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SPATIAL CONTROLS ON DISSOLVED ORGANIC CARBON IN UPLAND WATERS INFERRED FROM A SIMPLE STATISTICAL MODEL

FROM A SIMPLE STATISTICAL MODEL

Running title: Spatial controls on dissolved organic carbon

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Abstract

Dissolved organic carbon (DOC) concentrations in upland surface waters in many northern hemisphere industrialised regions are at their highest in living memory, provoking debate over their "naturalness". Because of the implications for drinking water treatment and supply there is increasing interest in the potential for mitigation through local land management, and for forecasting the likely impact of environmental change. However, the dominant controls on DOC production remain unresolved, hindering the establishment of appropriate reference levels for specific locations. Here we demonstrate that spatial variation in long-term average DOC levels draining upland UK catchments is highly predictable using a simple multiple logistic regression model comprising variables representing wetland soil cover, rainfall, altitude, catchment sensitivity to acidification, and current acid deposition. A negative relationship was observed between DOC concentration and altitude that, fro catchments dominated by organo-mineral soils, is plausibly explained by the combined effects of changing net primary production and temperature-dependent decomposition. However, the magnitude of the altitude effect was considerably greater for catchments with a high proportion of wetland cover, suggesting that additional controls influence these sites such as impeded respiratory loss of carbon in wet soils and/or an increased susceptibility to water level drawdown at lower altitudes. The model suggests 1) that continuing reductions in sulphur deposition on acid sensitive organo-mineral soils, will drive further significant increases in DOC and, 2) given the differences in the magnitude of the observed altitude-DOC relationships, that DOC production from catchments with peat-dominated soils may be more sensitive to climate change than those dominated by mineral soils. However, given that mechanisms remain unclear, the latter warrants further investigation.

Surface waters draining organic-rich soils (deep peats, and 'organo-mineral' soils with either a peaty or organic-matter rich upper horizon) typically contain significant amounts of dissolved organic matter (DOM), commonly quantified in terms of dissolved organic carbon (DOC) concentration. A contributor to both organic acidity and water "colour", DOM in these systems is derived predominantly from allocthonous organic matter, originating largely from decomposing vegetation and plant root exudates (Thurman 1985). Processes determining the terrestrial production and fluvial export of DOM from boreal landscapes are receiving mounting attention, reflecting growing recognition of the importance of DOC in the global carbon cycle (Bauer and Bianchi 2011) and wider soil biochemical processes (Taylor and Townsend 2010). More immediate economic concerns have arisen in regions such as the northern and western UK, parts of Scandinavia, and the Czech Republic (Oulehle and Hruska 2009), where surface waters supply drinking water to the majority of the population. Here, and elsewhere in northern Europe and North America, DOC concentrations have been rising over the last quarter century or more (Monteith et al. 2007; Skjelkvåle et al. 2005).

There is a widely held perception in the UK and elsewhere that current DOC concentrations in upland surface waters used for water supply are unnaturally high. In part this stems from observations of rising levels of DOC in waters draining catchments that have been significantly modified by human activities. In the UK, peat erosion is widespread in catchments used for water supply. This degradation has been attributed variously to loss of bryophyte cover through effects of air pollution (e.g. Ferguson and Lee (1983)) the effects of drainage schemes (Holden et al. 2007), over-grazing by sheep (Evans 1997) and excessive burning in the course of grouse moor management (Yallop and Clutterbuck 2009) – problems that also concern stakeholders tasked with conserving upland biodiversity. However, it is also clear that DOC concentrations vary markedly across upland catchments as a result of intrinsic geophysical factors. For example, concentrations tend to be higher in catchments dominated by peats, regardless of the extent of physical degradation (Hope et al. 1994).

Furthermore, upland soils have been shown to be biogeochemically sensitive to the influences of atmospheric pollutants, and particularly the acidifying effects of sulphur, nitrogen and hydrochloric acid (Evans et al.

2012; Evans et al. 2011). Over the past two decades, levels of acid deposition in the UK have fallen substantially in response to an international drive to control acidic emissions (Curtis and Simpson 2014) and overall, sulphur deposition in the UK is estimated to have declined by 80% from 1986 to 2006 (RoTAP 2012). DOC concentrations in remote surface waters have been observed to change in proportion to these reductions across the industrialised northern hemisphere (Monteith et al. 2007) in an apparent solubility-driven response to declining soil acidity (Ekstrom et al. 2011; Evans et al. 2012) and/or declining soil water ionic strength (Hruška et al. 2009). It is therefore feasible that recent increases in DOC in some areas represent a return toward pre-industrial (i.e. pre-acidification) conditions. There are very few long term records internationally of sufficient duration to chart DOC responses to rising and, more recently, falling acid deposition. However, a century long record of transparency in a Bohemian lake (Vrba et al. 2003), and a 420 nm absorbance record from Alsterälven in southern Sweden that reaches back to the 1960s (Forsberg 1992), both lend support for this "recovery" hypothesis.

Alternatively, deposition-induced increases in solubility may be leading to unprecedented levels of DOC if other factors favouring increased DOC leaching have also changed since the pre-industrial period. For example, it has been suggested that net primary productivity (NPP), and hence the supply of potentially soluble organic matter, is now higher than in pre-industrial times as a result of the accumulation of atmospherically deposited reactive nitrogen in these catchments (Rowe et al. 2014; Tipping et al. 2012). Various studies have also suggested that either total decomposition rates, or the proportion of decomposed organic matter leached as DOC rather than respired as CO_2, may have increased due to climatic and/or management changes (Freeman et al. 2001).

Increasingly, physical catchment-level intervention is being proposed to stabilise, or even reverse, inputs of DOC from physically degraded catchments to the water supply system (e.g. SCAMP (2013). However, there is currently no statistical or conceptual framework for deriving expected DOC concentrations for waters in a particular environmental setting, and therefore no way of gauging the extent to which observations may be deviating from those expected in the absence of local impacts. Hydrochemical records rarely, if ever, reach back prior to such disturbances, while palaeolimnological DOC reconstruction techniques that have the

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potential to predict historical concentrations in lakes (e.g. Rosén et al. (2011)) are still under development and cannot, in any case, be applied to running waters.

If spatial variation in DOC concentrations in surface waters draining largely physically undisturbed catchments could be modelled accurately from a set of variables representing dominant controls, this would not only guide the assessment of the DOC status of other sites of concern (e.g. to water authorities), but would also provide long-term baselines for these sites against which long term trends and shorter term variation could subsequently be modelled. The practice of defining long-term climatic baselines is already standard practice in the field of modelling and prediction of climate change. Finally, the structure of such a model should provide a clearer understanding of the relative roles of physical and biogeochemical factors in determining spatial variation in DOC and, consequently, in the prediction of future DOC trajectories in view of anticipated future climate change and further reductions in acid deposition.

In this paper we describe the development and structure of a simple multiple logistic regression model that explains spatial variation in long-term (20 year mean; 1992-2011) DOC concentrations for an intensively and continuously monitored set of 21 upland lakes and streams across the UK. By using as long a period as the dataset allowed we sought to minimise the effect of short-term, site-specific, variation in DOC that could otherwise cloud the spatial signal, thus providing the most robust baseline possible for future dynamic modelling. However, since most sites show long term changes in DOC that have slowed in recent years, we also describe an identically parameterised, although slightly poorer fitting model, based on a more contemporary dataset (2009-2013), that is arguably of more immediate value in the assessment of DOC status of other recently monitored sites. Finally, focussing on the structure of the most parsimonious (20 year mean) model, we consider the processes that may govern spatial variability in DOC and the potential value of the model as a predictive tool.

