statistical artefact resulting from the more extended
503 deposition records available for the grassland sites.

504
505 Temporal patterns in divalent base cations corresponded closely with those for acid anions at all
506 the forest sites indicating common dominant anthropogenic sources. In the case of the Zone 1 sites, this
507 was also true for Na^+ which is normally assumed to be entirely derived from sea salt. Sodium, however can
508 also originate from anthropogenic sources such as the manufacturing industry, iron production and
509 domestic and power station coal burning (Werner et al., 2011). As Na^+ was used to calculate marine
510 fractions of SO_4^{2-} and Cl^- real concentrations and rates of change in nmSO_4^{2-} and nmCl^- at the Zone 1 sites
511 may have been significantly underestimated at these sites.

512

513 **4.2. Soil water responses to trends in deposition**

514 The smoothed plots presented in Figure 4 demonstrate that recent changes in the chemistry of
515 atmospheric deposition have had a marked influence on solute concentrations and acidity of soil water
516 across a wide range of grassland and forest sites. Effects were particularly pronounced at forest sites,
517 where reductions in deposition were largest, and at those sites with the most acidic soils. Changes in
518 surficial concentrations of SO_4^{2-} , the dominant acid anion at most sites, mimicked deposition trends in
519 most cases. Soil water concentrations of SO_4^{2-} in podzol B horizons appeared to be in long-term (decadal-
520 scale) equilibrium with those in the upper soil, with gradual desorption from mineral horizons likely to
521 account for an apparent lagged response over the period of the sharpest reductions in nmSO_4^{2-} deposition.
522 Sulphate adsorption/desorption characteristics of soils are known to be strongly pH dependent. Specific
523 adsorption of SO_4^{2-} by soils tends to be favoured by high levels of free iron and aluminium oxides and
524 hydroxides (Fuller et al., 1986), and laboratory and field studies show that increasing soil pH often tends to
525 increase desorption of SO_4^{2-} (Singh, 1984, Nodvin et al., 1986). The absence of significant reductions in
526 SO_4^{2-} in the Moor House peats, despite large reductions in deposition, reflects the role of redox processes
527 in these soils - reduction to sulphide during long periods of anaerobic conditions punctuated by occasional
528 re-oxidation and release of sulphate following re-wetting after drought (Clark et al., 2005).

529

530 Unsurprisingly, there was little association between variation and trends in concentrations of
531 species in soil water at either depth and those in deposition. Bacterial nitrification of reduced N tends to be
532 rapid and generates NO_3^- which itself is highly reactive in soils and water (Galloway and Cowling, 2002). Soil
533 N process dynamics are dependent on a range of ecosystem properties including plant demand,
534 stoichiometric relationships with carbon and other nutrients, and the amount and form of N inputs
535 (Galloway et al., 2003, Shibata et al., 2014). Curtis et al. (2011) proposed a conceptual model of N
536 behaviour in semi-natural catchments, whereby retention and accumulation of N is maximised in carbon-
537 rich ecosystems, while carbon-poor ecosystems exposed to elevated N deposition leach most NO_3^- . In our
538 study the highest NO_3^- concentrations indeed occurred at the forest sites with very low soil organic carbon

539 content, i.e. Lady Bower and Thetford, although these were also the sites that experienced the highest
540 concentrations of N species in bulk deposition. At Thetford, NO_3^- was by far the most concentrated acid
541 anion throughout the monitoring period, and its large significant reduction detected in shallow samplers
542 will have dominated changes in surface soil acidity at this site. Changes in NO_3^- in the Lady Bower soils,
543 while not as great in magnitude as SO_4^{2-} , will also have made a significant contribution to reductions in total
544 acidity. Similarly the sharp post-2007 increase in NO_3^- in the surface soils at Llyn Brianne, possibly linked to
545 a major aphid infestation of the canopy (Pitman et al., 2010) also seems to account for a significant
546 reduction in soil pH over the same period.

