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

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Abstract

Long-term monitoring of surface water quality has shown increasing concentrations of Dissolved Organic Carbon (DOC) across a large part of the Northern Hemisphere. Several drivers have been implicated including climate change, land management change, nitrogen and sulphur deposition and CO_2 enrichment. Analysis of stream water data, supported by evidence from laboratory studies, indicates that an effect of declining sulphur deposition on catchment soil chemistry is likely to be the primary mechanism, but there are relatively few long term soil water chemistry records in the UK with which to investigate this, and other, hypotheses directly. In this paper, we assess temporal relationships between soil solution chemistry and parameters that have been argued to regulate DOC production and, using a unique set of co-located measurements of weather and bulk deposition and soil solution chemistry provided by the UK Environmental Change Network and the Intensive Forest Monitoring Level II Network . We used statistical non-linear trend analysis to investigate these relationships at 5 forested and 4 non-forested sites from 1993 to 2011. Most trends in soil solution DOC concentration were found to be non-linear. Significant increases in DOC occurred mostly prior to 2005. The magnitude and sign of the trends was associated qualitatively with changes in acid deposition, the presence/absence of a forest canopy, soil depth and soil properties. The strongest increases in DOC were seen in acidic forest soils and were most clearly linked to declining anthropogenic acid deposition, while DOC trends at some sites with westerly locations appeared to have been influenced by shorter-term hydrological variation. The results indicate that widespread DOC increases in surface waters observed elsewhere, are most likely dominated by enhanced mobilization of DOC in surficial organic horizons, rather than changes in the soil water chemistry of deeper horizons. While

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

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

1. Introduction

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

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

While statistical relationships between the rate of change in acid deposition and DOC concentrations in water, modified by acid sensitivity (Monteith et al., 2007), hint strongly at a controlling effect of atmospheric deposition on catchment soils, there is still no clear consensus regarding underlying mechanisms. The organic soils of upper horizons and near-stream zones are considered to be the main source of DOM in headwater catchments (e.g. Brooks et al., 1999, Billett et al., 2006, Evans et al., 2007, Winterdahl et al., 2011), but considerably fewer long term soil chemistry monitoring records exist in comparison with surface waters, and there are, therefore, relatively limited opportunities to test the various DOC trend driver hypotheses at source. Where monitoring of soil solution has been conducted in regions recovering from acidification, DOC concentrations in organic surficial layers have often been found to be increasing at a similar rate to those observed in surface waters (Borken et al., 2011, Stutter et al., 2011), but DOC trends in deeper horizons have both positive and negative gradients, with increases at some sites (Borken et al., 2011, Stutter et al., 2011, Ukonmaanaho et al., 2014) and decreases at others (Wu et al., 2010, Borken et al., 2011, Löfgren and Zetterberg, 2011, Stutter et al., 2011), possibly reflecting the adsorption/desorption properties of more mineral-dominated layers and differences in redox state. Differences in behaviour between surface waters and some soil waters may therefore result from differences in soil properties, in addition to land use type (e.g. Vanguelova et al., 2010, Borken et al., 2011, Stutter et al., 2011). Interactions with climatic factors also need to be taken into account since investigations into the influence of temperature and hydrology on DOC have demonstrated the potential for regional warming and changes in precipitation patterns to affect DOC production and export (Freeman et al., 2001, Pastor et al., 2003, Freeman et al., 2004, Clark et al., 2005). As acid deposition declines to very low levels, and significant changes in temperatures and precipitation are being forecast in response to the continuing accumulation of greenhouse gasses in the atmosphere, it is increasingly important that sensitivity to climatic parameters is quantified accurately.

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

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

2. Methods

2.1. Field sites

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

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

Soils at all FLII and ECN sites were surveyed between 1993 and 1995. In each plot the soil was described according to the FAO soil classification system and classified according to the World Reference base for soil classification (WRB, 2007). FLII were also classified using the Soil Classification for England and Wales (Avery, 1980) and the Scottish Soil Classification system (Soil Survey of Scotland Staff 1981). FLII soil sampling and analyses were carried out according to the UNECE ICP Manual for Soil Sampling and Analysis (2006). ECN sites surveys were conducted according to The UK Environmental Change Network Protocols for Standard Measurements at Terrestrial Sites (Sykes and Lane, 1996). Soil types were developed from a range of parent materials and include gleysols, histosols, podzols, cambisols and arenosols. Soil chemical characteristics also varied widely (Table 2): soil organic carbon (SOC) content ranged from 0.8 to 48.7 %; C:N ratios from3 to 70 and soil acidity from pH 3.6 to 7.0. Base Saturation (BS) and Al saturation (Al sat.), indicative of soil sensitivities to acid deposition, ranged from 1.1 to 100 % and <0.1 to 93.5 % respectively. Acid deposition spanned a gradient of 121 to 406 meq m^{-2} yr^{-1} (2002-2006 means).

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

2.2. Measurements and chemical analysis

Soil water samples were collected at FLII sites every two weeks using tension lysimeters (PRENART SuperQuartz soil water samplers, Plenart Equipment Aps, Denmark) between 1996 and 2011. Twelve lysimeters were installed at each site, six located at 10 cm soil depth and the other six at 50 cm soil depth (Figure 2). Soil water samples were collected and measured according to Level II protocols described in detail in the ICP forests manual (ICP, 2006). Water samples were filtered through a 0.45 µm membrane filter and analysed for pH; total aluminium (Al), calcium (Ca^{2+}), magnesium (Mg^{2+}), potassium (K^+), sodium (Na^+) and iron (Fe) by ICP-OES (Spectro-flame, Spectro Ltd.); ammonium N (NH_4–N) colorimetrically; DOC by total carbon analyser (Shimadzu 5000, Osaka, Japan) using catalytic or persulphate oxidation; and sulphate (SO_4^{2-}), nitrate (NO_3^-) and Cl^- by Ion Chromatography (Dionex DX-500). Quality assurance and quality control on dissolved ion concentrations in soil water are described by De Vries et al. (2001) and in the ICP manual (2006). Soil acidity indexes at all sites and depths are shown in Table 2.