Materials and methods

Study sites

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Our study was focussed primarily on sites from the UK Upland Waters Network (UWMN) (Table 1). The UWMN includes the outflows from small lakes (ranging in surface area from 2-114 ha, in volume from 3.6 x 10^4 - 7.4 x 10^6 m^3 and in residence time from around 2 weeks to 6 months) and streams (first or second order) from many regions of the UK uplands (Battarbee et al. 2014). The UWMN is an expansion of the former UK Acid Waters Monitoring Network, which was established to assess the efficacy of regional reductions in acid pollutants (see for example, Monteith and Evans (2005)). AWMN sites were selected originally on the criteria of low geological acid-buffering capacity and the absence of marked local catchment interference or point source contamination that might otherwise complicate acidification/recovery signals. The main exception to the latter criterion was the selection of a subset of sites with significant conifer plantation forestry. The remaining sites were either subject to low-intensity grazing (mainly by sheep or deer) which maintains a grassland or heathland cover, or were located above the natural tree line. Two southern English UWMN sites were excluded from our analysis on the grounds that their catchments were not glaciated in the last glacial period and active sulphur cycling in B horizons distorts the strong link between sulphur deposition and sulphate concentration in runoff that is seen across the rest of the network (Cooper 2005). In order to extend the geochemical gradient into more strongly buffered systems the dataset also included the Environmental Change Network (ECN) stream site, the Trout Beck (northern Pennines) that drains blanket peat overlying carboniferous limestone.

Water sampling and analysis

Water chemistry samples from the outflow of each lake were collected usually in the first week of March, June, September and December. The UWMN streams were sampled every month in order to better capture the larger hydrochemical variation of these systems. The second order ECN Troutbeck stream was sampled weekly. All water samples were filtered using 0.45 µm cellulose nitrate filters and analysed for DOC using a TOC analyser by first acidifying samples to purge inorganic carbon, followed by high temperature combustion and spectrometric analysis of the resulting CO_2. Acid anions were analysed by ion chromatography, and base cations using an Inductively Coupled Plasma Mass Spectrometer or Optical Emission Spectrometer (i.e. ICP-MS or ICP-OES). The laboratories participating in the UWMN operate a range of quality control procedures (Gardner 2008) and participate in an annual international AQC

assessment provided by the UNECE International Cooperative Programme on the Assessment of Acidification of Rivers and Lakes (or ICP Waters Network).

Physical data

Data for a number of mechanistically plausible metrics or surrogates for potential process drivers were compiled to predict spatial variability in DOC, several representing factors that have been linked to DOC in previous spatial assessments (see Supplementary Table 1 for full list and explanation of the derivation of the soils data).

Area-weighted mean catchment altitude (ALT) was determined from a digital terrain model. Site-specific daily precipitation data were obtained for the 1 km square most central to each catchment from the NERC Centre for Ecology and Hydrology's hydrological CHESS (Climate, Hydrological and Ecological research Support System) dataset, which is based on interpolated data from the UK Met Office's network of meteorological stations. These data were available at the time of analysis up to the end of 2007 only, so data for the period 1988-2007 were used to provide a 20 year annual mean. Precipitation was then corrected for evaporative loss (to provide effective precipitation (P_E)) by subtracting the UK Met Office's 1 km square resolution Standard-period Average Annual Rainfall (SAAR) evaporation estimate (representing the period 1961-1990).

Due to local variation in topography, 1 km interpolated air temperature data were unsuitable for determining air temperatures for the mid-altitude points of catchments. Mean annual air temperature (MAT) for each site was therefore estimated using a linear model describing the relationship between mean annual temperature, altitude and latitude for the 12 meteorological stations on the UK Environmental Change Network (ECN) which span gradients of altitude and latitude of 100 – 700 m and 50.8 – 57.1 °N respectively; i.e.

MAT(°C) = 28.5 - (0.343 x latitude) - (0.00612 x ALT)   ($R^2 = 0.97$)   (1)

- where latitude is in degrees North, and ALT in metres above sea level (masl).

Soil data were derived from the UK FAB database which is based on extracted shapefiles from the Soil Survey and Land Research Centre, Macaulay Land Use Research Institute, and Department of Environment Northern Ireland databases (Curtis pers. comm.). Soil map units were converted to the "Institute of Terrestrial Ecology Generic classes". Data were represented as percentage cover of each catchment for a range of soil types, and included the sum of proportions of peat and peaty gley soils (PPPG) to represent wetland soil coverage.

Non-marine concentrations of calcium and magnesium were calculated as an indicator of catchment sensitivity to acidification, using the difference between long-term mean concentrations of these ions and a hypothetical marine fraction based on long-term mean chloride concentration (cf. Evans et al. (2001). We also calculated long term mean sulphate [SO_4], nitrate and chloride concentration to represent the contribution of these acid anions in runoff.

Data representing spatial variation in the deposition of oxidised sulphur and oxidised and reduced N for the period 2001-2003 were obtained from 5km gridded estimates provided by the NERC Centre for Ecology and Hydrology and used to inform national air quality policy (RoTAP 2012). These were determined from estimates of dry and wet deposition derived from measurements of gas concentrations and of ion concentrations in rainfall respectively. Deposition estimates were modelled using the same procedures as for the UK deposition estimates (RoTAP 2012; Smith and Fowler 2001; Smith et al. 2000),) and include a vegetation canopy resistance model to estimate gas and particle deposition and an orographic enhancement for wet deposition.

Data Analysis

To accommodate a sub-set of UWMN sites for which monitoring started later than 1988, 20 year site means for DOC and other hydrochemical variables (see below) were derived for the period April 1992 to March 2011. While this period is out of sync with the 20 year precipitation estimates, we assumed between-site variation would be much greater than temporal variation in the 20 year means and that this discrepancy would therefore be unlikely to weaken the predictive power of this potential explanatory variable. Monitoring of

Loch Coire nan Arr was terminated at the end of 2007, but we established that there were only marginal differences in mean DOC concentrations for the period 1992-2007 compared to 1992-2011 (on average concentrations for the former period were 96% of those for the latter) and we therefore decided to keep this site in the dataset. We used the product of DOC and P_E to provide an approximation for DOC flux.

Exploratory data analysis involved inspection of a series of scatter plots and Pearson correlation coefficients comparing both mean annual DOC and mean annual DOC flux (i.e. DOC x P_E) with a broad range of potentially explanatory variables (correlation coefficients provided in Supplementary Table 2). Decisions on whether or not to log transform each variable were based on the structure of between-site variation. A range of candidate multiple logistic regression models, chosen on the basis of backward elimination to minimise the Akaike Information Criterion (AIC), were then produced to explain spatial variation in mean annual DOC using subsets of the variables that either showed strong individual relationships with either DOC variables, and/or have previously been identified in either spatial or temporal studies as being potentially influential (see Discussion). The latter included variables representing acid deposition and catchment sensitivity to acidification on the basis of observations by Monteith et al. (2007).