547
548 Sizeable reductions in Cl^- in the soil water of grassland sites were too large to be explained by at
549 most slight and non-significant reductions in Na^+ deposition, thus ruling out any dynamic response to a
550 change in sea salt deposition. Chloride is generally considered to undergo less adsorption, biological
551 retention and biogeochemical cycling than SO_4^{2-} or NO_3^- , and is hence more mobile in soils (Schlesinger,
552 1997). It has been proposed that long term declines in Cl^- in shallow and deep soils at these sites represent
553 responses to declining deposition of hydrochloric acid derived from industrial sources (Evans et al., 2011).
554 However, Na:Cl ratios in deposition at these sites were generally difficult to distinguish from those
555 expected in sea salt, thus providing little evidence for short-term effects of reductions in HCl deposition.
556 Marked downward trends in Cl^- in both horizons therefore most likely imply longer term retention and
557 release of Cl^- from organic complexes (Bastviken et al., 2006). Longer term reductions in either, or both,
558 marine- or industrially-derived Cl^- may therefore have contributed to observed reductions in soil solution
559 Cl^- concentrations. However, there were few such distinct trends in soil solution Cl^- at most forest sites,
560 perhaps reflecting greater short term variability resulting from enhanced canopy interception of sporadic
561 marine inputs. The major exception was the site most affected by anthropogenic Cl^- , Lady Bower and
562 Thetford, where the strong trend in soil water Cl^- prior to 2003 showed close correspondence with that for
563 the throughfall concentration of nmCl^- .

564
565 Forest sites with infertile soils and low base saturation are most vulnerable to the loss of base
566 cations as a result of sea-salt and acid deposition (Vanguelova et al., 2007). In addition, tree growth can
567 also contribute to long-term depletion in base cations (Sverdrup et al., 1992, Finzi et al., 1998, Högberg et
568 al., 2006). There was little consistent pattern across sites in trends in divalent base cation concentrations
569 and it was difficult to ascertain the relative effects of reductions in inputs from deposition (which were
570 particularly marked at forest sites), effects of reduced leaching resulting from reduced acid inputs and
571 effects of tree growth. However concentrations declined in the shallow samplers of most podzols, including
572 grassland sites (and the Moor House peats) where base cation deposition trends were insignificant,
573 indicating reduced rates of exchange with H^+ ions. Long-term declines in $\text{Ca}^{2+} + \text{Mg}^{2+}$ were also apparent in
574 the mineral horizons of most grassland and forest podzols, with the exception of Grizedale.

575

576 Soil water pH increased significantly in one or both horizons over various periods but changes were
577 mostly coincident with the period of most marked reductions in acid deposition. The most consistent
578 positive response across sites was observed for B horizons of the more acidic soils prior to 2000, with more
579 mixed behaviour in organic horizons. Significant increases in shallow sampler pH were seen during the
580 period of sharpest change in deposition at all four grassland sites, in addition to Lady Bower and Grizedale,
581 while upward trends at Moor House and Snowdon were sustained throughout the monitoring periods,
582 likely due the decrease in nm Cl⁻ deposition (Evans et al., 2011). However, organic horizons at Glensaugh,
583 Llyn Brienne, Thetford and Alice Holt showed no clear overall increase in pH. Morecroft et al. (2009) have
584 previously reported differential responses in soil pH in surficial and deeper horizons of ECN sites, and
585 similar patterns have been described for the UK Countryside Survey (RoTAP, 2012). It has been suggested
586 that increased release of organic acidity generated by organic rich surface horizons has served to buffer
587 reductions in acid inputs relative to changes in lower horizons (e.g. Erlandsson et al., 2010).

