Predicting nitrogen and acidity effects on long-term dynamics of dissolved organic matter

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Abstract

Increases in dissolved organic carbon (DOC) fluxes may relate to changes in sulphur and nitrogen pollution. We integrated existing models of vegetation growth and soil organic matter turnover, acid-base dynamics, and organic matter mobility, to form the ‘MADOC’ model. After calibrating parameters governing interactions between pH and DOC dissolution using control treatments on two field experiments, MADOC reproduced responses of pH and DOC to additions of acidifying and alkalising solutions. Long-term trends in a range of acid waters were also reproduced. The model suggests that the sustained nature of observed DOC increases can best be explained by a continuously replenishing potentially-dissolved carbon pool, rather than dissolution of a large accumulated store. The simulations informed the development of hypotheses that: DOC increase is related to plant productivity increase as well as to pH change; DOC increases due to nitrogen pollution will become evident, and be sustained, after soil pH has stabilised.

Keywords: DOC, dynamic models, carbon, soil, nitrogen
Introduction

Observed increases in dissolved organic carbon (DOC) concentration in many north-temperate surface waters (Evans et al., 2005; Findlay, 2005; Oulehle and Hruska, 2009) may indicate changes in soil carbon storage (Freeman et al., 2001), and give rise to increased water treatment costs (Chow et al., 2003). These increases have been attributed to various factors (Clark et al., 2010), such as pH increase resulting mainly from a decline in sulphur (S) pollution (De Wit et al., 2007; Evans et al., 2006; Evans et al., 2008a; Haaland et al., 2010; Monteith et al., 2007; SanClements et al., 2012); climate change (Freeman et al., 2001); nitrogen enrichment (Bragazza et al., 2006; Findlay, 2005; Pregitzer et al., 2004); changes in precipitation patterns (Hongve et al., 2004; Ledesma et al., 2012); or changes in management such as burning (Clutterbuck and Yallop, 2010; Holden et al., 2012). While it is doubtful that all of these proposed drivers have combined to cause an increase in DOC in all locations, it is likely that interactions among some factors, in particular acidification recovery and factors affecting plant productivity, will affect DOC fluxes. Several models of DOC dynamics have been developed (Futter et al., 2007; Jutras et al., 2011; Michalzik et al., 2003; Neff and Asner, 2001; Xu et al., 2012) but these generally focus on seasonal dynamics and require detailed inputs describing hydrological processes. There remains a need for a simple model, which simulates long-term controls on DOC fluxes and is suitable for large-scale applications. In the current study, we summarised key processes affecting DOC into a simple annual-timestep model, and applied this to experimental and long-term monitoring studies in which DOC and acid-base dynamics could be related.

Dissolved organic matter is defined as particles that pass through a 0.45 µm filter (Sleutel et al., 2009), and includes molecules of 100 to 100,000 Da (Aitkenhead-Peterson et al., 2003) with variable C/N ratio and surface charge. The formation and loss of DOC are affected by biological and surface exchange processes. The sorption and flocculation of potentially-dissolved organic carbon (PODOC) is mediated by hydrophobicity, ligand exchange between surface hydroxyl groups and organic acids, electrostatic interactions, and coadsorption and competition with other anions (Tipping, 1990). Several of these processes are influenced by soil solution acidity. At low pH, much low-molecular-weight organic matter stays in the solid phase, flocculated or adsorbed onto larger particles, in particular iron and/or aluminium oxyhydroxides (Sleutel et al., 2009). As pH increases, this organic matter tends to de-flocculate and desorb. In solution, acid groups on DOC partially buffer pH increases (Evans et al., 2008b; Krug and Frink, 1983).

Fluxes of DOC are greater from more organic soils, and correlate well with soil total C/N ratio (Aitkenhead-Peterson et al., 2005; van den Berg et al., 2012). Concentrations of DOC are determined not simply by soil solution acidity but also by the dynamics of soil C. During decomposition, DOC is produced by the action of microorganisms on plant litter and soil organic matter. Decomposition in organic soils is commonly impeded by anaerobic conditions, and may only proceed as far as soluble forms of C. Studies of 14C concentration indicate that much of the DOC in streams (Raymond et al., 2007; Tipping et al., 2010) and in peat pipes (Billett et al., 2012) results from recent inputs of plant-derived C. This recent origin implies that, other factors being equal, DOC concentrations are likely to be correlated with plant productivity. This inference is supported by the conclusion of Larsen et al. (2011a) from a study of Norwegian lakes that a correlation of DOC concentration with temperature was primarily due to increased vegetation cover. In a related study, by far the best predictor of lake DOC concentration among a set of catchment properties that included annual mean temperature, slope, and fractions of bog, forest and arable land, was the normalised-difference vegetation index, which indicates photosynthetic capacity (Larsen et al., 2011b). Evidence that DOC fluxes are correlated more strongly with solar radiation 1-2 months previously than with air or soil temperature (Harrison et al., 2008) also indicates the importance of recently fixed C.
Nitrogen deposition has variable effects on DOC flux. It has been suggested that N pollution will increase DOC flux due to the suppression of phenol oxidase activity by nitrate (DeForest et al., 2004), but no evidence was found for this effect in an experimental study (DeForest et al., 2005). Increased N deposition has been observed to decrease (De Wit et al., 2007), increase (Filep and Rekasi, 2011), or have no net effect on (Emmett et al., 1998; Fernandez and Rustad, 1990; Stuanes and Kjonaas, 1998) DOC flux. None of these studies reported effects on plant productivity, so it is difficult to judge which of these systems was N-limited. Productivity is limited by N supply in many terrestrial ecosystems, since N is energetically expensive to obtain through fixation and easily lost through leaching and gaseous pathways (LeBauer and Treseder, 2008; Vitousek and Howarth, 1991), but at a given site other limitations may predominate such as growing season length (Kerkhoff et al., 2005) or availability of other nutrients (Menge et al., 2012). Increases in plant productivity as a result of chronic pollution with reactive N have however been observed at least in the short term in many forest ecosystems (Bontemps et al., 2011; Hogberg et al., 2006; Lu et al., 2012; Wei et al., 2012) and are likely in other habitats where N has historically been limiting. Where increased N supply increases productivity, there will potentially be an increase in DOC flux, although this also depends on soil and hydrological properties that determine the retention, transport and mineralisation of DOC.