The transferability of the most parsimonious, or "final", spatial model, based on the lowest AIC, was tested both internally and externally. First, we carried out leave-one-out cross validation of the UWMN/ECN dataset. Second, we compiled the necessary mean DOC and explanatory data for an independent set of lake and streams sites. There are very few alternative multi-decadal hydrochemical records for UK upland surface waters of sufficient analytical quality available for this purpose. We therefore assembled a dataset for a range of sites that were all sampled at least quarterly (lakes) or monthly (streams) within one year between the period 1993 and 1997, and analysed for DOC and other hydrochemical variables using analytical methods appropriate for dilute waters (Gardner 2008). Effective precipitation for these sites was determined using SAAR long-term (1961-1990) average precipitation and evaporation data.

While we deliberately used the longest time series available (i.e. 1992-2011) to develop the most robust spatial model of long-term mean concentrations, further modelling of superimposed long-term trends and

shorter-term variability is beyond the scope of this paper. As DOC concentrations have increased over much of the time period represented, contemporary levels across the UK uplands are likely to exceed those predicted on the basis of modelled 20 year means. We therefore repeated the modelling approach using the same parameters on a five year dataset covering the period 2009-2013, during which concentrations have been relatively stable, in order to provide a more contemporary predictive tool. In this case Loch Coire nan Arr was replaced with the neighbouring site Loch Coire Fionnaraich which replaced the former site in 2008.

Results and Discussion

Exploratory analysis

Long-term mean DOC in our dataset ranged from 1.6 mg L^{-1} at the second highest site with a catchment dominated by peat ranker soils (Scoat Tarn, northern England), to 13.9 mg L^{-1} at a relatively low elevation peatland site (Beagh's Burn, Northern Ireland) (Table 1). Mean DOC draining the highest altitude site, Lochnagar (northeast Scotland) was slightly higher (0.2 mg L^{-1}) than Scoat Tarn, but showed the lowest mean annual DOC flux (2.4 g DOC m^{-2} yr^{-1}) as a consequence of significantly lower annual effective precipitation. The three sites with the highest peat and peaty gley cover (i.e. >0.95%; Beagh's Burn, Loch Tinker (central Scotland) and Troutbeck (northern England) had moderate to high mean concentrations and the three highest DOC fluxes (ranging from 13.5 to 16.8 g DOC m^{-2} yr^{-1}).

Correlation coefficients summarising relationships between long-term mean DOC and long-term mean DOC flux, and a range of explanatory variables included in our analysis are provided in Supplementary Information (Table 2). Relatively few variables showed statistically significant ($p<0.05$) relationships with either log DOC or log DOC flux. However, log DOC was particularly strongly (positively) correlated with the percentage cover of wetland soils (PPPG), negatively correlated with effective precipitation (P_E) and positively correlated with divalent base cation concentration ([xBC]). Log DOC flux was negatively correlated with altitude (ALT) and positively correlated with mean annual temperature (MAT). A positive correlation with log chloride concentration (log Cl) might reflect the strong negative relationship between log Cl and ALT. There were no clear relationships between either DOC or DOC flux and any of the deposition-based predictors, i.e. log sulphate concentration (log [SO_4]) or estimated reduced, oxidised or total nitrogen deposition. The four sites with the highest log DOC also showed the highest non-marine divalent base cation concentrations, but there was no apparent structure in this relationship for the remaining sites. Scatter plots revealed little covariant structure between potential explanatory variables with the obvious exception of strong negative relationships between altitude and temperature, a negative relationship between altitude and chloride concentration reflecting distance from the coast and hence vulnerability to seasalt deposition, and positive relationships between the sulphate concentration and the three nitrogen deposition variables.

Final model structure

The most parsimonious logistic regression model (lowest AIC) for explaining spatial variation in 1992-2011 log DOC concentration comprised five variables and two interactions representing both physical and chemical determinands and is structured as follows:

$$\mathbf{log_{10}\,DOC} = 2.75 - 6.18 \times 10^{-4}\mathbf{ALT} - 1.12 \times 10^{-4}\mathbf{P_E} + 1.22\mathbf{PPG} - 1.8 \times 10^{-3}\mathbf{ALT*PPG} \tag{2}$$

$$- 1.05\mathbf{log[SO_4]} - 9.32 \times 10^{-3}\mathbf{[xBC]} + 5.41\mathbf{log[SO4]*[xBC]}$$

All model terms were highly significant ($p = 0.001$ or less), and together explained 96.5 % (adjusted R^2) of the spatial variation in DOC (Table 2). The model included four terms based on three physical parameters: a positive effect of the proportion of peat and peaty gley soil in the catchment (PPPG); negative effects of altitude (ALT) and effective precipitation (P_E), and a negative interaction between ALT and PPPG. The combination of these three variables in isolation was sufficient to explain 79% of the variance in DOC. The final model also included two hydrochemical parameters - negative effects of non-marine base cation concentration ([xBC]) and sulphate concentration log[SO4] – and a positive interaction term between the two.

Leave-one-out cross validation of the primary dataset resulted in a very tight relationship between observed and predicted values ($R^2 = 0.92$) and a Root Mean Square Error (RMSE) of 1.06 mg DOC L^{-1} (Figure 1). A further independent test of the model, based solely on data obtained from other sites from the mid-1990s, also demonstrated strong predictive power with a single exception. Following the removal of this major outlier (Cottage Hill Syke – a small tributary of the Troutbeck, discussed below), the remaining DOC observations for the sites were strongly correlated with model predictions ($R^2 = 0.85$, $p<0.001$) with a slope of 1.16 and a statistically insignificant intercept of 0.11 (Figure 2).

The structure of the final model has several features in common with previous analyses of spatial determinants of DOC, but the model's overall predictive strength is perhaps unparalleled and provides some

confidence that DOC draining upland catchments might be predicted over wide spatial scales on the basis of physical catchment characteristics, and estimates of sulphate and divalent base cation leaching.

The same set of predictor variables (but with hydrochemical variables representing 2009-13 means), all again statistically significant, were found to explain a slightly lower proportion of spatial variance (adjusted R^2 = 93.7) in mean 2009-2013 DOC concentrations (Table 2b). Coefficients were generally very similar to those in the 1992-2011 baseline model but were 32% and 57% smaller for $log[SO_4]$ and the $log[SO4]$ x $[xBC]$ interaction term respectively (both of which also showed higher p values). This possibly reflects the greatly reduced spatial variation in sulphate concentration in UK waters in recent years resulting from large reductions in sulphur deposition that have led to a convergence of sulphate concentrations in surface waters nationally (Monteith et al. 2014).