588
589 Along with increases in pH, total Al started decreasing as a result of declining acid deposition, since
590 pH controls Al solubility (Walker et al., 1990). Decreases in total Al were most pronounced in podzols and
591 gleysols with soil pH < 5. These patterns were consistent in surface waters across Europe in 1990s
592 (Skjelkvale et al., 2005) and in surface and soil waters at national scales over the past few decades
593 (Vuorenmaa et al., 2006, Wu et al., 2010, Löfgren and Zetterberg, 2011, Monteith et al., 2014).

594

595 **4.3. Temporal links between trends in DOC and potential drivers**

596 Our analysis demonstrates that soil water DOC concentrations increased significantly over
597 extended periods at most of our study sites, particularly in organic surficial horizons. As the sites are
598 distributed across much of Great Britain, the observation is consistent with the widely accepted
599 assumption that regional scale increases in DOC seen in surface waters (e.g. Monteith et al., 2007) have
600 been driven by changing processes within catchment soils. Differences in the periods over which
601 monitoring data were available, both between ECN and FLII sites and between measurement types,
602 restricted the extent to which the precise timing of DOC changes could be compared across all sites or
603 linked with the timing of changes in potential drivers. However, where records overlapped sufficiently,
604 comparisons with trends in other solutes, bulk deposition and climate variables, provided a number of
605 clues regarding likely dominant drivers and mechanisms behind the DOC trends.

606

607 We found relatively little evidence for an association between both long term variation and periods
608 of significant change in soil water DOC and periods of significant change in either temperature or
609 precipitation (with the exception of Snowdon – see below). Figure 5 provides very little indication of shifts
610 in monthly mean air temperatures over the relatively short period covered by most sites. Periods of
611 significant change in air temperatures were largely restricted to phases of slight cooling from around 2005-

612 2006 to the end of the datasets. There was little indication for significant changes in monthly rainfall totals
613 at most sites. The modelled GAM curves hint at a general tendency for slight increases in precipitation but,
614 with the exception of Glensaugh, changes were generally not found to be statistically significant. Despite
615 significant increases in summer precipitation during the course of ECM monitoring, but mostly during the
616 most recent decade (Monteith et al. (this issue), temporal variation in precipitation at other times of year
617 appears to have largely balanced these changes, resulting in little overall trend in monthly precipitation.
618 There was, therefore, little evidence that the long-term shifts in soil chemistry described earlier could be
619 linked to changes in either temperature or precipitation.

620

621 Widespread correspondence of temporal patterns in acid anions in deposition and soil water, and
622 acid anions and DOC in organic horizons, provided further strong support for the argument that these are
623 the key causal pathways for DOC increases. Similar relationships have previously been identified for FLII
624 site soils in Germany, where sulphate concentration was found to be the only parameter that correlated
625 with DOC trends (Borken et al., 2011). As in the case of the German FLII sites, monitoring of DOC at the UK
626 forest sites began only after most substantial reductions in acid deposition had occurred. Borken et al.
627 (2011) suggested that time lags between the major reductions in SO_4^{2-} deposition and changes in DOC
628 could reflect chronic retention of S by organic and inorganic binding sites and more gradual release (Mörth
629 et al., 2005), resulting in a partial de-coupling of deposition and soil solution SO_4^{2-} trends.

630

631 Our results show that the major changes in SO_4^{2-} in deposition were almost synchronous with those
632 in shallow samplers, but statistically significant reductions in the latter continued for 1-3 years after trends
633 in deposition appeared to terminate. The late commencement of monitoring of DOC at FLII sites appears to
634 have caught only the tail end of the deposition-induced, but lagged, changes in soil chemistry at Lady
635 Bower, Llyn Brianne and Grizedale. Indeed, rates of decline in SO_4^{2-} concentrations at these sites were
636 already levelling off, and most had ceased to be statistically significant, over the relatively short period
637 significant increases in DOC were detected. By contrast, significant increases in DOC in organic horizons
638 were sustained at two of the three Zone 1 deposition sites throughout the monitoring period. This
639 conforms with the hypothesis of “de-coupling” at heavily impacted forest sites, but while there was an
640 overall long-term reduction in SO_4^{2-} in the organic horizon of Alice Holt, there was no comparable change
641 in this acid anion at Thetford. Here, the primary change in soil chemistry was a large and continuously
642 significant reduction in NO_3^- , thus supporting the hypothesis that changes in either soil acidity or ionic
643 strength are the key driver of change in DOC, rather than changes in SO_4^{2-} specifically.