ECN soil waters were also sampled fortnightly by tension lysimetry using the same Prenart SuperQuartz samplers between 1992 and 2010. In accordance with the Environmental Change Network (ECN) protocols, six samplers were placed at the base of each A and B horizon, except for deep peats where fixed depths of 10 and 50 cm depths were used (Figure 2). Soil water was analysed for pH, then filtered (<0.45 µm) and analysed for DOC by combustion oxidation and IR (infra-red) gas detection; total metals (Al, Ca^{2+}, Fe, K^+, Mg^{2+}, Na^+) by ICP-OES; Cl^-, SO_4^{2-} by Dionex ion chromatography; and NO_3^- colorimetrically.

At each FLII site, samples from two bulk precipitation (installed in the open ground near the forest plots) and 10 throughfall collectors (installed under the stands canopy) were collected every two weeks from 1995 until 2006 and precipitation volumes determined by weighing. Water samples were filtered and analysed for the same determinands and by the same methods as soil water samples. Bulk precipitation samples from single bulk collectors at ECN sites were collected weekly and were analysed using the same methods for the same determinands as soil water.

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

2.3. Data preparation

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

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

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

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

$nmSO_4^{2-} = Total\ SO_4^{2-} - 0.104\ [Cl^-]$ [µeq L^{-1}] (Eq. 1).

For this purpose all Cl^- in soil water was assumed to be from a marine source (Evans et al., 2001). While it now appears likely that several sites would have been impacted by hydrochloric acid deposition in the past, it is thought that levels of this pollutant (derived from coal-burning) are likely to have fallen to very low levels in the last 20 years (Evans et al., 2011). For these reasons, nmSO_4^{2-} concentrations in bulk deposition were calculated using the ratio with Na^+ rather than Cl^-:

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

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

$nmCl^- = Total\ Cl^- - (1/0.86)\ [Na^+]$ [µeq L^{-1}] (Eq. 3).

2.4. Trends analysis

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

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

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 days since the start of the series and the day of the year respectively; $s_1(Date_i)$ represents the trend in the response and describes how the level of the response varies through time; $s_2(DayOfYear_i)$ represents the seasonal, within year signal in the data); ε_i and ε are model residuals assumed to be zero mean, normal random variables with variance $\sigma^2\Lambda$, and Λ is a correlation matrix describing the dependence structure in the residuals.

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

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

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

3. Results

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

3.1. Trends in bulk deposition chemistry

The initial and mean concentrations respectively of $nmSO_4^{2-}$ in bulk deposition were mostly much higher in the throughfall collectors in the FLII forested sites than the ECN grassland bulk collectors (Figure 4, Table 3). All sites showed a relatively monotonic decline in $nmSO_4^{2-}$ in bulk deposition. Concentrations at three out of four grassland sites, Glensaugh, Moor House and Snowdon, declined significantly (as indicated by thickened lines) throughout the available monitoring records. Concentrations at the forested sites, and the ECN site Sourhope, declined significantly up to around the year 2000. Changes in $nmSO_4^{2-}$ in bulk deposition at these sites were not statistically significant over the period 2000-2005, but concentrations at four (Lady Bower, Thetford, Alice Holt and Grizedale) then showed a brief second significant downturn to the end of the record in 2007. In common with initial concentrations, overall rates of change in bulk deposition of $nmSO_4^{2-}$ at forested sites were substantially greater than those for the ECN sites but were similar relative to mean levels; on average, mean $nmSO_4^{2-}$ in the last year of the record was about 60% lower than in the first year.

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

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

3.2. Trends in soil water chemistry

The lower panels of Figures 4a and 4b represent the smoothed trends in selected indicators of soil water chemistry measured at two depths at the ECN grassland and FLII forested sites respectively. Periods of significant decreases in soil water SO_4^{2-} were observed at the majority of sites, and mostly coincided with periods of significant declines in $nmSO_4^{2-}$ deposition. Reductions in SO_4^{2-} occurred in both shallow and deep samplers, but in most cases patterns of change in the shallow, and generally more organic, layers more closely mimicked change in bulk deposition concentrations. Sharp initial declines in the shallow samplers of several sites often ceased to be significant by around 2002-2003, indicating a slight lag relative to the termination of significant reductions in deposition. At Glensaugh, where reductions in SO_4^{2-} in bulk deposition were significant across the full monitoring period, shallow soil water SO_4^{2-} declined significantly over two extended periods, i.e. prior to 2000 and after 2007. Despite large reductions in nmSO_4^{2-} in bulk deposition, SO_4^{2-} in shallow samplers in the Moor House peat, the Snowdon cambisol and the Thetford arenosol did not change significantly. However, mean concentrations still showed overall downward tendencies, so the absence of clear trend at these sites may at least partly reflect greater short term variability relative to other sites. An overall decline in shallow soil water SO_4^{2-} at Alice Holt was interrupted by a temporary pulse centred around year 2006, coinciding both with the termination of a major drought and significant insect infestation of the canopy (Pitman et al., 2010).