The role of soil type

The combined proportional cover of the two 'wetland' organic soil types, peats and peaty gleys (PPPG), provided by far the strongest single predictor of log DOC (positive correlation) – a finding that accords with a number of studies from other regions (Aitkenhead et al. 1999; Creed et al. 2008; Dillon and Molot 1997; Hope et al. 1994; Xenopoulos et al. 2003), and in isolation explained 63.2% of the total spatial variance. While the often highly coloured water draining peatland catchments is sometimes considered a product of the peat itself, analyses of carbon isotopes in DOC draining relatively undisturbed upland UK catchments indicate DOC from these systems is mostly of very recent origin, i.e. <5 years (Evans et al. 2007; Tipping et al. 2010), as has also been found elsewhere (Moore et al. 2013). In this context PPPG would seem to act primarily as an indicator of a) soil anoxia, limiting the respiratory loss of newly deposited/exuded organic matter, and b) the impediment of vertical routing of drainage waters, and consequently of reduced potential for adsorption of DOC by ion-exchange complexes in mineral soil horizons (McDowell and Wood 1984; Moore and Jackson 1989), rather than as a simple indicator of the size of the catchment's terrestrial organic carbon store. It is also feasible the DOC draining peat soils may be more recalcitrant than that draining other soil types (Moody et al. 2013),

The role of precipitation

Effective precipitation provided a strong negative effect in the final model. While this is consistent with a net diluting influence on DOC the effect was relatively muted. The model predicts that a four-fold increase in P_E, (i.e. 500 to 2000 mm) would reduce DOC concentration by circa 40%. Other influences, including the shift from vertical to more lateral drainage with increasing precipitation - reducing the potential for DOC adsorption by mineral strata, the fact that wetter environments are more likely to be characterised by organic soils, and the effect of precipitation in reducing residence time and hence exposure to photo-mineralisation, may all have partially counteracted the dilution effect.

The role of altitude

When P_E is held constant the model predicts that DOC, and hence DOC flux, will increase exponentially with declining altitude (ALT) (Figure 3 – solid black line). Strong negative relationships between DOC and altitude have also been reported widely before (Sobek et al. 2007; Weyhenmeyer and Karlsson 2009; Xenopoulos et al. 2003). While effective as a spatial predictor, from a mechanistic view its inclusion in the model has limited direct explanatory value because a wide range of environmental parameters tend to correlate with altitude (Creed et al. 2008).

Inter-annual variability in total organic carbon concentrations has been shown to be tightly correlated with terrestrial gross primary productivity in waters draining a Scottish peatland (Dinsmore et al. 2013), while field experiments in the northern Pennines have demonstrated a strong temporal correlation between DOC production and net primary production (NPP) as inferred from cumulative solar radiation during the growing season (Harrison et al. 2008). These findings therefore support previous spatial modelling exercises in which effects of altitude on DOC have been linked to primary productivity through: the number of days in the year that mean daily air temperature exceeds 0°C (Sweden) (Weyhenmeyer and Karlsson 2009); the number of growing degree days (north-eastern Canada) (Creed et al. 2008); and, the extent of plant cover as inferred by the remotely sensed Normalised Difference Vegetation Index (Norway) (Larsen et al. 2011). However, these spatial studies have not compared the magnitude of the proposed effect of these drivers with the size of the apparent response in DOC.

In comparison, the influence of temperature (which also declines markedly with increasing altitude) on soil organic matter decomposition rates has been reported widely. The kinetic theory of Arrhenius suggests that organic matter decomposition rates should increase exponentially with increasing temperature, and that decomposition of more recalcitrant substrates, such as the "low quality" organic matter that characterises highly organic soils, will show more sensitive relationships with temperature because of their relatively high activation energies (Davidson and Janssens 2006). In a meta-analysis of 494 studies of soils worldwide, the median relative change in soil respiration rate per 10 °C rise in temperature (or Q_{10}) was 2.39 (Hamdi et al. 2013). However a study of Scottish peats (Chapman and Thurlow 1998), which are likely to be more representative of the organic soils of our calibration sites, reported Q_{10} values ranging from 2.2 – 19, with a mean of 4.8, while a maximum Q_{10} of 3.53 was observed for peat cores taken from the UK ECN Moor House site under drained conditions (Clark et al. 2009).

In the final model selected here, altitude influences DOC both as a single term and in a positive interaction with PPPG. We first consider its effect in catchments dominated exclusively by better drained soils, i.e. when PPPG = 0 (and the interaction term is therefore redundant). Here the model shows DOC concentration and flux to increase by a factor of 2.34 over an altitude gradient of 900 – 300 masl - approximately the range covered by the calibration sites and equivalent to a gradient in mean annual air temperature of 4.2 – 7.9 °C for a mid-latitude UK site (Figure 3). ECN meteorological data indicates that cumulative solar radiation over the growing season (CSR_G) (i.e. the total solar radiation over the months of the year when mean air temperature exceeds 5°C) increases by a factor of 1.45 over the same altitude gradient (Supplementary Information Figure 2). Even if NPP responds proportionally, this alone would be insufficient to explain the observed change in DOC with altitude in organo-mineral soil dominated catchments. However, if the microbial production of DOC from the organic matter pool generated by NPP is temperature dependent, then NPP and temperature dependent decomposition (TDD) might be expected to exert a multiplicative effect. In this case the TDD effect required to explain the modelled change in DOC is given by 2.34/1.45 = 1.62, equivalent to a Q_{10} response of 3.7, and therefore broadly consistent with mid-range values reported for Scottish peats (Chapman and Thurlow 1998). Figure 3 demonstrates that the product of CSR_G and TDD (Q_{10} = 3.7) changes with altitude in a similar exponential manner to that shown by DOC. However it is likely

that other altitude-related factors, such as slope, susceptibility to soil freezing, snow accumulation, windspeed effects on plant growth, or microbial cycling of nutrients, also contribute to the overall effect, in which case the effect of temperature alone would not need to be so pronounced.

In contrast to organo-mineral soils, the modelled response of DOC to declining altitude for catchments exclusively covered by wetland soils (i.e. PPPG =100), is far too large to be explained purely by the simple product of NPP and TDD, even if Q_{10} levels were substantially higher for these soils (Figure 4). The model predicts no difference between catchments for which PPPG = 0 and PPPG = 1 at an altitude of 690 masl, but by 300 masl production is almost five times higher from than the latter (Figure 4c). Further mechanisms contributing to this apparent amplification of DOC export may relate to soil hydrological status, and might include: 1) greater accumulation of potentially soluble organic matter carbon in wetland soils; 2) an increase in the ratio of organic matter exported as DOC relative to that being respired as CO_2 in wetter environments; and, 3) effects of water table variation in peats (Clark et al. 2009; Fenner and Freeman 2011; Mitchell and McDonald 1992; Toberman et al. 2008) which might be expected to greater at lower altitudes due to lower levels of precipitation and greater evaporation.

Hydrological factors may also account for the significant model underestimate for Cottage Hill Syke catchment, the only major outlier we have encountered to date (Figure 2 – point R). This peat dominated site has by far the smallest catchment (circa 17.4 ha) considered in this study and is heavily gullied. Low pH and base cation concentration implies very little contribution from groundwater, while the water table remains within 5 cm of the surface for 83% of the time (Holden et al. 2012), implying that run-off is likely to be particularly heavily dominated by saturated and overland flow, minimising the potential for retention of DOC by the underlying substrata.

The role of catchment sensitivity to acid deposition
Despite explaining relatively little of the overall variance in logDOC all three hydrochemical terms were highly significant in the full model. A negative effect on DOC of acid deposition, as inferred by log [SO_4], dampened by an interactive effect with [xBC], is consistent with the relationship reported for trends in DOC

and these variables across a wide range of sites in northern Europe and North America by Monteith et al. (2007). Negative effects of sulphuric acid additions on DOC production in organic and B horizons of soil samples taken from a range of UWMN sites have been shown to be greater in soils with lower base saturation and higher exchangeable aluminium levels (Clark et al. 2009; Palmer et al. 2013). The coefficient for log [SO_4] is large relative to between-site variation, suggesting DOC is sensitive to even small changes in sulphur deposition. The negative sign for the individual [xBC] term may reflect the extent to which DOC in catchment drainage waters interacts with, and is subsequently retained by, mineral soil horizons.