644

645 The relative importance of soil acidity and ionic strength in influencing organic matter solubility has
646 been widely debated and is yet to be fully resolved (e.g. Evans et al., 2012; Hruska, 2009). While the ionic
647 strength of soil solution will have declined substantially at all sites, and particularly at the forest sites,
648 changes in soil solution pH of organic horizons are often not clear and it is therefore difficult to associate

649 DOC changes at some sites directly with soil acidity changes. However, there is mounting evidence that
650 both rates of change and spatial variation in DOC in surface waters (Monteith et al., 2007, Monteith et al.,
651 2015) and spatial variation in DOC in soils (Sawicka, 2015) are linked to interactive effects of SO_4^{2-} and base
652 cation levels, suggesting that DOC in acid-sensitive soils is most responsive to reductions in acid anion
653 inputs. Such relationships are consistent, therefore, with the humic substance partitioning model of Tipping
654 and Woof (1991), where increased negative charge on humic surfaces associated with increased pH
655 promoted increased movement of organic matter from solid to dissolved phases.

656
657 We found relatively little agreement in DOC trends, either with respect to direction or persistence,
658 between shallow and deep horizons, and at nearly all sites DOC concentrations in the former were
659 substantially higher than in the latter. Assuming DOC is produced predominantly at the soil surface from
660 litter or humus (Kalbitz et al., 2000), the apparent loss of DOC from percolating soil water at depth and
661 differences in temporal behaviour is likely to reflect effects of both mineralisation and sorption desorption
662 processes. DOC concentrations in B horizons at two of our highly acidic coniferous forest sites increased
663 significantly over extended periods but at slower rates relative to briefer changes in organic horizons,
664 indicating a lagged response at depth to increased DOC production at the surface. Forest soils, and
665 coniferous soils particularly, tend to be more acidic (Harriman and Morrison, 1982, Ormerod et al., 1989,
666 Helliwell et al., 2001, Langan and Hirst, 2004), and often exhibit relatively high concentrations of reactive Al
667 (Harriman and Morrison, 1982, Ormerod et al., 1989, Harriman et al., 2003). The two coniferous sites had
668 the highest soil Al saturation and total Al concentrations of all sites monitored, and were also characterised
669 by lighter mineral soil texture which is likely to have limited the potential for DOC sorption relative to
670 heavier clay mineral soils. In laboratory examinations of DOC leaching from forest subsoils Kaiser and Zech
671 (1999) and Münch et al. (2002) both found that increased pH favoured DOC desorption, although Kaiser &
672 Zech (1999) found much stronger responses to reductions in ionic strength and argued that mobilisation of
673 colloidal organic matter was, therefore, likely to be a key mechanism.

674
675 In contrast to the positive DOC trends in B horizons described above, trends in the heavy clay soil at
676 forested Alice Holt and the peaty gley podzol beneath the Sourhope grassland were strongly negative, thus
677 counteracting significant increases in their organic horizons. Borken et al. (2011) also reported negative
678 DOC trends in mineral horizons of German forest soils, despite positive trends in organic horizons while
679 Stutter et al. (2011) made similar observations for grassland Glensaugh and Sourhope. Furthermore,
680 Löfgren and Zetterberg (2011), found that DOC in lower-B horizon soil solution of 46% of 68 forested sites
681 in southern Sweden decreased over the period 1987 – 2008 over a period of significant reductions in acid
682 deposition, while a further 47% showed no trend. Simple competitive sorption theory suggests that a
683 declining presence of sulphate anions would lead to stronger DOC binding to soils (Wu et al., 2010), and
684 hence removal from soil water. Mineral soils might be expected to show the most marked increases in
685 sorption capacity for DOC in these circumstances. Decreasing SO_4^{2-} concentrations resulting from reduced

686 deposition of S and the continuing pH-dependent desorption of sulphate may, therefore, both have
687 contributed to enhances adsorption of DOC in these soils.