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

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

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

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

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

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

3.3. Trends in soil water DOC

With the exception of Alice Holt, DOC concentrations were markedly higher in shallow samplers than in deep samplers throughout the records (Figure 4, Table 4), demonstrating both a dominance of DOC production in the surficial soils and varying degrees of adsorption in deeper mineral soils. There was no strong linear relationship between mean DOC and %SOC across all sites in either shallow or deep samplers. While mean DOC concentrations in the shallow samplers of the four sites with particularly organic upper horizons, i.e. %SOC > 30 (i.e. Moor House, Sourhope, Glensaugh and Llyn Brianne were invariably high (i.e. above 20 mg L^{-1}), and were mostly 12 mg L^{-1} or less in the deeper samplers in B horizons (where %SOC was invariably <8), Ah and Bw horizons of the Thetford Arenosol, both with very low %SOC, exhibited the highest DOC of all sites.

At all three grassland sites with DOC records extending back to 1993 (Moor House, Glensaugh and Sourhope), DOC increased significantly during periods up to 2000, but in shallow soil samplers only, while significant increases beyond this time were confined to a brief period at Glensaugh only. The main changes in shallow soil DOC at Glensaugh and Sourhope broadly coincided, therefore, with the periods of steepest reductions in SO_4^{2-} in the same samplers and the period of strongest reductions in $nmSO_4^{2-}$ and other acid anions in deposition observed at Sourhope and all five forested sites. DOC trends in the deep samplers of these grassland sites showed contrasting behaviours. Concentrations in the peaty gleyed podzol B horizon of Sourhope showed a continuously significant downward trend, while those for the Glensaugh podzol B horizon indicated a very slight upward step (although concentrations were very low throughout). Deep peat concentrations at Moor House, oscillated at concentrations between 15 – 20 mg L^{-1} and were more variable than in the shallow samplers.

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

3.4. Trends in precipitation and temperature

Smoothed trends in monthly total precipitation and average air temperatures observed at or near each site are presented in Figure 5. All sites showed similar air temperature profiles with a general indication of slight (but insignificant) increases over the first 10 years of these records, followed by significant downturns at the majority of sites from around 2006. There was no evidence for any periods of significant temperature increases that were common between two or more sites.

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

4. Discussion

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

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

Our analysis demonstrates that responses in bulk deposition chemistry to reductions in the emission of S, N and Cl species were most marked at the forest sites, where initial concentrations of $nmSO_4^{2-}$, NO_3^-, NH_4^+, divalent cations and, to a lesser extent $nmCl^-$, in bulk deposition were invariably considerably higher than at the grassland sites. Differences in rates of change between FLII and ECN sites likely reflect both geographical distribution and the role of forest canopies in enhancing deposition. In an assessment of regional variation in trends of acid deposition across the UK Acid Deposition Network for the period 1986-2002 (Fowler et al, 2005), rates of decline in $nmSO_4^{2-}$ were shown to be greatest in the close-to-source areas of southern and eastern England (classified as Zone 1- see Figure 1) and weakened in a north-westerly direction with the least affected region (northwest Scotland) classified as Zone 4 (Figure 1, Fowler et al., 2005). Of the sites assessed in this paper, three forest sites, Alice Holt, Thetford and Lady Bower, but no grassland sites, fell within Zone 1 of this classification. These three sites exhibited both the highest mean concentrations of major ions of all sites and the most marked reductions. Nevertheless, a comparison of mean chemistry of sites that fall within Zone 2 (i.e., Moor House, Sourhope, Glensaugh, Grizedale and Llyn Brianne) show that concentrations and trends in major ions in the former three grassland sites were consistently lower than those at the latter two forest sites. The role of forests relative to other vegetation types in ecosystem acidification and recovery has been widely recognised with respect to both soils (Stuanes et al., 1992, Hruska et al., 2002, Vanguelova et al., 2010, Nisbet and Evans, 2014) and surface waters (Fölster and Wilander, 2002, Oulehle et al., 2013, Malcolm et al., 2014, Nisbet and Evans, 2014). Forests have a much higher capacity to scavenge air pollutants than grasslands (Fowler et al., 1989, Miller et al., 1991, Harriman et al., 2003) resulting in considerably higher fluxes of acidifying ions being deposited in throughfall collectors, and hence also to soils, relative to bulk collectors in open ground (Ivens et al., 1990).

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

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

4.2. Soil water responses to trends in deposition

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

Unsurprisingly, there was little association between variation and trends in concentrations of species in soil water at either depth and those in deposition. Bacterial nitrification of reduced N tends to be rapid and generates NO_3^- which itself is highly reactive in soils and water (Galloway and Cowling, 2002). Soil N process dynamics are dependent on a range of ecosystem properties including plant demand, stoichiometric relationships with carbon and other nutrients, and the amount and form of N inputs (Galloway et al., 2003, Shibata et al., 2014). Curtis et al. (2011) proposed a conceptual model of N behaviour in semi-natural catchments, whereby retention and accumulation of N is maximised in carbon-rich ecosystems, while carbon-poor ecosystems exposed to elevated N deposition leach most NO_3^-. In our study the highest NO_3^- concentrations indeed occurred at the forest sites with very low soil organic carbon content, i.e. Lady Bower and Thetford, although these were also the sites that experienced the highest concentrations of N species in bulk deposition. At Thetford, NO_3^- was by far the most concentrated acid anion throughout the monitoring period, and its large significant reduction detected in shallow samplers will have dominated changes in surface soil acidity at this site. Changes in NO_3^- in the Lady Bower soils, while not as great in magnitude as SO_4^{2-}, will also have made a significant contribution to reductions in total acidity. Similarly the sharp post-2007 increase in NO_3^- in the surface soils at Llyn Brianne, possibly linked to a major aphid infestation of the canopy (Pitman et al., 2010) also seems to account for a significant reduction in soil pH over the same period.