Soils often change considerably in organic matter content, biotic activity and surface chemistry with depth. Mineral soil horizons with large concentrations of iron and/or aluminium oxyhydroxides generally have greater DOC sorption capacity than organic horizons. In a study of Belgian forests, sorption was responsible for substantial retention (67-84%) of DOC entering the mineral soil profile with forest floor leachate (Sleutel et al., 2009). Reductions in S pollution and sulphate concentrations may free up anion exchange sites in lower soil horizons, increasing the sorption of DOC (Borken et al., 2011). Much of the retained organic matter is likely to be mineralised before it can be leached, resulting in lower DOC concentrations in streams than in soil solution. This process also releases mineral N, which may be re-immobilised or taken up by plants, depending on the amount of labile C-rich organic matter and the presence of plant roots within deeper soil layers. These processes can result in considerable decoupling between fluxes of dissolved organic N (DON) and DOC (Kalbitz et al., 2000).

The concentrations of DOC in rivers and lakes are affected by DOC efflux from different landscape elements depending on the flow regime (Laudon et al., 2011). Flow pathways through soil vary with rainfall intensity. During high-flow periods, much of the streamflow derives from near-surface drainage through more organic horizons (Hagedorn et al., 2000), resulting in greater stream DOC concentrations and considerably greater DOC fluxes during storm events (Buffam et al., 2001). Conversely, during periods of low water flow, DOC concentrations in streams are reduced by surface interactions and mineralisation within the mineral soil. As well as affecting flow pathways and (via effects on anaerobiosis) DOC formation, water flux directly affects the solubilisation of DOC since greater volumes of water allow more dissolution of POC. Thus DOC concentrations do not show a strong decline with precipitation (Haaland et al., 2008; van den Berg et al., 2012), as would be expected from simple dilution.

Previous approaches to modelling DOC fluxes (Futter et al., 2007; Jutras et al., 2011; Michalzik et al., 2003; Xu et al., 2012) have most often focused on seasonal and episodic variation in DOC production and in flow pathways through soil layers, and consequently require detailed hydrological and meteorological parameterisation. For modelling long-term changes in DOC flux we assume that the key processes are the production, mineralisation and solubilisation of DOC. A similar approach was taken by Neff and Asner (2001), who based their DOC model on a three-pool soil C model instantiated in four soil layers and with an hourly-timestep hydrology model. In the current study we
propose a much simpler approach to modelling DOC changes using a Model of Acidity Dynamics and Organic Carbon (MADOC), developed by integrating models of: a) plant production and soil total C and N dynamics; b) partitioning of DOC between solid and dissolved phases; and c) acid-base kinetics. The MADOC model simulates the effects on long-term trends of DOC of large-scale ecosystem drivers such as air pollution by N and S. The aim of the study was to determine whether observed changes in soil solution and stream chemistry across a range of experimental and long-term monitoring sites can be simulated using a combination of these relatively simple models.

Methods

Model development

Three annual-timestep models of vegetation and soil dynamics were dynamically integrated to form the MADOC model: N14C (Tipping et al., 2012), VSD (Posch and Reinds, 2009), and a simplified version of DyDOC (Michalzik et al., 2003). A major goal in developing the model was to limit structural detail and number of parameters wherever possible, resulting in a model that is generalisable and widely applicable. The model simulates dynamics within a one dimensional vegetation-soil column and is suitable for simulating experimental plots, and larger-scale areas where spatially-lumped parameters can be used. The integrated model was developed in Fortran90; an executable version is available on request. Data for calibrating the model were obtained from control treatments on experimental N addition sites, and the model was tested against data from acidified and alkalised treatments from these sites, and from long-term monitoring sites.

The VSD model (Posch and Reinds, 2009) was developed as the simplest dynamic model compatible with the computation of critical loads for S and N deposition by simple mass balances (UBA, 2004), and is based on solving equations that describe competition among cations for exchange sites and thus the partitioning of ions between the solution and adsorbed phases. The model was run using Gapon exchange kinetics. Whereas the original model assumed complete nitrification (and thus zero concentration of NH$_4^+$ in soil solution), the version included in MADOC uses the concentrations of NO$_3^-$ and NH$_4^+$ supplied by the N14C model, as described below. A retained fraction of deposited S can be specified to simulate retention of reduced and organic S. A version of VSD without surface exchange processes was used to simulate the chemistry of subsoil solution and of surface waters.

The N14C model (Tipping et al., 2012) simulates C and N dynamics in vegetation and soils, tracking three organic matter pools with mean residence times at 10 °C of 2, 20 and 1000 years. The turnover of these pools is divided between a mineralisation flux (into CO$_2$ or inorganic N) and a proportion becoming low-molecular-weight PDOM. In the version used within MADOC the proportions of C and N turnover were allowed to differ, to represent uncoupling of solution DOC and DON. The year is subdivided into a cold season, when mineralised N is either re-immobilised or leached, and a growing season, when plant uptake can occur before immobilisation or leaching. Litterfall returns C and N to the soil organic matter pool, although a vegetation-type-specific proportion of plant biomass is retained from year to year.