Potential space-for-time implications

While our spatial model essentially represents "steady state" relationships between DOC and environmental factors, it may also provide some indication of the sensitivity of these systems to future environmental change. Medium emissions climate change scenarios projected by UKCP09 for conditions in 2080 relative to 1961-1990 predict all parts of the UK to become warmer (Murphy et al. 2009). The main temperature increases are forecast for summer, with the greatest increases in mean summer temperatures of 4.2 °C in southern England, declining to around 2.5 °C for remoter parts of Scotland. Effects of warming on NPP in the uplands should be most dependent on the rate of advance in spring and retreat in autumn of the temperature threshold for net production to occur, but given the relatively modest response over a considerable altitudinal gradient we show here these effects are unlikely to be substantial. However, a projected increase in annual average temperatures of circa 3 °C for the UK as a whole (equivalent in temperature terms to a decline in altitude of around 500 m), would be sufficient to increase concentrations draining organo-mineral soils on average by circa 150% relative to current levels if decomposition rates were to respond to temperature at a rate described by a Q_{10} of 3.7. For the northern and western UK, negligible change is predicted in summer precipitation that dominates the magnitude of wet dry cycling in peats, although a forecast increase in winter precipitation could if anything reduce these fluctuations. The effect of soil type on the magnitude of the relationship between altitude and DOC has potential implications for catchment sensitivity to future warming and thus requires further investigation. Over the 20 year duration of the UWMN to date, however, there have been no clear trends in either air temperature or precipitation, and it should be noted that Zhang et al. (2010) did not detect any change in DOC in lakes in regions of eastern

Canada that had experienced two decades of warming. Climatic effects on the long-term DOC trend to date are therefore likely to have been small, although effects of inter-annual variability in temperature should be detectable.

For the majority of sites we found relatively good agreement between the relationship between log [SO$_4$] and DOC measured in individual samples at the calibration sites, and the spatially modelled response of DOC to changing [SO$_4$], when all other variables (including [xCa^{2+}+xMg^{2+}]) were held constant (Figure 5). However, relationships for some peatland dominated sites, i.e., River Etherow, Coneyglen Burn and Troutbeck were poor. These sites show a similar curvilinear pattern in the DOC - [SO$_4$] relationship in individual samples to the other sites, but the model appears too sensitive to the effect of the [xBC] * log [SO4] interaction term, which results in a reversal of the net effect of [SO4] at higher base cation concentrations. Further modifications will therefore be necessary to enable prediction of effects of changing deposition on peatland systems. Nevertheless, close agreement for the organo-mineral dominated sites provides further strong support for the hypothesis that reducing acid deposition has dominated the long-term trend in DOC in this region over recent decades (Clark et al. 2010). For these sites the model predicts that the sensitivity of DOC to unit declines in surface water [SO$_4$] is increasing as the latter approaches low-to-background levels. Although sulphur deposition has fallen substantially over the last two decades, further, relatively small, reductions are expected according to current national and international emission abatement policy, and are therefore likely to result in further significant increases in DOC at unprecedented rates per unit reduction in the acid load.

Certain factors that have been identified elsewhere as potentially influential appeared to be relatively unimportant in explaining spatial variation in DOC within our dataset. For example, we were unable to detect any systematic differences between sites with significant cover of managed coniferous forest and moorland sites. However, any effects of increased interception of sulphur deposition by forest canopies will have been taken into account by inclusion of the log[SO$_4$] term. Aside from the effects of enhanced deposition, differences in annual inputs of organic matter to the soil, or other factors related to forestry, appear to have not been sufficiently marked at this national scale (and given the substantial effect size of the other controls)

to exert a significant effect on the model. We were also unable to detect any fertilising influence of nitrogen deposition on DOC. Nitrogen deposition has been identified as a key factor explaining gradients in upland floristic diversity across the UK (Henrys et al. 2011; Stevens et al. 2006) and it has been argued that levels of NPP in the most polluted upland regions will have also been stimulated, with a consequent effect on DOC - an effect that is included in some recent process-based models (Rowe et al. 2014; Tipping et al. 2012). It is possible that nitrogen deposition effects on DOC have been masked by the variable log[SO_4] (despite the expectation of opposite effects) as S and N deposition are reasonably well correlated spatially. Alternatively it is feasible that NPP in upland catchments throughout the regions covered by our dataset is now effectively N-saturated resulting in no detectable differential effect. Whether recovery from acidification, in conjunction with other intensifying anthropogenic pressures, is resulting in unprecedented levels of DOC or simply reflects a return to pre-industrial levels will require further exploration.

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Table 1. Physical parameters and mean annual DOC data for the study sites.

Site no.	Site	latitude	longitude	Mean catchment altitude (masl)	modelled mean annual temperature (°C)	modelled effective precipitation (mm yr^{-1})	DOC concentration (1992-2011) (mg L^{-1})	modelled DOC flux (g m-2 yr-1)
1	Loch Coire nan Arr	57.4171	-5.65186	446	6.08	2838	3.0	8.5
2	Allt a'Mharcaidh	57.1178	-3.84959	706	4.59	773	3.2	2.4
3	Allt na Coire nan Con	56.7584	-5.61215	333	6.99	2262	5.6	12.7
4	Lochnagar	56.9583	-3.23157	914	3.37	1295	1.8	2.4
5	Loch Chon	56.2122	-4.54755	275	7.54	2099	4.9	10.3
6	Loch Tinker	56.2282	-4.5099	469	6.35	2179	6.2	13.5
7	Round Loch of Glenhead	55.0937	-4.43045	377	7.30	2014	4.1	8.2
8	Loch Grannoch	55.0031	-4.28109	318	7.69	2050	6.1	12.5
9	Dargall Lane Burn	55.0775	-4.43103	416	7.06	2156	2.3	5.0
10	Scoat Tarn	54.482	-3.29955	717	5.43	2914	1.6	4.6
11	Burnmoor Tarn	54.4285	-3.25931	329	7.82	1676	3.0	5.0
12	River Etherow	53.493	-1.82663	480	7.21	1087	8.2	8.9
15	Llyn Llagi	53.0149	-4.0153	549	6.95	2420	3.0	7.4
16	Llyn Cwm Mynach	52.7955	-3.96212	360	8.19	1815	2.6	4.8
17	Afon Hafren	52.4741	-3.70337	527	7.28	2142	2.5	5.3
18	Afon Gwy	52.4542	-3.70555	558	7.10	2136	2.5	5.3
19	Beaghs Burn	55.1005	-6.16357	332	7.57	1210	13.9	16.9
20	Bencrom River	54.1573	-6.00503	422	7.34	1358	5.4	7.3
21	Blue Lough	54.1585	-5.96976	459	7.12	1236	4.8	5.9
22	Coneyglen Burn	54.7393	-7.00599	360	7.52	1120	10.5	11.8
30	Troutbeck	54.695	-2.38784	600	6.07	1434	9.8	14.0

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Table 2a   Multivariate logistic regression model statistics for the most parsimonious (lowest AIC) model explaining spatial variation in $\log_{10}$ 20 year (1992 – 2011) mean DOC concentration.