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

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

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

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

4.3. Temporal links between trends in DOC and potential drivers

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

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

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

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

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

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

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

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

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

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

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

4.4. Implications for observations of rising DOC in surface waters

Overall, the trends in soil water DOC, both positive and, with respect to some B horizons, negative are consistent with a dominant control from declining acid deposition, while the more consistently significant and positive changes observed in organic horizons indicate that changes in organic matter solubility close to the soil surface provides the most likely explanation for regional-scale increases in DOC in surface waters. Linking spatially- and depth-restricted observations of changes in soil chemistry with the catchment-wide signal provided by surface waters is highly problematic, as extensive understanding of geology, soil heterogeneity, hydraulic flowpaths etc., are required and these will vary greatly between locations. It has been argued that in some boreal environments, much of the hydraulic catchment is largely irrelevant with respect to DOC supply to streams, and that most DOC is provided from a relatively narrow riparian zone (Lofgren et al., 2010, Ledesma et al., 2015). However, Hruška et al. (2014), in their detailed modelling study of the upland Lysina catchment in the Czech republic noted that it was unfeasible for stream water DOC concentrations to be sustained from DOC production from the riparian zone alone. The apparent high predictive ability of various spatial DOC models (e.g. Monteith et al., 2015) that tend not to factor in riparian extent would also suggest that soils from across catchments, rather than just stream margins, are likely to have a significant influence on fluvial export of DOC in various upland environments. The increase in DOC concentrations seen in stream waters often appear most marked for seasonal peak concentrations. In the UK, these tend to occur during wet weather in the early autumn when wetted soils facilitate lateral flow paths. In these circumstances it would seem intuitive that potential adsorption of DOC by B horizons of organo-mineral soils is likely to exert little influence relative to enhanced production in the organic layer.

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

5. Conclusions

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

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

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

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References

AVERY, B. W. 1980. Soil Classification for England and Wales (Higher Categories). Harpender: Soil Survey Technical Monograph.

BASTVIKEN, D., SANDÉN, P., SVENSSON, T., STÅHLBERG, C., MAGOUNAKIS, M. & ÖBERG, G. 2006. Chloride Retention and Release in a Boreal Forest Soil: Effects of Soil Water Residence Time and Nitrogen and Chloride Loads. *Environmental Science & Technology,* 40**,** 2977-2982.

BILLETT, M. F., DEACON, C. M., PALMER, S. M., DAWSON, J. J. C. & HOPE, D. 2006. Connecting organic carbon in stream water and soils in a peatland catchment. *Journal of Geophysical Research: Biogeosciences,* 111**,** G02010.

BORKEN, W., AHRENS, B., SCHULZ, C. & ZIMMERMANN, L. 2011. Site-to-site variability and temporal trends of DOC concentrations and fluxes in temperate forest soils. *Global Change Biology,* 17**,** 2428-2443.

BROOKS, P. D., MCKNIGHT, D. M. & BENCALA, K. E. 1999. The relationship between soil heterotrophic activity, soil dissolved organic carbon (DOC) leachate, and catchment-scale DOC export in headwater catchments. *Water Resources Research,* 35**,** 1895-1902.

CHANDLER, R. & SCOTT, M. 2011. *Statistical Methods for Trend Detection and Analysis in the Environmental Sciences*, John Wiley & Sons, Ltd.

CLARK, J. M., BOTTRELL, S. H., EVANS, C. D., MONTEITH, D. T., BARTLETT, R., ROSE, R., NEWTON, R. J. & CHAPMAN, P. J. 2010. The importance of the relationship between scale and process in understanding long-term DOC dynamics. *Science of the Total Environment,* 408**,** 2768–2775.

CLARK, J. M., CHAPMAN, P. J., ADAMSON, J. K. & LANE, S. N. 2005. Influence of drought-induced acidification on the mobility of dissolved organic carbon in peat soils. *Global Change Biology,* 11, 791-809.

CLARK, J. M., VAN DER HEIJDEN, G. M. F., PALMER, S. M., CHAPMAN, P. J. & BOTTRELL, S. H. 2011. Variation in the sensitivity of DOC release between different organic soils following H2SO4 and sea-salt additions. *European Journal of Soil Science,* 62, 267–284.

COUTURE, S., HOULE, D. & GAGNON, C. 2012. Increases of dissolved organic carbon in temperate and boreal lakes in Quebec, Canada. *Environmental Science and Pollution Research,* 19, 361-371.

CURTIS, C., EVANS, C., GOODALE, C. & HEATON, T. E. 2011. What Have Stable Isotope Studies Revealed About the Nature and Mechanisms of N Saturation and Nitrate Leaching from Semi-Natural Catchments? *Ecosystems,* 14, 1021-1037.

CURTIS, C. J. & SIMPSON, G. L. 2014. Trends in bulk deposition of acidity in the UK, 1988–2007, assessed using additive models. *Ecological Indicators,* 37, Part B, 274-286.

DE VRIES, W., REINDS, G. J., VAN DER SALM, C., DRAAIJERS, G. P. J., BLEEKER, A., ERISMAN, J. W., AUEE, J., GUNDERSEN, P., KRISTENSEN, H. L., VAN DOBBEN, H., DE ZWART, D., DEROME, J., VOOGD, J. C. H. & VEL, E. M. 2001. Intensive monitoring of forest ecosystems in Europe. Technical report 2001. Geneva/Brussels: UN/ECE, EC.

DE WIT, H. A., MULDER, J., HINDAR, A. & HOLE, L. 2007. Long-Term Increase in Dissolved Organic Carbon in Streamwaters in Norway Is Response to Reduced Acid Deposition. *Environmental Science & Technology,* 41, 7706-7713.

EKSTRÖM, S. M., KRITZBERG, E. S., KLEJA, D. B., LARSSON, N., NILSSON, P. A., GRANELI, W. & BERGKVIST, B. 2011. Effect of Acid Deposition on Quantity and Quality of Dissolved Organic Matter in Soil-Water. *Environmental Science & Technology,* 45, 4733 – 4739.