The DyDOC model (Michalzik et al., 2003) simulates the formation, transport and retention of DOC within soil profiles. We adapted the model by simplifying the original three-horizon structure and removing hydrological detail. The simplified model is described below, and parameters are listed in Table 1. A pool of PDOM was defined in terms of stocks of C and of N. The annual change in these pools (Equations 1 and 2) was determined from input fluxes (fixed proportions of overall soil C and N turnover as calculated using the N14C model), mineralisation calculated using a first-order exponential function, and leaching.
where \( C_{pd} \) and \( N_{pd} \) are single pools of potentially-dissolved C and N in g m\(^{-2}\), \( T_c \) and \( T_n \) are the net annual turnovers of C and N in g m\(^{-2}\) yr\(^{-1}\) as calculated by the N14C model, \( k_{inp}^{C} \) and \( k_{inp}^{N} \) are the proportions of these turnovers entering the potentially-dissolved pools, \( k_{min}^{pd} \) is the rate constant for mineralisation of both \( C_{pd} \) and \( N_{pd} \) pools in yr\(^{-1}\), \( W_d \) is the water drainage flux in g m\(^{-2}\) yr\(^{-1}\), and \( C_{DOC} \) and \( C_{DON} \) are concentrations in the soil solution in g g\(^{-1}\). These concentrations were calculated from the stocks of potentially-dissolved C and N, assuming that in the absence of soil the whole stock would be dissolved, resulting in a concentration determined by water mass. Soil reduced this concentration according to soil mass and a pH-dependent coefficient determining partitioning between solid and solution phases (Equations 3 and 4).

\[
\begin{align*}
\text{[3]} & \\
\text{[4]} & \\
\end{align*}
\]

where \( M_W \) is the mass of water (g m\(^{-2}\)), including both annual average water content and annual drainage flux, \( M_s \) is the mass of soil (g m\(^{-2}\)), and \( k_p \) is a partitioning coefficient calculated as the average coefficient for mineral and organic soil, weighted by the thickness of these horizons (Equation 5).

\[
\begin{align*}
\text{[5]} & \\
\end{align*}
\]

where \( k_{Dorg} \) and \( k_{Dmin} \) are partitioning coefficients for organic and mineral soil, and \( L_{org} \) and \( L_{min} \) are the thicknesses in m of the organic and mineral horizons. The partitioning coefficients were dependent on soil solution H\(^+\) activity, and were calculated for organic soil (Equation 6) and mineral soil (Equation 7) using different values for a partition constant.

\[
\begin{align*}
\text{[6]} & \\
\text{[7]} & \\
\end{align*}
\]

where \( k_{Dorg} \) and \( k_{Dmin} \) are the partitioning coefficients for organic and mineral soil, \( \alpha_{org} \) and \( \alpha_{min} \) are the partition constants (m\(^{-1}\) g\(^{-1}\) L mol\(^{-1}\)) for organic and mineral soil, and \( a_{H^+} \) is the soil solution H\(^+\) activity (mol L\(^{-1}\)).

Quantities passing among the component models are illustrated in Figure 1. In the current study, the main drivers of interest were N and S deposition. Nitrogen dynamics in soil and vegetation were simulated using N14C. The original N14C model calculated a flux of DOM, which in the current model was assumed to enter a PDOM as described above. With mineralisation of this potentially-dissolved pool, there was further release of mineral N, which was then leached. The DON flux calculated by MADOC was assumed not to contribute to plant uptake. Total mineral N release as calculated by the N14C and DyDOC models was split between reduced and oxidised forms, using a soil-type-specific constant nitrate proportion, \( P_{nit} \). The VSD model determined ion exchange dynamics according to this supply of ammonium and nitrate, deposition rates of S and other elements, and DOC flux as calculated by DyDOC. A constant proportion, \( P_{sites} \), of the DOC was assumed to be able to form acid anions, i.e. a fixed value for dissociation site density. The value of pH influenced DOC dissolution in the DyDOC model.
The N14C model allows for the adsorption of DOC to mineral surfaces in deeper soil horizons, using a simplified version of the algorithm used for the upper horizons. Surface waters were assumed to have undergone these deeper soil processes, so stream and lake DOC measurements were compared with simulated DOC flux flowing from the deeper soil. Of the DOC flux from the upper horizons, a proportion is assumed to bypass the deeper soil, with the remainder entering the deeper-soil pool. The proportion bypassing the deeper soil pool was assumed to be one for peats and gley soils, and zero for other soils. A temperature-dependent proportion of the deeper-soil pool is mineralised each year, and a proportion leached. In the original N14C model this proportion was fixed, but the rapid changes in UK surface-water DOC concentrations (Monteith and Evans, 2005) suggest that pH changes are also affecting the subsoil sorbed C pool. The dissolution of potentially-dissolved subsoil C was therefore made pH-dependent, using the same partition constant (\(k_{\text{min}}\)) as for shallower mineral soil. The DOC flux from deeper soil was converted to a concentration, based on precipitation surplus, and other solute concentrations were as predicted for topsoil leachate by MADOC. The pH values for the subsoil and surface waters were calculated using instances of a simplified version of VSD that does not include weathering or cation exchange. To avoid the need to seek solutions to simultaneous equilibria, the N14C and DyDOC models used pH values calculated for the previous year.

**Data sources**

An experiment to study the effects of acid anion and base cation deposition on soil solution chemistry was set up in 2007, on British upland moor sites on the Migneint range (52° 59.6’ N, 3° 48.8’W) and in the Peak District (53° 28.3’ N, 1° 54.5’ W) (Evans et al., 2012b). On each site, additions of acidifying solution (\(\text{H}_2\text{SO}_4\)) or alkalisising solution (mainly NaOH, with some \(\text{CaCl}_2\), \(\text{MgCl}_2\) and KCl) were made to both peat and podzol soils, with four replicate plots. Equivalent volumes of rainwater were added to control plots. The trajectories of deposition, including atmospheric and experimental additions, are illustrated in Figure 2. The current study related MADOC predictions of yearly mean soil solution chemistry to yearly mean soil solution measurements for each of the treatments. Soil solution was sampled using suction lysimeters at 5-10 cm depth, and the simulations were run for soil above 10 cm depth. The soil was organic to at least the depth of the samplers in both the peat and the podzol treatments. Following calibration of the MADOC model using the control treatments of the experimental study (see below), the performance of the model against an independent dataset was evaluated, with minimal additional calibration. This dataset was obtained from the Acid Waters Monitoring Network (AWMN), a set of 22 lakes and streams in upland areas of the UK that has been monitored since 1988 (18 sites) or 1990-1991 (four sites) (Evans et al., 2010b; Monteith and Evans, 2005; Patrick et al., 1991).