Predictor	Coefficient	SE Coefficient	P value
Constant	2.747	0.378	<0.001
Altitude(m) **(ALT)**	-0.00062	0.0001	<0.001
Effective precipitation (mm) **(PE)**	-0.000112	0.000024	0.001
Proportion peat + peaty gley soil **(PPPG)**	1.217	0.158	<0.001
ALT * PPPG	-0.00182	0.00035	<0.001
log [sulphate] (μeq L^{-1}) **(log[SO4])**	-1.051	0.186	<0.001
[Non-marine divalent base cation] (μeq L^{-1}) **([xBC])**	-0.0093	0.0021	0.001
Log[SO4] * [xBC]	0.00542	0.0011	<0.001
	S = 0.0488 R^2 = 97.7% Adjusted R^2 = 96.5%		

Table 2b Multivariate logistic regression model statistics explaining spatial variation in $\log_{10}$ DOC concentration for the period 2009-2013 based on the same parameters selected for the most parsimonious model (see Table 2a). Note data for Loch Coire nan Arr, monitoring of which ceased in 2007, has been replaced with data for nearby Loch Coire Fionnaraich.

Predictor	Coefficient	SE Coefficient	P value
Constant	2.089	0.371	<0.001
Altitude(m) **(ALT)**	-0.00053	0.0001	<0.001
Effective precipitation (mm) **(PE)**	-0.000091	0.00003	0.010
Proportion peat + peaty gley soil **(PPPG)**	1.126	0.218	<0.001
ALT * PPPG	-0.00172	0.00047	0.003
log [sulphate] (μeq L^{-1}) **(log[SO4])**	-0.715	0.181	0.002
[Non-marine divalent base cation] (μeq L^{-1}) **[xBC]**	-0.0040	0.0012	0.006
Log[SO4] * [xBC]	0.00629	0.0022	0.013
	S = 0.0632 R^2 = 95.9% Adjusted R^2 = 93.7%		