ERLANDSSON, M., BUFFAM, I., FOLSTER, J., LAUDON, H., TEMNERUD, J., WEYHENMEYER, G. A. & BISHOP, K. 2008. Thirty-five years of synchrony in the organic matter concentrations of Swedish rivers explained by variation in flow and sulphate. *Global Change Biology,* 14, 1191-1198.

ERLANDSSON, M., CORY, N., FÖLSTER, J., KÖHLER, S., LAUDON, H., WEYHENMEYER, G. A. & BISHOP, K. 2011. Increasing Dissolved Organic Carbon Redefines the Extent of Surface Water Acidification and Helps Resolve a Classic Controversy. *BioScience,* 61, 614-618.

ERLANDSSON, M., CORY, N., KÖHLER, S. & BISHOP, K. 2010. Direct and indirect effects of increasing dissolved organic carbon levels on pH in lakes recovering from acidification. *J. Geophys. Res.,* 115, G03004.

EVANS, C. D., CHAPMAN, P. J., CLARK, J. M., MONTEITH, D. T. & CRESSER, M. S. 2006. Alternative explanations for rising dissolved organic carbon export from organic soils. *Global Change Biology,* 12, 2044-2053.

EVANS, C. D., FREEMAN, C., CORK, L. G., THOMAS, D. N., REYNOLDS, B., BILLETT, M. F., GARNETT, M. H. & NORRIS, D. 2007. Evidence against recent climate-induced destabilisation of soil carbon from 14C analysis of riverine dissolved organic matter. *Geophysical Research Letters,* 34, L07407.

EVANS, C. D., JONES, T. G., BURDEN, A., OSTLE, N., ZIELIŃSKI, P., COOPER, M. D. A., PEACOCK, M., CLARK, J. M., OULEHLE, F., COOPER, D. & FREEMAN, C. 2012. Acidity controls on dissolved organic carbon mobility in organic soils. *Global Change Biology,* 18, 3317-3331.

EVANS, C. D., MONTEITH, D. T. & COOPER, D. M. 2005. Long-term increases in surface water dissolved organic carbon: Observations, possible causes and environmental impacts. *Environmental Pollution,* 137, 55-71.

EVANS, C. D., MONTEITH, D. T., FOWLER, D., CAPE, J. N. & BRAYSHAW, S. 2011. Hydrochloric Acid: An Overlooked Driver of Environmental Change. *Environmental Science & Technology,* 45, 1887-1894.

EVANS, C. D., MONTEITH, D. T. & HARRIMAN, R. 2001. Long-term variability in the deposition of marine ions at west coast sites in the UK Acid Waters Monitoring Network: impacts on surface water chemistry and significance for trend determination. *Science of the Total Environment,* 265, 115-129.

EVANS, C. D., MONTEITH, D. T., REYNOLDS, B. & CLARK, J. M. 2008. Buffering of recovery from acidification by organic acids. *Science of the Total Environment,* 404, 316-325.

FINDLAY, S. E. G. 2005. Increased carbon transport in the Hudson River: unexpected consequence of nitrogen deposition? *Frontiers in Ecology and the Environment,* 3, 133-137.

FINZI, A. C., CANHAM, C. D. & VAN BREEMEN, N. 1998. CANOPY TREE–SOIL INTERACTIONS WITHIN TEMPERATE FORESTS: SPECIES EFFECTS ON pH AND CATIONS. *Ecological Applications,* 8, 447-454.

FÖLSTER, J. & WILANDER, A. 2002. Recovery from acidification in Swedish forest streams. *Environmental Pollution,* 117**,** 379-389.

FOWLER, D., CAPE, J. N., COYLE, M., FLECHARD, C., KUYLENSTIERNA, J., HICKS, K., DERWENT, D., JOHNSON, C. & STEVENSON, D. 1999. The Global Exposure of Forests to Air Pollutants. *Water, Air, and Soil Pollution,* 116**,** 5-32.

FOWLER, D., CAPE, J. N., UNSWORTH, M. H., MAYER, H., CROWTHER, J. M., JARVIS, P. G., GARDINER, B. & SHUTTLEWORTH, W. J. 1989. *Deposition of Atmospheric Pollutants on Forests [and Discussion]*.

FOWLER, D., SMITH, R. I., MULLER, J. B. A., HAYMAN, G. & VINCENT, K. J. 2005. Changes in the atmospheric deposition of acidifying compounds in the UK between 1986 and 2001. *Environmental Pollution,* 137**,** 15-25.

FREEMAN, C., EVANS, C. D., MONTEITH, D. T., REYNOLDS, B. & FENNER, N. 2001. Export of organic carbon from peat soils. *Nature,* 412**,** 785-785.

FREEMAN, C., FENNER, N., OSTLE, N. J., KANG, H., DOWRICK, D. J., REYNOLDS, B., LOCK, M. A., SLEEP, D., HUGHES, S. & HUDSON, J. 2004. Export of dissolved organic carbon from peatlands under elevated carbon dioxide levels. *Nature,* 430**,** 195-198.

FULLER, R. D., DRISCOLL, C. T., SCHINDLER, S. C. & MITCHELL, M. J. 1986. A simulation model of sulfur transformations in forested Spodosols. *Biogeochemistry,* 2**,** 313-328.

FUTTER, M., VALINIA, S., LÖFGREN, S., KÖHLER, S. & FÖLSTER, J. 2014. Long-term trends in water chemistry of acid-sensitive Swedish lakes show slow recovery from historic acidification. *AMBIO,* 43**,** 77-90.

GALLOWAY, J. N., ABER, J. D., ERISMAN, J. W., SEITZINGER, S. P., HOWARTH, R. W., COWLING, E. B. & COSBY, B. J. 2003. The Nitrogen Cascade. *BioScience,* 53**,** 341-356.