Present-day S and mineral N deposition estimates for all sites were obtained using CBED model estimates for the years 2006-2008 (Smith et al., 2000). The history of depositions at each site after 1910 was estimated by scaling to historic sequences obtained using the FRAME model (Dore et al., 2009). Following Tipping et al. (2012), pre-1850 N deposition was assumed to be zero, with ecosystem N during this period supplied entirely from \(\text{N}_2\) fixation at a rate of 0.3 g m\(^{-2}\) yr\(^{-1}\). Atmospheric N deposition during the 1850-1910 period was assumed to increase linearly from zero to the rate calculated by the deposition model for 1910.

Fixed inputs for the MADOC model are listed in Table 1, and site-specific inputs are listed in Table 2. Organic acids were assumed to be triprotic, and mean values from a study by Oulehle et al. (in press) were used for dissociation constants for the three protons and for \(P_{\text{site}}\). The partial pressure of CO\(_2\) in solution in soil was assumed to be 0.037 atm, i.e. 100 times atmospheric concentration, and to decline in streams to twice atmospheric concentration, and in lakes to atmospheric concentration. Net plant uptake was assumed to be zero, since there was little or no harvest of nutrient elements.
from the modelled catchments. Weathering of N, chloride (Cl\textsuperscript{-}), sulphate, phosphate and sodium were assumed to be zero. The temperature range (difference between growing season and non-growing season in mean temperature) was set to 7 °C for all sites. Values for several MADOC inputs which are difficult to ascertain experimentally were obtained by calibrating the model to observations, as described below. Values for other input parameters for the N14C submodel were as described in (Tipping et al., 2012).

**Calibration of model parameters**

The model was calibrated to measurements from control treatments on the experimental sites, by minimising the sum of absolute differences using the Nelder-Mead simplex method (Nelder and Mead, 1965). For simultaneous calibrations to more than one type of measurement, the error for each was weighted by the inverse of the mean measured value. Simulations began 12000 years before present, to allow organic matter pools to stabilise. Parameter values were fitted in sequence. Firstly, Cl\textsuperscript{-} deposition as estimated for each of the two sites by the CBED model was adjusted to minimise error in soil solution Cl\textsuperscript{-}, assuming that Cl\textsuperscript{-} is fully conservative in the soil. Soil solution Cl\textsuperscript{-} provides a proxy measurement of the deposition input which is more accurate than modelled deposition estimates. The marine component of inputs of other ions was adjusted in the same ratio. Next, the sodium (Na\textsuperscript{+}) weathering rate was adjusted for each site and soil type to minimise error in soil solution Na\textsuperscript{+}. The VSD parameter f\textsubscript{Sset}, i.e. the proportion of S deposition that is immobilised and does not contribute to SO\textsubscript{4}\textsuperscript{2-} leaching, was then adjusted for each site and soil type to minimise error in soil solution SO\textsubscript{4}\textsuperscript{2-}. Next, the aluminium (Al\textsuperscript{3+}) equilibrium constants for each site and soil type were adjusted to minimise error in soil solution total inorganic Al\textsuperscript{3+}. VSD considers exchange of calcium (Ca\textsuperscript{2+}), magnesium (Mg\textsuperscript{2+}) and potassium (K\textsuperscript{+}) together, so the total weathering rate of these cations for each site and soil type was adjusted to minimise error in total concentration of Ca\textsuperscript{2+}, Mg\textsuperscript{2+} and K\textsuperscript{+}. Once the simulations had been constrained to match these major ion fluxes as closely as possible given sampling error in the measurements, model parameters governing organic matter dynamics were adjusted. The k\textsubscript{ingapd} parameter has a major influence on the long-term development of soil C and N pools, and was adjusted for each site and soil type to minimise error in soil total C/N ratio. To minimise error in DOC flux, firstly k\textsubscript{minpd} and \textalpha\textsubscript{org} were adjusted using single values for all soils and sites, and then the k\textsubscript{ingada} parameter was adjusted separately for each site and soil type. The DOC site density was then adjusted separately for each site and soil type to minimise error in pH.

A similar calibration procedure was followed for the AWMN sites, fitting Cl\textsuperscript{-} deposition to minimise error in surface water Cl\textsuperscript{-}, Na\textsuperscript{+} weathering to minimise error in surface water Na\textsuperscript{+}, and f\textsubscript{Sset} to minimise error in surface water SO\textsubscript{4}\textsuperscript{2-}. Base cation fluxes in surface water include subsoil base cation weathering. To avoid unrealistically high Ca\textsuperscript{2+} concentrations in surface soil, published values for surface soil Ca\textsuperscript{2+} weathering were used (Aherne et al., 2007) and the error in surface water Ca\textsuperscript{2+} was minimised by adjusting subsoil Ca\textsuperscript{2+} weathering. Parameters governing DOM dynamics were not calibrated separately for the AWMN sites, to determine whether the values established at the experimental sites are applicable more widely. The means of previously fitted values of k\textsubscript{ingapd}, k\textsubscript{ingadn} and P\textsubscript{sset} for peat and podsol were used, and the area proportions of peat and podsol within the lake or stream catchment were used to derive a weighted mean value for the catchment for these parameters.

The accuracy of simulated data was assessed in relation to observations using the Nash-Sutcliffe coefficient of determination (NSCD), calculated as (1 – residual variance/variance of measured data) (Nash and Sutcliffe, 1970). For the AWMN sites, the NSCD was calculated using mean observations and mean simulated values for the study period.
The sensitivity of predicted DOC fluxes to variation in deposition fluxes of S and N, and variation in mean annual temperature and precipitation surplus, was explored for an example site, the control treatment on Migneint podzol. Simulations were carried out using historic and projected deposition fluxes, as above, until 2020. Different rates of S and N deposition, or different combinations of mean annual temperature and precipitation surplus, were then applied and kept constant until 2100. The DOC flux, pH and NPP were assessed in the year following the change (2021) and in 2100.