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Figure 1 Comparison of long term observed mean annual DOC concentration of UWMN/ECN sites and predicted DOC concentration based on leave-one out cross validation. Site numbers according to Table 1. 1:1 line = feint grey; linear regression line = black.
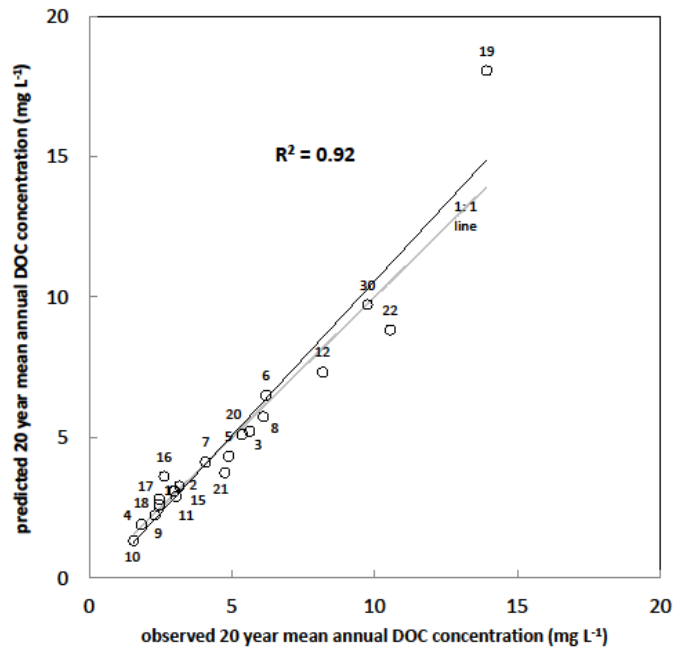
Figure 2 Relationship between measured mean DOC concentrations for upland lake and stream sites in Scotland and Wales (sampled repeatedly over the course of one year only during the early-mid 1990s) and concentrations predicted by the final model on the basis of long-term modelled effective precipitation, mean catchment altitude, proportion of peat and peaty gley soil in terrestrial catchment, and mean sulphate and non-marine divalent base cation concentration for the year of sampling. A list of sites and locations are provided in Supplementary Information (Table 3) .
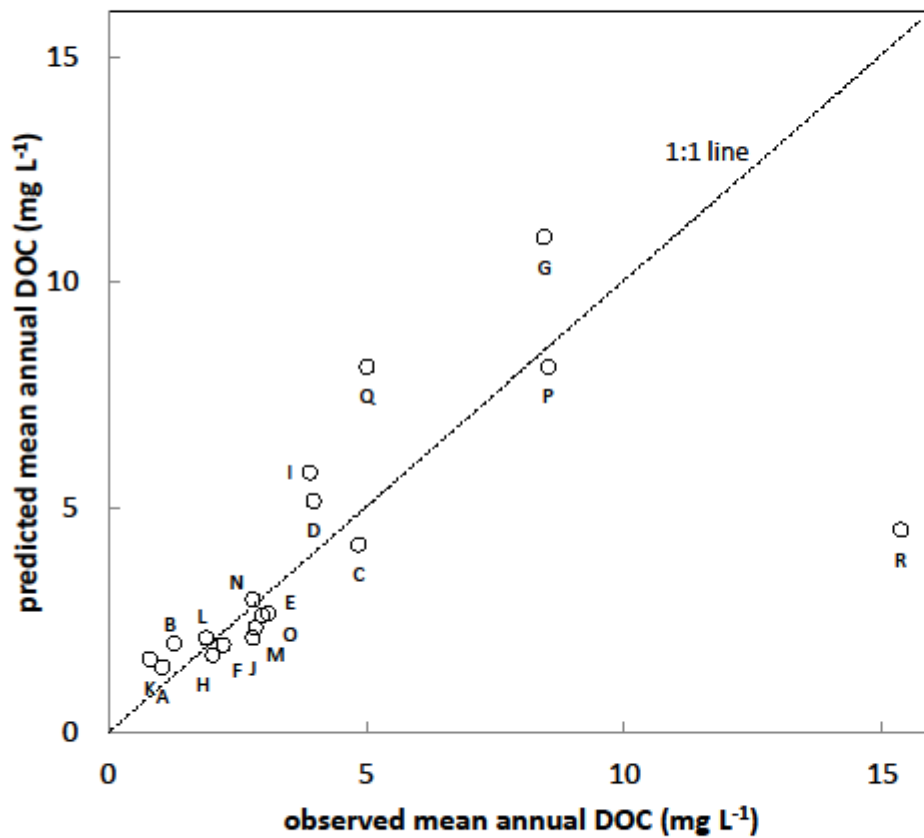
Figure 3 Modelled effect of altitude on DOC concentration, or flux, for UK upland catchments devoid of peats or peaty gley soils, relative to levels at 900 masl (solid line). Other lines represent: the modelled effects of altitude on cumulative growing season solar radiation over the growing season (CSR_G), assumed to be a surrogate for net primary production (filled squares); modelled temperature dependent decomposition (TDD) assuming a Q_{10} of 3.7 (empty squares); and, the product of the above effects of CSR_G and TDD (dotted line).
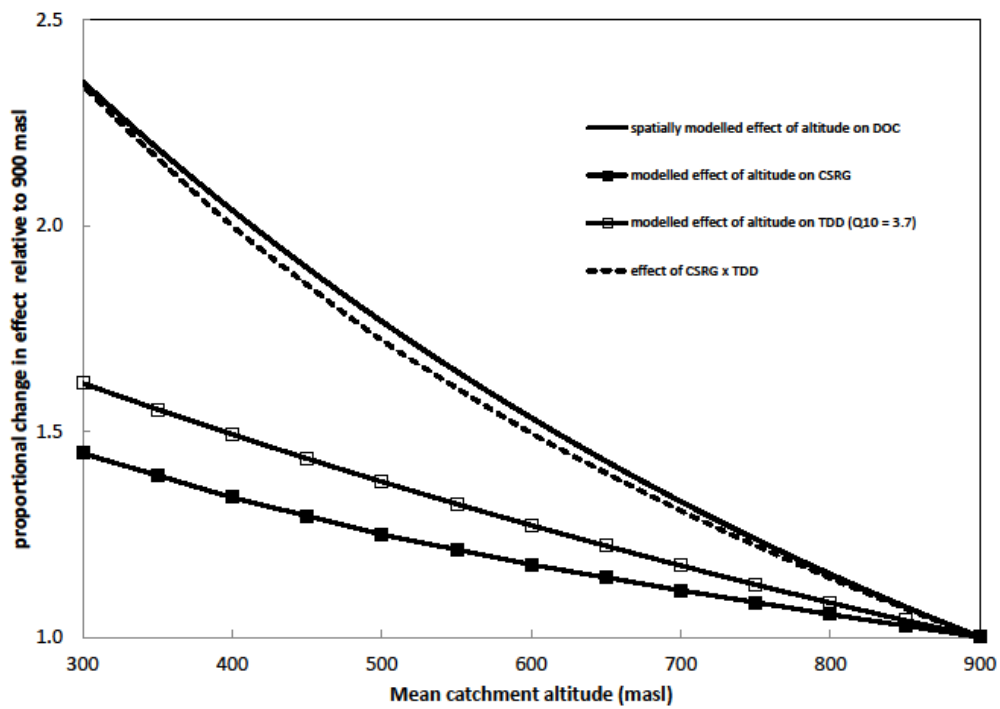
Figure 4 a-b) Modelled change in DOC concentration with altitude for hypothetical sets of sites representing peat or peaty gley dominated catchments (black lines) and other upland soil types (grey lines). a) poorly buffered and acidified sites with rainfall, and sulphate and non-marine divalent cation concentration equivalent to the Round Loch of Glenhead in Galloway. b) strongly buffered non-acidified sites with rainfall, and sulphate and non-marine divalent cation concentration equivalent to the Trout Beck in the northern Pennines. c) The effect of altitude on the ratio of concentrations between the two soil type end-members (i.e. PPPG=1: PPPG=0) regardless of other factors. Dotted line = unity.
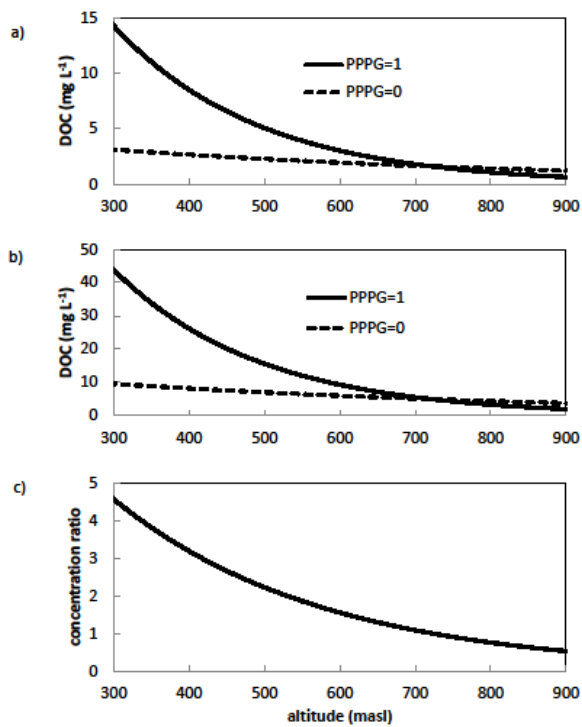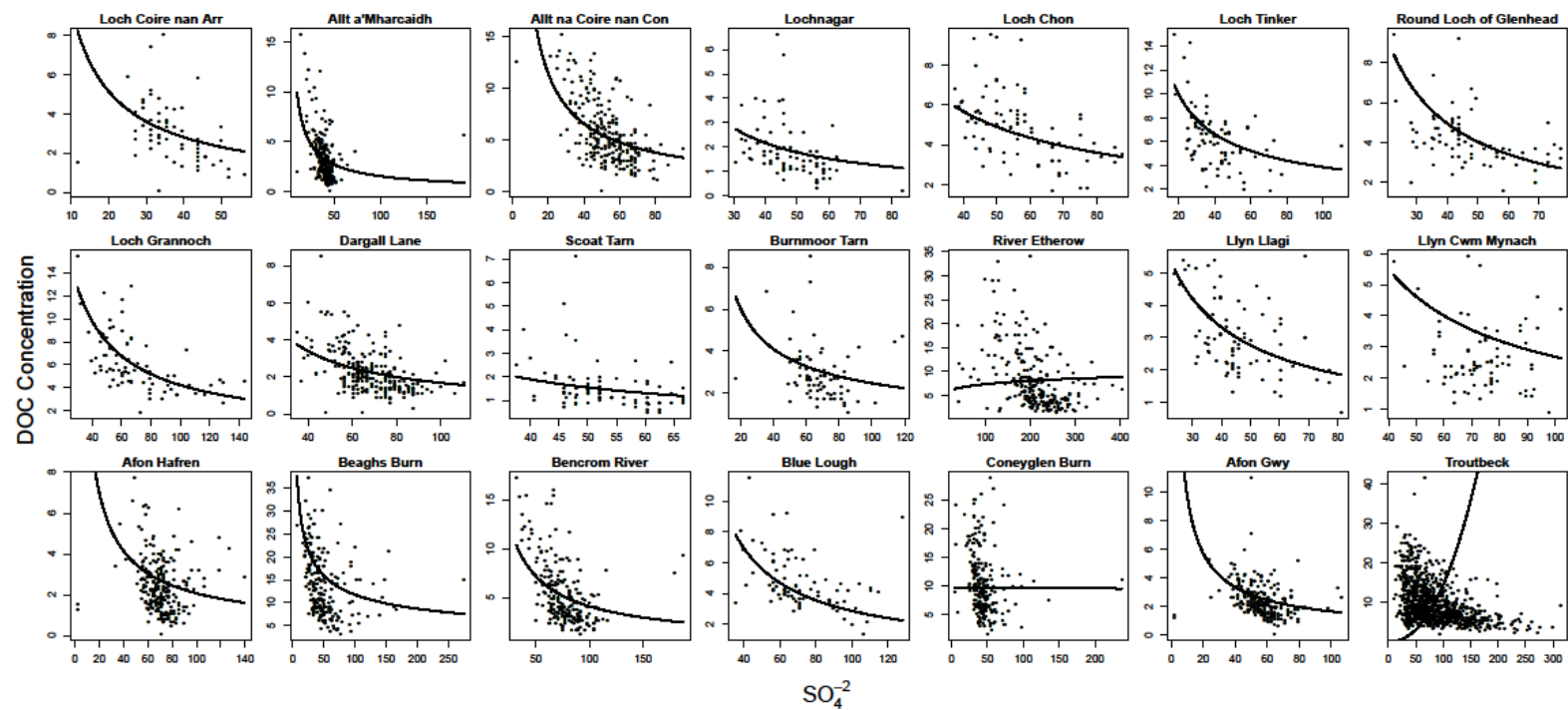
Figure 5