GALLOWAY, J. N. & COWLING, E. B. 2002. Reactive nitrogen and the world: 200 years of change. *Ambio,* 31**,** 64-71.

HAALAND, S., HONGVE, D., LAUDON, H., RIISE, G. & VOGT, R. D. 2010. Quantifying the Drivers of the Increasing Colored Organic Matter in Boreal Surface Waters. *Environmental Science & Technology,* 44**,** 2975-2980.

HARRIMAN, R. & MORRISON, B. R. S. 1982. Ecology of streams draining forested and non-forested catchments in an area of central Scotland subject to acid precipitation. *Hydrobiologia,* 88**,** 251-263.

HARRIMAN, R., WATT, A. W., CHRISTIE, A. E. G., MOORE, D. W., MCCARTNEY, A. G. & TAYLOR, E. M. 2003. Quantifying the effects of forestry practices on the recovery of upland streams and lochs from acidification. *Science of the Total Environment,* 310**,** 101-111.

HELLIWELL, R. C., FERRIER, R. C., JOHNSTON, L., GOODWIN, J. & DOUGHTY, R. 2001. Land use influences on acidification and recovery of freshwaters in Galloway, south-west Scotland. *Hydrology and Earth System Sciences,* 5**,** 451–458.

HÖGBERG, P., FAN, H., QUIST, M., BINKLEY, D. A. N. & TAMM, C. O. 2006. Tree growth and soil acidification in response to 30 years of experimental nitrogen loading on boreal forest. *Global Change Biology,* 12**,** 489-499.

HRUSKA, J., KRAM, P., MCDOWELL, W. H. & OULEHLE, F. 2009. Increased dissolved organic carbon (DOC) in Central European streams is driven by reductions in ionic strength rather than climate change or decreasing acidity. *Environ Sci Technol,* 43**,** 4320-6.

HRUŠKA, J., KRÁM, P., MOLDAN, F., OULEHLE, F., EVANS, C., WRIGHT, R., KOPÁČEK, J. & COSBY, B. 2014. Changes in Soil Dissolved Organic Carbon Affect Reconstructed History and Projected Future Trends in Surface Water Acidification. *Water, Air, & Soil Pollution,* 225**,** 1-13.

HRUSKA, J., MOLDAN, F. & KRÁM, P. 2002. Recovery from acidification in central Europe--observed and predicted changes of soil and streamwater chemistry in the Lysina catchment, Czech Republic. *Environmental Polluion,* 120**,** 261-274.

ICP 2006. Manual on Methods and criteria for harmonised sampling, assessment, monitoring, and analysis of the effects of air pollution on forests, 2006. . Elaborated by the EU Expert Panel on Soil.

KAISER, K. & ZECH, W. 1999. Release of Natural Organic Matter Sorbed to Oxides and a Subsoil. *Soil Science Society of America Journal,* 63**,** 1157-1166.

KALBITZ, K., SOLINGER, S., PARK, J.-H., MICHALZIK, B., MATZNER & E. 2000. *Controls on the dynamics of dissolved organic matter in soils : A review,* Hagerstown, MD, ETATS-UNIS, Lippincott Williams & Wilkins.

LANGAN, S. J. & HIRST, D. 2004. An analysis of the long-term variation in stream water quality for three upland catchments at Loch Dee (Galloway, S.W. Scotland) under contrasting land management. *Hydrology and Earth System Sciences,* 8**,** 422-435.

LEDESMA, J. L., GRABS, T., BISHOP, K. H., SCHIFF, S. L. & KOHLER, S. J. 2015. Potential for long-term transfer of dissolved organic carbon from riparian zones to streams in boreal catchments. *Glob Chang Biol,* 21**,** 2963-79.

LOFGREN, S., GUSTAFSSON, J. P. & BRINGMARK, L. 2010. Decreasing DOC trends in soil solution along the hillslopes at two IM sites in southern Sweden--geochemical modeling of organic matter solubility during acidification recovery. *Sci Total Environ,* 409**,** 201-10.

LÖFGREN, S. & ZETTERBERG, T. 2011. Decreased DOC concentrations in soil water in forested areas in southern Sweden during 1987–2008. *Science of the Total Environment,* 409**,** 1916-1926.

MALCOLM, I. A., GIBBINS, C. N., FRYER, R. J., KEAY, J., TETZLAFF, D. & SOULSBY, C. 2014. The influence of forestry on acidification and recovery: Insights from long-term hydrochemical and invertebrate data. *Ecological Indicators,* 37, Part B**,** 317-329.

MILLER, J. D., ANDERSON, H. A., COOPER, J. M., FERRIER, R. C. & STEWART, M. 1991. Evidence for enhanced atmospheric sulphate interception by Sitka spruce from evaluation of some Scottish catchment study data. *Science of the Total Environment,* 103**,** 37-46.

MONTEITH, D., HENRYS, P., EVANS, C., MALCOLM, I., SHILLAND, E. & PEREIRA, M. G. 2015. Spatial controls on dissolved organic carbon in upland waters inferred from a simple statistical model. *Biogeochemistry***,** 1-15.

MONTEITH, D. T., EVANS, C. D., HENRYS, P. A., SIMPSON, G. L. & MALCOLM, I. A. 2014. Trends in the hydrochemistry of acid-sensitive surface waters in the UK 1988–2008. *Ecological Indicators,* 37, Part B**,** 287-303.

MONTEITH, D. T., STODDART, J. L., EVANS, C. D., DE WIT, H. A., FORSIUS, M., HØGÅSEN, T., WILANDER, A., SKJELKVÅLE, B. L., JEFFRIES, D. S., VUORENMAA, J., KELLER, B., KOPÁCEK, J. & VESELY, J. 2007. Dissolved organic carbon trends resulting from changes in athmospheric deposition chemistry. *Nature,* 450**,** 537-541.