The MADOC model was developed to use a relatively small parameter set, for model parsimony and to facilitate upscaling. The MADOC model uses many of the same inputs as VSD, and a regional application to British peat bogs was carried out based on data collated by the UK National Focal Centre for critical loads mapping, as described in Evans et al. (2012a). Spatial data were derived under the Defra Critical Loads and Dynamic Modelling project, http://cldm.defra.gov.uk/.

Results

Simulated responses of pH and DOC flux corresponded to the measured increases in these quantities in response to acidification and decreases in response to alkalinization (Figure 3). Some instability was observed in predicted trajectories of pH and DOC in the alkalised treatments, due to the simplification whereby DOC solubility in the model is determined by pH in the preceding year. This instability was only observed following an abrupt increase in pH. The model predicted DOC fluxes across all measurement years and treatments reasonably well (Figure 4; NSCD = 0.61). Values for pH were predicted with less accuracy (Figure 4; NSCD = 0.24) but the overall trend of experimental responses was reproduced.

Model runs for the AWMN surface waters dataset showed reasonable correspondence between MADOC predictions and measured trends in pH and in DOC flux, although there was some inaccuracy in predicted mean values, as illustrated by time-series plots of observations and predictions from an example site (Figure 5). After calibration of Cl deposition rate, Ca weathering rate and the Al equilibrium constant for each site, the MADOC model reproduced measured Cl⁻, Al³⁺ and total base cation concentrations (not shown). Without further calibration, values were predicted with limited accuracy for pH (NSCD = 0.47, Figure 6a) and better accuracy for DOC flux (NSCD = 0.11, Figure 6b). The upward trends in DOC and pH at many sites were reproduced (Figure 6c, 6d), although in most cases the model over-predicted increases in pH, and under-predicted increases in DOC.

Responses of the model to different N and S deposition rates applied from 2020 are shown in Figure 7. Soil solution pH responded as expected, showing an effect of S in the year immediately following application of the new loading. Initially, N loading did not affect pH, since all of the applied N was either immobilised or taken up by plants, and was therefore not leached. After 80 years, greater N deposition rates gave rise to N-saturation, more N leaching, and somewhat lower pH. The DOC flux initially responded only to changes in S deposition, with more S giving lower pH and decreased DOC flux. However, after 80 years the effects of N deposition are also evident, and the cumulative effects of N on net primary productivity (NPP) and therefore the release of DOC from relatively young organic material led to greater DOC fluxes at higher N loadings.

Responses of the model to changes in precipitation surplus and mean annual temperature, applied from 2020-2100, showed only minor differences in initial response and response after 80 years (Figure 8). There was a clear increase in NPP with mean annual temperature, but little effect of precipitation surplus on NPP. The DOC flux increased with temperature, principally as a result of greater NPP at higher temperatures, and also increased with precipitation surplus, since a greater
The example maps (Figure 9) illustrate the spatial variation in pH and DOC across UK peat bogs, as simulated by the MADOC model. Larger DOC fluxes were simulated in peat towards the south and east than in the north and west, and coincided with lower simulated pH. Areas with low pH and large DOC fluxes were associated with large rates of N and also S deposition. A simple interpretation that DOC flux is controlled within the model by productivity stimulation rather than by acid suppression would be incorrect, however, since areas with high current S deposition also historically received very large S inputs and have therefore recovered from acidification more strongly. The simulations suggest that the spatial pattern of DOC in the UK is determined by both pH increase with reductions in S deposition, and by productivity stimulation by ongoing N pollution.

### Discussion

Increases in pH and DOC in alkalised experimental treatments, and decreases in acidified treatments, were reproduced by the MADOC model. The changes were largely due to increased solubilisation of PDOC as a result of higher pH, reflecting observations in field studies which have attributed DOC increase to recovery from acidification (Haaland et al., 2010; Monteith et al., 2007; SanClements et al., 2012). The buffering effect of DOC on pH was well represented. The model also reproduced changes in pH and DOC in the independent dataset from the AWMN with minimal extra calibration. In contrast to the soil solution sampled in the experimental treatments, the AWMN samples were obtained from stream and lake samples, and hence many had greater pH and base cation concentrations due to the influence of basal flow paths through deeper mineral soil. By calibrating the aluminium equilibrium constant and base cation weathering rates, stream and lake base cation concentrations were successfully reproduced. Without further calibration, the predicted pH and DOC fluxes for the independent dataset matched observations reasonably well (Figure 6). Further calibration could be used to increase accuracy – for example, fitting site-specific values for \( k_{\text{diss}} \) resulted in considerable improvements in prediction accuracy for pH (\( NSCD = 0.01 \)) and DOC flux (\( NSCD = 0.64 \)) (data not shown). These results give some confidence that the MADOC model can simulate DOC and pH change in a range of environments.

The observed lack of pH response to experimental acid and alkali additions on the Migneint peat site (Figure 3a) was not simulated by the model, and was the main cause of inaccuracy in overall performance (Figure 4a). This lack of response may have been due to the dilution of treatments by lateral water movement at this very wet site, where water tables frequently come close to the surface, above the zone in which soil solution samplers were located. This interpretation is supported by small observed changes in Na\(^+\) concentrations in the alkaline (NaOH) addition treatments on this site (data not shown). On this basis, we conclude that poor performance of the model at this site was at least partially explained by issues relating to the experimental site itself.