688
689 Trends in DOC in the Snowdon soils differed from all other sites – with reductions occurring in both
690 soil horizons. While the long-term trend in the deeper soil is consistent with those observed at Sourhope
691 and Alice Holt and thus with the hypothesis of competitive anion adsorption, the timing of the more brief
692 reduction in DOC, which occurred after 2006, is not consistent with the major changes in deposition-driven
693 changes in soil chemistry. It would seem more likely, in this case, that the change is linked to changes in
694 weather. Snowdon receives much greater amounts of precipitation than any other site, and while the trend
695 fitting to monthly met data provided no clear evidence for anomalous post-2006 changes in precipitation,
696 Monteith et al. (this issue), identified significant increases in summer precipitation linked to post-2006
697 increases in the summer North Atlantic Oscillation. Simple dissolution can diminish DOC concentrations
698 (van den Berg et al., 2012) and a substantial increase in water flux around the time of year associated with
699 peak DOC production may therefore have been the key determinant at this site.

700
701 Moor House was the only site where reductions in nmSO_4^{2-} deposition were not expected to elicit
702 dynamic responses in soils solution chemistry, including DOC. However, episodic increases in DOC in
703 peatlands, such as at Moor House, have previously been clearly linked to episodic release of sulphate
704 following drought. Such episodes were particularly visible in years 1994 and 1995 during which the site
705 experienced severe drought (Clark et al., 2005), which could in turn influence the trend at the beginning of
706 the analysed time series.

707 ***4.4. Implications for observations of rising DOC in surface waters***

708 Overall, the trends in soil water DOC, both positive and, with respect to some B horizons, negative
709 are consistent with a dominant control from declining acid deposition, while the more consistently
710 significant and positive changes observed in organic horizons indicate that changes in organic matter
711 solubility close to the soil surface provides the most likely explanation for regional-scale increases in DOC in
712 surface waters. Linking spatially- and depth-restricted observations of changes in soil chemistry with the
713 catchment-wide signal provided by surface waters is highly problematic, as extensive understanding of
714 geology, soil heterogeneity, hydraulic flowpaths etc., are required and these will vary greatly between
715 locations. It has been argued that in some boreal environments, much of the hydraulic catchment is largely
716 irrelevant with respect to DOC supply to streams, and that most DOC is provided from a relatively narrow
717 riparian zone (Lofgren et al., 2010, Ledesma et al., 2015). However, Hruška et al. (2014), in their detailed
718 modelling study of the upland Lysina catchment in the Czech republic noted that it was unfeasible for
719 stream water DOC concentrations to be sustained from DOC production from the riparian zone alone. The
720 apparent high predictive ability of various spatial DOC models (e.g. Monteith et al., 2015) that tend not to
721 factor in riparian extent would also suggest that soils from across catchments, rather than just stream

722 margins, are likely to have a significant influence on fluvial export of DOC in various upland environments.
723 The increase in DOC concentrations seen in stream waters often appear most marked for seasonal peak
724 concentrations. In the UK, these tend to occur during wet weather in the early autumn when wetted soils
725 facilitate lateral flow paths. In these circumstances it would seem intuitive that potential adsorption of DOC
726 by B horizons of organo-mineral soils is likely to exert little influence relative to enhanced production in the
727 organic layer.