Change in mean DOC concentration (mg L^{-1}) with changing sulphate concentration (μeq L^{-1}) at the study sites estimated by the final model with all other parameters held constant (line),

superimposed on a scatter plot of DOC concentration against sulphate concentration in individual water samples taken from these sites over the last two decades.
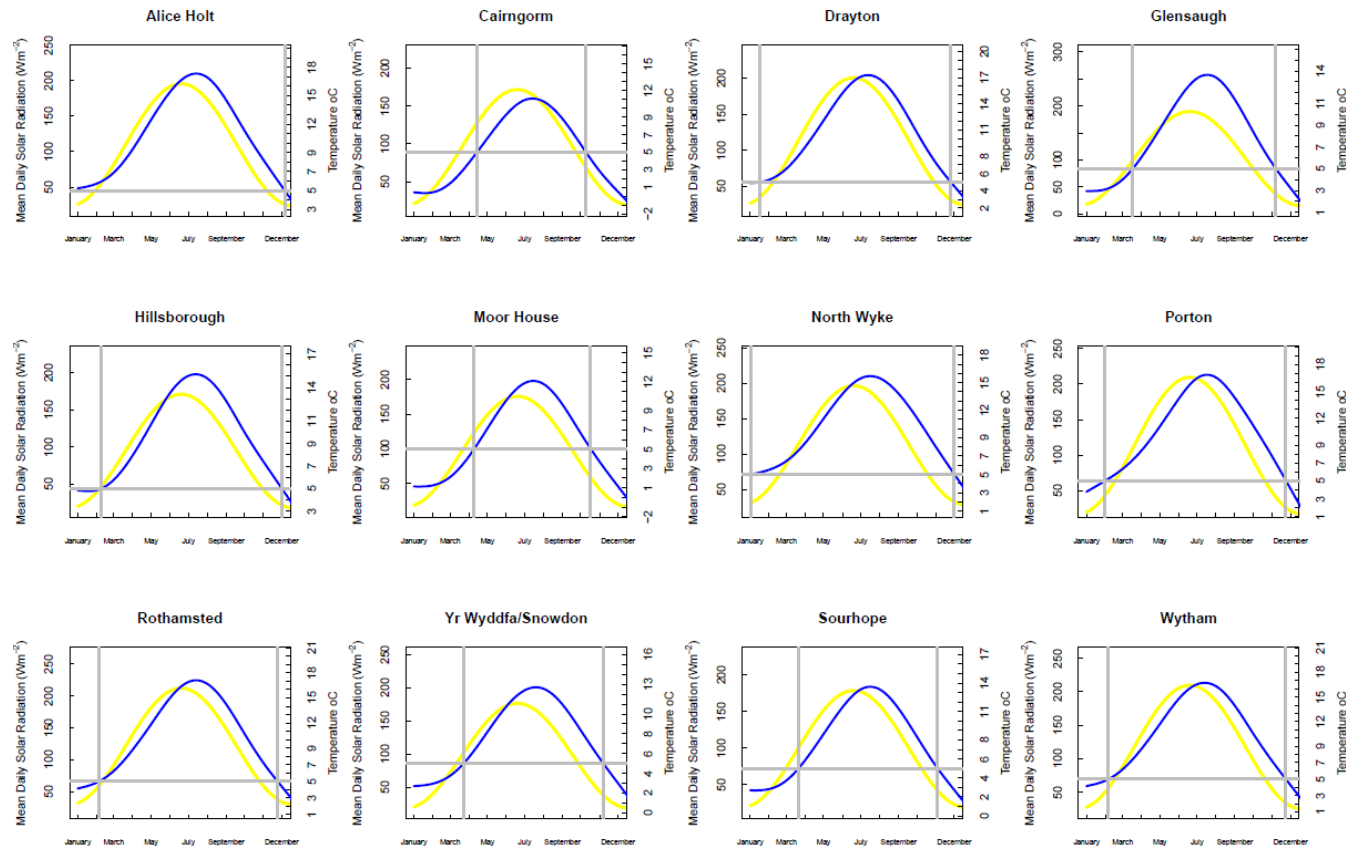
Supplementary Information Table 1

Variables included within candidate multivariate logistic regression models to explain spatial variability in long-term mean dissolved organic carbon concentration.

Variable	Abbreviation	Units
Log_{10} Mean annual DOC concentration	[DOC]	mg C L^{-1}
Log_{10} Mean annual DOC flux	DOC flux	g C m^{-2} yr^{-1}
Altitude	ALT	Metres above sea level
Total annual effective precipitation	P_E	Mm yr^{-1}
Mean annual temperature	MAT	°C
Mean annual reduced nitrogen deposition (5 km resolution)	RED_N_DEP	keq ha^{-1} yr^{-1}
Mean annual oxidised nitrogen deposition (5 km resolution)	OX_N_DEP	keq ha^{-1} yr^{-1}
Total annual nitrogen deposition (5 km resolution)	TOT_N_DEP	
Mean annual sulphur deposition (5 km resolution)	S_DEP	keq ha^{-1} yr^{-1}
% of catchments covered by coniferous forestry	%FOREST	%
Proportion of catchment occupied by brown podsolic soils	BPS	proportion
Proportion of catchment occupied by Gley podsols	GP	proportion
Proportion of catchment occupied by humic-sandy gley soils	HSG	proportion
Proportion of catchment occupied by Peat soils	PEAT	proportion
Proportion of catchment occupied by Podsols	POD	proportion
Proportion of catchment occupied by Rankers	RANK	proportion
Proportion of catchment occupied by Sandy gley soils	SG	proportion
Proportion of catchment occupied by peaty gley soils	PG	proportion
Proportion of catchment occupied by Stagnopodsols	SP	proportion
Proportion of catchment occupied by peat + peaty gley soil	PPPG	proportion
Log_{10} Mean annual sulphate concentration	Log [SO_4]	µeq L^{-1}
Divalent non-marine base cation concentration	[xBC]	µeq L^{-1}

Supplementary Information Figure 1. Seasonal variation in mean monthly air temperature and mean monthly solar radiation measured at Environmental Change Network terrestrial monitoring sites. Solar radiation curves (yellow) fitted using a sin function with peak centred on the summer solstice. Air temperature curves fitted using a GAM function. Horizontal grey lines correspond with an air temperature of 5 °C. Vertical grey lines provide period of year air temperature exceeds 5°C and primary production is assumed to occur. Integration of the area between the the pairs of vertical grey lines, bounded by the solar radiation curve provides the cumulative annual solar radiation over the hypothetical growing season (CSRG).

Supplementary Information Figure 2.

Relationship between modelled cumulative solar radiation over the growing season (CSR_G) and the altitude of Environmental Change Network meteorological stations. A GAM function (blue line), is used to represent the response of CSR_G to changing altitude in the Discussion section.