When applied at catchment scale the model performed less well, in particular overestimating the rate of pH change and underestimating the rate of DOC change over the approximately 20 year period. This suggests that the simulations should have included a greater effect of pH increase on DOC dissolution from mineral soil layers, which would have buffered the simulated pH increase. Complexation of DOC with aluminium in the mineral soil at lower pH, which was not simulated, may also partially explain the greater apparent sensitivity of DOC concentrations in surface waters to changes in sulphur deposition, compared to those surface organic soil horizons, and thus the larger observed versus modelled rate of increase of surface water DOC with recovery from acidification (Evans et al., 2012b).
Simulated DOC fluxes proved sensitive to several factors that have been highlighted by previous authors, notably soil solution pH, but were also strongly affected by plant productivity and the resultant increase in soil organic matter in the fast-turnover pool. The main processes governing DOC concentration within the model are illustrated by sensitivity plots (Figure 7, Figure 8). In the year following a change in simulated N and S load, effects on DOC flux are dominated by pH change on the solubility of the pre-existing PDOM pool, and hence DOC flux is correlated with changes to the S load rather than to the N load. However, after maintaining simulated application rates for 80 years, changes in simulated DOC flux were also strongly affected by the effects of N deposition on plant productivity. The DOC flux is simulated as a constant proportion of total organic matter decomposition, most of which is of the active organic matter pool that is derived from plant production in the previous year. This matches observations that much DOC is of recent origin (Evans et al., 2007; Raymond et al., 2007; Tipping et al., 2010).

The simulated productivity increase due to release from N limitation is realistic, although whether this increase will be sustained is questionable. Limitation by N is widespread (LeBauer and Treseder, 2008) and so an initial increase in productivity with more N deposition is likely. Other limitations to plant growth may then start to dominate, such as temperature, drought, water saturation or deficiencies in other nutrients (Braun et al., 2010). Nitrogen can be obtained from the atmosphere, so the supply of phosphorus and other elements obtained from mineral weathering may be a more fundamental long-term constraint (Menge et al., 2012). However, increased N availability can increase the supply of other plant nutrients (Olander and Vitousek, 2000; Rowe et al., 2008) leading to eventual nutrient element co-limitation in many ecosystems (Elser et al., 2007; Vitousek et al., 2010). In a review of the effects on DOC fluxes of experimental N additions, Evans et al. (2008a) concluded that direct effects of N on plant growth and organic matter cycling were often obscured by pH changes resulting from the ionic form of the N applied and counter-ion additions. In a gradient study, (Bragazza et al., 2006) concluded that DOC concentrations increased with N deposition, noting that N deposition can increase enzyme fluxes, increase plant productivity, and drive changes in plant species composition towards more easily-decomposed species. The predicted increase in DOC flux with N deposition corresponds to this trend, and suggests that effects of recovery from acidification on DOC solubility may not be acting in isolation, but rather are reinforcing a more gradual long-term increase in DOC linked to rising productivity. Further research is needed to test this hypothesis.

Oulehle et al. (in press) proposed a switch in determination of DOC fluxes from ‘solubility control’ to ‘supply control’. Supply control implies that a change in pH and therefore DOC solubility will change the PDOC pool, eventually causing DOC fluxes to become more similar to fluxes before the pH change. Increased pH will increase PDOC dissolution, depleting the PDOC pool, whereas decreased pH will allow a larger PDOC pool to build up and eventually increase DOC fluxes again. However, retained PDOC is susceptible to mineralisation, so DOC fluxes are unlikely to revert entirely to values observed before the pH change. In the simulations presented, changes to DOC fluxes due to acidification or alkalisation were maintained, with only a small tendency for concentrations to revert towards the values in the control treatment. A given increase in DOC flux may be explained equally well by a PDOC pool that turns over slowly or rapidly, although these alternatives affect the speed and extent with which the DOC flux returns to its previous value following a change in pH (Figure 10). A PDOC pool with a large turnover rate results in more sustained increase in DOC as a result of pH increase, whereas if input and output PDOC fluxes are smaller, the rise is more short-lived. The experimental dataset has not run for long enough to distinguish these effects, and we are uncertain as to which type of response prevails. Increases in DOC with recovery from acidification seem likely to have been sustained, given that they are noticeable in long-term monitoring datasets and across sites with distinct deposition histories (Evans et al., 2005). However, many of these observations have taken place against a background of continuously declining S deposition, so it is not certain that concentrations will remain high once S inputs have stabilised.
The predicted increase in DOC flux with precipitation surplus (Figure 8) corresponded to observations that DOC flux is correlated with water flux (Buckingham et al., 2008) and that DOC concentrations are less strongly reduced by precipitation than would be suggested by a simple dilution model (Haaland et al., 2008; van den Berg et al., 2012). Although the increase in simulated DOC flux was not proportionate to the increase in precipitation surplus, greater volumes of water increased the partitioning of PDOC into the dissolved phase. Simulated DOC fluxes increased with temperature, mainly because higher temperatures stimulated organic matter turnover and N mineralisation. This effect seems likely to be masked by continuing N pollution in many ecosystems.

The simulated effects and interactions may be formulated as hypotheses generated by the model:

**H1**: Spatial and/or temporal patterns of DOC increase are related to patterns of plant productivity increase as well as to recovery from acidification.

**H2**: The cumulative effects of fertilisation by reactive N deposition, and reduced mineralisation of PDOC resulting from more rapid solubilisation and leaching, will cause a sustained increase in DOC even after soil pH has stabilised.

These hypotheses could be tested against survey and long-term monitoring datasets, although controlled field or lab experiments may be necessary to separate the effects of N and S pollution.

Predictive representations of DOC dynamics are essential for closing C budgets in ecosystem models and understanding interactions between pollutant deposition, changes in C stock, water quality and climate change. Despite the existence of significant feedbacks between pH and DOC flux, and between NPP and N flux, a relatively simple integrated model proved capable of reproducing the effects of key drivers as observed in experiments and surveys. The study illustrates the value of constraining the overall complexity and parameter requirement of an integrated model by using simple components. As well as predicting changes to DOC and pH, the MADOC model can be used to explore the effects of multiple pollutant and climate drivers on multiple endpoints including soil total C and N, plant-available N, plant productivity and nitrate leaching, and so will be useful for analysing a range of policy scenarios.

### Acknowledgements

The development of the MADOC model was funded by the Department for Environment, Food and Rural Affairs of the UK under the project “Critical loads and dynamic modelling for acidity and nitrogen” [http://cldm.defra.gov.uk/](http://cldm.defra.gov.uk/), by the European Union under the ECLAIRE project, and by the Natural Environment Research Council under the EHFI project. We are grateful to Rachel Helliwell of the James Hutton Institute for providing AWMN data.