728
729 Our observations are therefore largely consistent with those based on the analysis of UK long-term
730 stream water data alone (e.g. Evans et al., 2006, Evans et al., 2008) and international datasets together
731 (Monteith et al., 2007), experimental and field work (Clark et al., 2011, Evans et al., 2012), and a range of
732 studies from other countries (de Wit et al., 2007, Erlandsson et al., 2008, Haaland et al., 2010, Ekström et
733 al., 2011, SanClements et al., 2012, Futter et al., 2014, Hruška et al., 2014), adding support for an acid
734 deposition-based control. Whether recent trends in both soils and waters represent a gradual return to
735 previous low deposition conditions, however, depends on whether atmospheric nitrogen enrichment has
736 played a role (Findlay, 2005, Rowe et al., 2014), via enhanced stimulation of net primary production leading
737 to increased litter generation. This would act as substrate for DOC production, and/or increased
738 rhizodeposition and priming of organic matter decomposition. This would, however, depend on prevailing
739 levels of ecosystem N saturation. For example, at the N limited grassland sites (indicated by relatively very
740 low NO_3^- leaching) such as Glensaugh, Moor House and Sourhope, nitrogen might be expected to exert a
741 fertilising effect. In contrast, the extremely high levels of NO_3^- concentrations at Lady Bower imply that
742 additional nitrogen input would have an acidifying effect, thus counterbalancing recovery from the large
743 reductions in sulphur and non-marine chloride in the past.

744

745 **5. Conclusions**

746 Our evaluation of long term monitoring datasets provides valuable insight into changing soil
747 chemistry as a result of declines in acid deposition over the last two decades. The grassland and forest soils
748 monitored have undergone substantial recovery from anthropogenic acidification, and while variations in
749 soil chemistry are likely to have been influenced by climatic variations, there is little indication that long
750 term changes can be attributed to climatic shifts in most cases. The observed trends in DOC in soil water in
751 this data set were often non-linear, and periods of significant change in DOC have often been temporally
752 restricted. Temporal patterns of long-term trends in DOC varied between sites for reasons that can be
753 linked to soil properties, vegetation cover, and acid deposition magnitude and source (anthropogenic or
754 natural). DOC trends were mainly related to temporal changes in acid deposition with strongest trends
755 seen in forest soils and drier locations.

756

757 These findings suggest that the DOC trends observations from surface waters correspond strongly
758 to changes in topsoil DOC. Different responses were observed in mineral horizons, but this clearly does not
759 negate declining acid deposition as a viable mechanism explaining increased DOC in surface soils and
760 stream waters. This in turn implies that if the acid deposition continues declining to even lower levels,
761 further increases of DOC concentrations in surface horizons and adjacent surface waters may be observed.
762 Although it is difficult to draw general conclusions for the surface waters from a study based on soil
763 solution chemistry only, because of the complexity of the hydraulic flowpaths, these conclusions do
764 provide a strong base for further research into the direct links between terrestrial and stream water DOC.

765

766 The ECN and FLII monitoring programmes are unique terrestrial surveillance networks, providing
767 continuous, detailed information on the different ecosystems properties and their responses to the
768 anthropogenic and natural change on both local and regional scales. This integrated monitoring provides
769 unparalleled opportunities to study the evolving relationships between climate, pollutant exposure and
770 biogeochemical and biological responses.

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Table 1 Site descriptions. Mean annual daily temperature (MAT), precipitation (MAP) and acid deposition load (max 1993 – 2011). World Reference Base (WRB) classification used to define soil types.