MONTEITH ET AL. this issue.

MORECROFT, M. D., BEALEY, C. E., BEAUMONT, D. A., BENHAM, S., BROOKS, D. R., BURT, T. P., CRITCHLEY, C. N. R., DICK, J., LITTLEWOOD, N. A., MONTEITH, D. T., SCOTT, W. A., SMITH, R. I., WALMSLEY, C. & WATSON, H. 2009. The UK Environmental Change Network: Emerging trends in the composition of plant and animal communities and the physical environment. *Biological Conservation,* 142**,** 2814-2832.

MÖRTH, C.-M., TORSSANDER, P., KJØNAAS, O. J., O STUANES, A., MOLDAN, F. & GIESLER, R. 2005. Mineralization of Organic Sulfur Delays Recovery from Anthropogenic Acidification. *Environmental Science & Technology,* 39**,** 5234-5240.

MÜNCH, J. M., TOTSCHE, K. U. & KAISER, K. 2002. Physicochemical factors controlling the release of dissolved organic carbon from columns of forest subsoils. *European Journal of Soil Science,* 53**,** 311-320.

NISBET, T. & EVANS, C. D. 2014. Forestry and surface water acidification. Forestry Comission.

NODVIN, S. C., DRISCOLL, C. T. & LIKENS, G. E. 1986. The effect of pH on sulfate adsorption by a forest soil. *Soil Science,* 142.

ORMEROD, S. J., DONALD, A. P. & BROWN, S. J. 1989. The influence of plantation forestry on the pH and aluminium concentration of upland welsh streams: A re-examination. *Environmental Pollution,* 62**,** 47-62.

OULEHLE, F., CHUMAN, T., MAJER, V. & HRUŠKA, J. 2013. Chemical recovery of acidified Bohemian lakes between 1984 and 2012: the role of acid deposition and bark beetle induced forest disturbance. *Biogeochemistry,* 116**,** 83-101.

OULEHLE, F. & HRUŠKA, J. 2009. Rising trends of dissolved organic matter in drinking-water reservoirs as a result of recovery from acidification in the Ore Mts., Czech Republic. *Environmental Pollution,* 157**,** 3433-3439.

PASTOR, J., SOLIN, J., BRIDGHAM, S. D., UPDEGRAFF, K., HARTH, C., WEISHAMPEL, P. & DEWEY, B. 2003. Global warming and the export of dissolved organic carbon from boreal peatlands. *Oikos,* 100**,** 380-386.

PITMAN, R. M., VANGUELOVA, E. I. & BENHAM, S. E. 2010. The effects of phytophagous insects on water and soil nutrient concentrations and fluxes through forest stands of the Level II monitoring network in the UK. *Science of the Total Environment,* 409**,** 169-181.

RITSON, J. P., GRAHAM, N. J. D., TEMPLETON, M. R., CLARK, J. M., GOUGH, R. & FREEMAN, C. 2014. The impact of climate change on the treatability of dissolved organic matter (DOM) in upland water supplies: A UK perspective. *Science of the Total Environment,* 473–474, 714-730.

ROTAP 2012. Review of transboundary air pollution (RoTAP).

ROWE, E. C., TIPPING, E., POSCH, M., OULEHLE, F., COOPER, D. M., JONES, T. G., BURDEN, A., HALL, J. & EVANS, C. D. 2014. Predicting nitrogen and acidity effects on long-term dynamics of dissolved organic matter. *Environmental Pollution,* 184, 271-282.

RUSTAD, L. E., KAHL, J. S., NORTON, S. A. & FERNANDEZ, I. J. 1994. Underestimation of dry deposition by throughfall in mixed northern hardwood forests. *Journal of Hydrology,* 162, 319-336.

SANCLEMENTS, M. D., OELSNER, G. P., MCKNIGHT, D. M., STODDARD, J. L. & NELSON, S. J. 2012. New insights into the source of decadal increases of dissolved organic matter in acid-sensitive lakes of the northeastern United States. *Environ Sci Technol,* 46, 3212-9.

SAWICKA, K. 2015. *Multi-scale investigation of soil water DOC dynamics with respect to long-term trends.* PhD, University of Reading.

SCHINDLER, D. W. 1988. Effects of Acid rain on freshwater ecosystems. *Science,* 239, 149-57.

SCHLESINGER, W. H. 1997. *Biogeochemistry: An Analysis of Global Change,* San Diego, California, USA, Academic Press.

SHIBATA, H., CATTANEO, L. R., LEACH, A. M. & GALLOWAY, J. N. 2014. First approach to the Japanese nitrogen footprint model to predict the loss of nitrogen to the environment. *Environmental Research Letters,* 9, 115013.

SIER ET AL. this issue.

SINGH, B. R. 1984. Sulphate sorption by acid forest soils: 3. Desorption of sulphate from adsorbed surfaces as a function of time, desorbing ion, pH, and amount of adsorption. . *Soil Science,* 138, 346-353.

SKJELKVALE, B. L., MANNIO, J., WILANDER, A. & ANDERSEN, T. 2001. Recovery from acidification of lakes in Finland, Norway and Sweden 1990-1999. *Hydrology and Earth System Sciences,* 5, 327-337.

SKJELKVALE, B. L., STODDARD, J. L., JEFFRIES, D., TORSETH, K., HOGASEN, T., BOWMAN, J., MANNIO, J., MONTEITH, D. T., MOSELLO, R., ROGORA, M., RZYCHON, D., VESELY, J., WIETING, J., WILANDER, A. & WORSZTYNOWICZ, A. 2005. Regional scale evidence for improvements in surface water chemistry 1990 - 2001. *Environmental Polluion,* 137, 165-176.