### References


Hongve, D., Riise, G., Kristiansen, J.F., 2004. Increased colour and organic acid concentrations in Norwegian forest lakes and drinking water - a result of increased precipitation? Aquatic Sciences 66, 231-238.


UABA, 2004. Manual on methodologies and criteria for modelling and mapping critical loads & levels
and air pollution effects, risks and trends. Umwelt Bundes Amt (Federal Environment Agency), Berlin., p. 235.

concentrations in UK soils and the influence of soil, vegetation type and seasonality. Science of
the Total Environment 427, 269-276.

Biogeochemistry 13, 87-115.

Vitousek, P.M., Porder, S., Houlton, B.Z., Chadwick, O.A., 2010. Terrestrial phosphorus limitation:


matter export from a forested watershed. Water Resources Research 48, W05519,

750 751 752 753 754 755 756 757 758 759 760 761 762 763 764 765 766 767
### Table 1. Fixed input values for the MADOC model.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{\text{minpd}}$</td>
<td>Proportion of potential DOC mineralised, yr$^{-1}$</td>
<td>0.432 $^a$</td>
</tr>
<tr>
<td>$\alpha_{\text{org}}$</td>
<td>DOC sorption constant in organic soil, m$^3$ g$^{-1}$ L mol$^{-1}$</td>
<td>$2.20 \times 10^6$ $^a$</td>
</tr>
<tr>
<td>$\alpha_{\text{min}}$</td>
<td>DOC sorption constant in mineral soil, m$^3$ g$^{-1}$ L mol$^{-1}$</td>
<td>$7.62 \times 10^6$ $^a$</td>
</tr>
<tr>
<td>$pK_{\text{par(1)}}$</td>
<td>1$^{\text{st}}$ dissociation constant for triprotic organic acids</td>
<td>3.5 $^b$</td>
</tr>
<tr>
<td>$pK_{\text{par(2)}}$</td>
<td>2$^{\text{nd}}$ dissociation constant for triprotic organic acids</td>
<td>4.4 $^b$</td>
</tr>
<tr>
<td>$pK_{\text{par(3)}}$</td>
<td>3$^{\text{rd}}$ dissociation constant for triprotic organic acids</td>
<td>5.5 $^b$</td>
</tr>
<tr>
<td>$K_{\text{HBc}}$</td>
<td>selectivity constant for H-Bc exchange</td>
<td>199.5 $^c$</td>
</tr>
<tr>
<td>$\text{exp}_{\text{Al}}$</td>
<td>aluminium equilibrium exponent</td>
<td>1.85 $^d$</td>
</tr>
<tr>
<td>$k_{\text{inpdN}}$</td>
<td>Proportion of N turnover entering potentially-dissolved pool</td>
<td>0.0274 $^a$</td>
</tr>
</tbody>
</table>

$^a$ fitted; $^b$ (Oulehle et al., in press); $^c$ (Hall et al., 2003); $^d$ (UBA, 2004).
Table 2. Site-specific inputs for the MADOC model. Values used for the experimental sites: Migneint peat (MPT); Migneint podzol (MPZ); Peak District peat (PPT) and Peak District podzol (PPZ), and the ranges of values used for Acid Waters Monitoring Network sites (AWMN) and for UK peat bog (UK peat) are shown.

<table>
<thead>
<tr>
<th>Input</th>
<th>Description</th>
<th>MPT</th>
<th>MPZ</th>
<th>PPT</th>
<th>PPZ</th>
<th>AWMN</th>
<th>UK peat</th>
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<tbody>
<tr>
<td>$k_{elev}$</td>
<td>aluminum equilibrium constant</td>
<td>0.059</td>
<td>0.295</td>
<td>0.531</td>
<td>0.567</td>
<td>0.16–54.5</td>
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<tr>
<td>$k_{impDC}$</td>
<td>Proportion of C turnover entering potentially-dissolved pool</td>
<td>0.347</td>
<td>0.493</td>
<td>0.825</td>
<td>0.472</td>
<td>0.534</td>
<td>0.586 b</td>
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<tr>
<td>$p_{diss}$</td>
<td>Dissociable protons per mol DOC, $\text{mol}^{-1}$</td>
<td>0.080</td>
<td>0.076</td>
<td>0.191</td>
<td>0.118</td>
<td>0.116 c</td>
<td>0.136 b</td>
</tr>
<tr>
<td>$p_{W}$</td>
<td>Proportion of leachate from topsoil that does not interact with subsoil weathering rate for Na, meq m$^{-2}$ yr$^{-1}$</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0.2</td>
<td>1.8–182 a</td>
<td>1.8 a</td>
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<tr>
<td>$W_{Ca}$</td>
<td>topsoil weathering rate for Ca, meq m$^{-2}$ yr$^{-1}$</td>
<td>264 a</td>
<td>786 a</td>
<td>271 a</td>
<td>202 a</td>
<td>127–383 a</td>
<td>268 b</td>
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<tr>
<td>$W_{Ca,b}$</td>
<td>subsoil weathering rate for Ca, meq m$^{-2}$ yr$^{-1}$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.297 a</td>
<td>-</td>
<td>-</td>
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<td>$T_{org}$</td>
<td>thickness of organic soil horizon, m</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.02–0.35 h</td>
<td>0.5</td>
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<tr>
<td>$T_{min}$</td>
<td>thickness of mineral soil horizon, m</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0–0.29 h</td>
<td>0</td>
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<tr>
<td>PPTN</td>
<td>annual precipitation, m</td>
<td>2.20 i</td>
<td>2.20 i</td>
<td>1.20 j</td>
<td>1.20 j</td>
<td>852–3820 h</td>
<td>548–3792 i</td>
</tr>
<tr>
<td>$W_{a}$</td>
<td>precipitation surplus or drainage flux, m yr$^{-1}$</td>
<td>1.99 j</td>
<td>1.99 j</td>
<td>0.95 j</td>
<td>0.95 j</td>
<td>0.40–3.47 h</td>
<td>0.12–3.62 j</td>
</tr>
<tr>
<td>$BD$</td>
<td>soil field bulk density, kg dry mass L$^{-1}$</td>
<td>0.08 a</td>
<td>0.34 a</td>
<td>0.16 a</td>
<td>0.23 a</td>
<td>0.19–1.22</td>
<td>0.16–0.22 a</td>
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<tr>
<td>$theta$</td>
<td>average annual volumetric water content, m$^3$ L$^{-1}$</td>
<td>0.91 h</td>
<td>0.66 a</td>
<td>0.86 a</td>
<td>0.71 a</td>
<td>0.78 c</td>
<td>0.88 a</td>
</tr>
<tr>
<td>$P_{nit}$</td>
<td>nitrate proportion of (nitrate + ammonium)</td>
<td>0.22 a</td>
<td>0.73 a</td>
<td>0.16 a</td>
<td>0.66 a</td>
<td>0.07–0.93 h</td>
<td>0.19 a</td>
</tr>
<tr>
<td>$MAT$</td>
<td>mean annual temperature, °C</td>
<td>8.1 a</td>
<td>8.1 a</td>
<td>7.8 a</td>
<td>7.8 a</td>
<td>3.3–10.0 h</td>
<td>7.2 a</td>
</tr>
<tr>
<td>Planttype</td>
<td>1=Broadleaf, 2=Conifer, 3=Herbs, 4=Shrub</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>2–4 h</td>
<td>4</td>
</tr>
<tr>
<td>$CEC$</td>
<td>cation exchange capacity, meq kg$^{-1}$</td>
<td>621 j</td>
<td>83 j</td>
<td>621 j</td>
<td>83 j</td>
<td>154–997 h</td>
<td>621 a</td>
</tr>
<tr>
<td>$f_{org}$</td>
<td>proportion of S deposition retained</td>
<td>0.49 a</td>
<td>0 a</td>
<td>0 a</td>
<td>0 a</td>
<td>0 a</td>
<td>0.69 a</td>
</tr>
<tr>
<td>$K_{sC}$</td>
<td>selectivity constant for Al-Bc exchange</td>
<td>8.7 j</td>
<td>6.3 j</td>
<td>8.7 j</td>
<td>6.3 j</td>
<td>7.5 c</td>
<td>8.7 a</td>
</tr>
</tbody>
</table>