Network	Site name	Soil type (WRB)	Soil drainage	Geology	Vegetation type	Altitude [m]	MAT [°C]	MAP [mm]	Acid deposition (Cl ⁻ + NO ³⁻ + SO ₄ ²⁻) [meq m ⁻¹ y ⁻¹]
ECN	Glensaugh	Humus Iron Podzol	Well drained	Old red sandstone, Schists	Grassland (Moorland)	300	7.8	1505	152
ECN	Moor House	Histosol	Very poorly drained	Limestone, Sandstone, Shale	Grassland (Moorland)	540	6.1	1910	178
ECN	Snowdon	Cambisol	Well drained	Rhyolite and Dolerite and moraines	Grassland	690	7.5	3395	406
ECN	Sourhope	Peat Gleyed Podzol	Well drained	Old red sandstone	Grassland	495	7.7	1170	121
FLII	Alice Holt	Gleysol	Poorly drained	Clay	Deciduous	80	10.7	685	159
FLII	Grizedale	Cambic Podzol	Well drained	Mudstone, siltstone and sandstone	Deciduous	115	9.6	1810	316
FLII	Lady Bower	Cambic Podzol	Well drained	Mudstone, siltstone and sandstone	Coniferous	265	10.6	1260	268
FLII	Llyn Brianne	Gleysol	Imperfectly drained	Mudstone, siltstone and sandstone	Coniferous	450	10.1	2100	376
FLII	Thetford	Arenosol	Poorly drained	Cretaceous	Coniferous	20	11.7	600	149

1 **Table 2 Soil acidity indexes for the sampled sites and depths.**

Site	Samplers Depth [cm]	Horizon		Soil pH	SOC [%]	C/N	BS [%]	Al sat. [%]
Glensaugh	10	H	Shallow	3.9	34.5	28	5	0.07
Moor House	10	O		3.8	40.6	32	11	2.5
Snowdon	8	Ah		5.5	4.4	19	8	28.6
Sourhope	10	O		3.6	48.7	18	5	0.1
Alice Holt FLII	10	Ah		5.4	2.7	5	95	0.4
Grizedale	10	Bs		5.1	5.0	17	7	37.7
Lady Bower	10	Ah		4.1	2.7	16	4	93.5
Llyn Brianne	10	H		3.6	40.1	17	15	50.9
Thetford	10	Ah		5.3	2.0	4	92	1.3
Glensaugh	50	Bs	Deep	4.7	5.3	22	1	2.0
Moor House	50	O		4.0	33.0	31	14	2.1
Snowdon	30	Bw		5.5	2.3	16	4	32.2
Sourhope	40	Bf		4.6	7.0	23	1	1.2
Alice Holt FLII	50	Bcg		6.2	1.1	39	96	0
Grizedale	50	Bs		5.1	5.0	17	7	37.7
Lady Bower	50	Bc		4.5	1.4	21	7	92.3
Llyn Brianne	50	Bg		4.3	3.5	63	2	42.9
Thetford	50	Bw		7.0	0.8	3	100	0

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5 **Table 3 Annual mean concentrations of wet deposited chemical species in precipitation. Means calculated from all**
 6 **available data (see Table S1) during the period 1993-2011.**

Site	nmSO_4^{2-}	nmCl^-	NO_3^-	NH_4^+	$\text{Ca}^{2+} + \text{Mg}^{2+}$	Na^+	pH
$\mu\text{eq L}^{-1}$							
Glensaugh	30.78	< 0	33.56	40.01	36.74	100.42	4.8
Moor House	21.05	< 0	17.51	25.47	24.25	56.18	5.2
Snowdon	16.42	3.10	11.64	16.82	24.33	74.05	5.3
Sourhope	27.84	< 0	27.61	32.92	47.97	90.03	5.0
Alice Holt FLII	88.58	20.08	42.08	48.60	139.13	128.64	6.0
Grizedale	43.14	6.22	23.96	33.23	66.25	136.77	5.3
Lady Bower	119.42	19.19	63.71	55.59	125.32	199.79	4.7
Llyn Brianne	63.71	7.02	37.35	22.64	86.92	190.62	5.2
Thetford	133.15	20.30	111.24	148.24	130.97	201.78	5.4

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8

10 **Table 4 Annual mean concentrations of chemical species in soil water at two depths: shallow and deep. Means**
 11 **calculated from all available data (see Table S1) during the period 1993-2011.**