STUANES, A. O., VAN MIEGROET, H., COLE, D. W. & ABRAHAMSEN, G. 1992. Recovery from Acidification. *In:* JOHNSON, D. & LINDBERG, S. (eds.) *Atmospheric Deposition and Forest Nutrient Cycling.* Springer New York.

STUTTER, M. I., LUMSDON, D. G. & ROWLAND, A. P. 2011. Three representative UK moorland soils show differences in decadal release of dissolved organic carbon in response to environmental change. *Biogeosciences,* 8, 3661-3675.

SVERDRUP, H., WARFVINGE, P. & ROSÉN, K. 1992. A model for the impact of soil solution Ca: Al ratio, soil moisture and temperature on tree base cation uptake. *Water, Air, and Soil Pollution,* 61, 365-383.

SYKES, J. M. & LANE, S. N. 1996. The UK Environmental Change Network: Protocols for Standard Measurements at Terrestrial Sites. London: The Stationery Office.

THURMAN, E. M. 1985. *Organic geochemistry of natural waters,* Dordrecht, Martinus Nijhoff/Dr W. Junk Publishers.

TIPPING, E. & WOOF, C. 1991. The distribution of humic substances between the solid and aqueous phases of acid organic soils; a description based on humic heterogeneity and charge-dependent sorption equilibria. *Journal of Soil Science,* 42, 437-448.

TRUDGILL, S. T. 1995. *Solute Modelling in Catchment Systems,* Chichester, UK, Wiley.

UKONMAANAHO, L., STARR, M., LINDROOS, A.-J. & NIEMINEN, T. 2014. Long-term changes in acidity and DOC in throughfall and soil water in Finnish forests. *Environmental Monitoring and Assessment,* 186, 7733-7752.

VAN DEN BERG, L. J. L., SHOTBOLT, L. & ASHMORE, M. R. 2012. Dissolved organic carbon (DOC) concentrations in UK soils and the influence of soil, vegetation type and seasonality. *Science of the Total Environment,* 427–428, 269-276.

VANGUELOVA, E. I., BARSOUM, N., BENHAM, S., BROADMEADOW, M., MOFFAT, A. J., NISBET, T. & PITMAN, R. 2007. Ten Years of Intensive Environmental Monitoring in British Forests. Edinburgh: Forestry Commission.

VANGUELOVA, E. I., S., B., PITMAN, R., MOFFAT, A. J., BROADMEADOW, M., NISBET, T., DURRANT, D., BARSOUM, N., WILKINSON, M., BOCHEREAU, F., HUTCHINGS, T., BROADMEADOW, S., CROW, P.,

TAYLOR, P. & DURRANT HOUSTON, T. 2010. Chemical fluxes in time through forest ecosystems in the UK – Soil response to pollution recovery. *Environmental Pollution,* 158**,** 1857-1869.

VISGILIO, G., WHITELAW, D. & NADELHOFFER, K. 2007. Atmospheric Nitrogen Deposition: Implications for Terrestrial Ecosystem Structure and Functioning. *Acid in the Environment.* Springer US.

VUORENMAA, J., FORSIUS, M. & MANNIO, J. 2006. Increasing trends of total organic carbon concentrations in small forest lakes in Finland from 1987 to 2003. *Science of the Total Environment,* 365**,** 47-65.

WALKER, W. J., CRONAN, C. S. & BLOOM, P. R. 1990. Aluminium Solubility in Organic Soil Horizons from Northern and Southern Forested Watersheds. *Soil Sci. Soc. Am. J.,* 54**,** 369-374.

WERNER, M., KRYZA, M., DORE, A. J., BLAŚ, M., HALLSWORTH, S., VIENO, M., TANG, Y. S. & SMITH, R. I. 2011. Modelling of marine base cation emissions, concentrations and deposition in the UK. *Atmos. Chem. Phys.,* 11**,** 1023-1037.

WINTERDAHL, M., FUTTER, M., KÖHLER, S., LAUDON, H., SEIBERT, J. & BISHOP, K. C. W. 2011. Riparian soil temperature modification of the relationship between flow and dissolved organic carbon concentration in a boreal stream. *Water Resources Research,* 47**,** n/a-n/a.

WOOD, S. N. 2004. Stable and Efficient Multiple Smoothing Parameter Estimation for Generalized Additive Models. *Journal of the American Statistical Association,* 99**,** 673-686.

WOOD, S. N. 2006. *Generalized Additive Models: An Introduction with R*, Chapman and Hall/CRC.

WOOD, S. N. 2011. Fast stable restricted maximum likelihood and marginal likelihood estimation of semiparametric generalized linear models. *Journal of the Royal Statistical Society: Series B (Statistical Methodology),* 73**,** 3-36.

WOOD, S. N. 2012. mgcv: Mixed GAM Computation Vehicle with GCV/AIC/REML smoothness estimation (v.1.7-28). CRAN.

WRB, I. W. G. 2007. World Reference Base for Soil Resources 2006, first update 2007. Rome: FAO.

WU, Y., CLARKE, N. & MULDER, J. 2010. Dissolved Organic Carbon Concentrations in Throughfall and Soil Waters at Level II Monitoring Plots in Norway: Short- and Long-Term Variations. *Water, Air, and Soil Pollution,* 205**,** 273-288.

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 [^{o}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

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

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

Site	$nmSO_4^{2-}$	$nmCl^-$	NO_3^-	NH_4^+	$Ca^{2+} + Mg^{2+}$	Na^+	pH
	$\mu eq\ L^{-1}$						
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

Table 4 Annual mean concentrations of chemical species in soil water at two depths: shallow and deep. Means 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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Figure 1 Site location map and the geographical locations of pollution zones adapted from Fowler et al. (2005).

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

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

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

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

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