Site	Samplers Depth [cm]	Horizon		SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	Ca ²⁺ + Mg ²⁺	pH	Al	DOC
				μeq L ⁻¹					mg L ⁻¹	
Glensaugh	10	O	Shallow	67.26	2.87	194.94	51.21	4.1	0.59	21.00
Moor House	10	Bs		29.15	0.83	87.70	50.78	4.2	0.09	23.30
Snowdon	10	Ah		33.96	5.84	157.02	115.46	6.2	0.06	3.19
Sourhope	10	H		82.03	7.25	187.44	85.59	4.2	0.75	19.40
Alice Holt FLII	10	H		127.53	3.35	252.37	264.69	5.7	0.13	12.06
Grizedale	8	Ah		79.76	12.36	250.30	92.50	4.9	0.48	9.27
Lady Bower	10	O		256.06	321.17	229.31	214.54	3.9	1.74	24.13
Llyn Brianne	10	Ah		91.79	24.38	280.09	40.36	3.9	0.49	21.67
Thetford	10	Ah		265.08	1264.41	391.20	1994.53	5.0	1.20	74.00
Glensaugh	50	O	Deep	97.88	1.88	214.44	40.63	4.8	0.75	3.09
Moor House	50	Bs		1.94	0.76	107.11	72.27	4.6	0.03	17.27
Snowdon	50	Bc		41.74	9.81	128.73	129.59	5.9	0.03	1.37
Sourhope	50	Bg		97.66	5.56	196.42	77.47	4.8	1.20	10.80
Alice Holt FLII	50	Bs		352.18	2.80	661.96	608.45	5.7	0.12	13.44
Grizedale	30	Bw		129.28	4.76	294.31	108.20	5.0	0.34	2.06
Lady Bower	40	Bf		358.01	225.44	269.66	141.09	4.3	3.82	3.11
Llyn Brianne	50	Bcg		103.60	3.71	322.83	40.40	4.3	0.97	3.98
Thetford	50	Bw		396.21	2054.27	406.55	4930.96	7.6	0.29	40.82

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14 **List of Figures**

15 Figure 1 Site location map and the geographical locations of pollution zones adapted from Fowler
16 et al. (2005).

17

18 Figure 2 Location of shallow and deep soil water samplers within the sites' soil profiles.

19

20 Figure 3 Graphical representation of the fitted additive model for the shallow samplers DOC
21 concentrations time series at Glensaugh. Panel a) shows the fitted smoother for the trend ($s_1(\text{Date}_i)$). Panel
22 b) shows the fitted smoother for the seasonal term ($s_2(\text{DayOfYear}_i)$). Both figures illustrate how the
23 response (in this case DOC) changes relative to its mean over time. The dashed lines are point-wise 95%
24 confidence intervals on the fitted smoothers and indicate the uncertainty in the estimate of each smooth
25 term.

26

27 Figure 4a Modelled trends in deposition and soil water chemistry chosen chemical determinants at
28 non-forest ECN sites. Black colour denotes shallow samplers, grey colour denotes deep samplers. Periods
29 of significant change, determined by the derivative analysis, are denoted by thickened lines on the fitted
30 trend. Dashed lines indicate 95% point-wise confidence intervals of the fitted trend. For presentation
31 purposes, the real scale model predictions were obtained.

32

33 Figure 4b Modelled trends in deposition and soil water chemistry chosen chemical determinants at
34 forest FLII sites. Black colour denotes shallow samplers, grey colour denotes deep samplers. Periods of
35 significant change, determined by the derivative analysis, are denoted by thickened lines on the fitted
36 trend. Dashed lines indicate 95% point-wise confidence intervals of the fitted trend. For presentation
37 purposes, the real scale model predictions were obtained.

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39 Figure 5 Modelled trends in monthly precipitation and air temperature at the studied sites. Periods
40 of significant change, determined by the derivative analysis, are denoted by thickened lines on the fitted
41 trend. Dashed lines indicate 95% point-wise confidence intervals of the fitted trend. For presentation
42 purposes, the real scale model predictions were obtained.

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