a fitted; b mean of values fitted for experimental peat sites; c mean of values fitted for all experimental sites; d mean weighted by areas of soil types in catchments, Rachel Helliwell pers. com.; e UK NFC values, based on soil and vegetation type (Evans et al., 2004); f Aherne et al., 2007; g (Evans et al., 2010a); h (Monteith and Shilland, 2007); i Standard-period Average Annual Rainfall 1961-1990 (SAAR6190) provided by UK Met Office; j (Hall et al., 2003); k mean of AWMN sites.
Figure captions

Figure 1. Model of Acidity Dynamics and Organic Carbon (MADOC): structure in terms of component models (N14C, VSD and DyDOC) and quantities passed among these. DOC = Dissolved Organic Carbon.

Figure 2. Trajectories of deposition rates of: a) total reactive nitrogen, g N m\(^{-2}\) yr\(^{-1}\); b) total sulphate, meq(-) m\(^{-2}\) yr\(^{-1}\); c) total chloride, meq(-) m\(^{-2}\) yr\(^{-1}\); and d) total base cations (Ca, Mg, K and Na), meq(+) m\(^{-2}\) yr\(^{-1}\), on control (Con), acidified (Acid) and alkalised (Alk) treatments, on peat and podzol (Pod) on the Migneint (Mig) and Peak District (Peak) experimental sites.

Figure 3. Observations (symbols) and predicted trajectories of change (lines) in pH and dissolved organic carbon (g C leached m\(^{-2}\) yr\(^{-1}\)) following additions from 2008 of rainwater (“Control”; ANC -188 meq m\(^{-2}\) yr\(^{-1}\) in 2010), alkalising solution (ANC +258 meq m\(^{-2}\) yr\(^{-1}\) in 2010), and acidifying solution (ANC -396 meq m\(^{-2}\) yr\(^{-1}\) in 2010) to two soil types on each of two sites: a) Migneint peat; b) Migneint podzol; c) Peak District peat; d) Peak District podzol. Details of the experiment are given in Evans et al. (2012b).

Figure 4. Comparison of annual measurements 2008-1011 on two experimental sites with values predicted by MADOC for: a) pH; and b) dissolved organic carbon (g C leached m\(^{-2}\) yr\(^{-1}\)) in control (triangles; “Con”), acidified (squares; “Acid”) and alkalised (circles; “Alk”) treatments, on each of two soil types: peat (filled shapes) and podzol (outline shapes; “Pod”). The model was fitted to data from the control treatments. Equivalence (1:1) plots are shown as dotted lines.

Figure 5. Observed (dots) and predicted (lines) values for: a) pH and b) DOC at an example Acid Waters Monitoring Network site (Dargall Lane).

Figure 6. Comparisons of mean measured values with mean MADOC predictions for the period 1988-2010, across all Acid Waters Monitoring Network sites: a) pH; b) dissolved organic carbon (DOC) flux, g C m\(^{-2}\) yr\(^{-1}\); and comparisons of observed with predicted rate of change for the period 1988-2010: c) pH, pH units yr\(^{-1}\); d) DOC flux, g C m\(^{-2}\) yr\(^{-1}\). Equivalence (1:1) lines are also shown.

Figure 7. Sensitivity to different combinations of N and S deposition (during the period 2020-2100), of a range of modelled chemical variables: a) pH; b) dissolved organic carbon, g C m\(^{-2}\) yr\(^{-1}\); and c) net primary productivity, g C m\(^{-2}\) yr\(^{-1}\). Outputs shown here were simulated by the MADOC model for the Migneint Podzol site (control treatment), in 2021 (top row) and in 2100 (bottom row).

Figure 8. Sensitivity to different combinations (during the period 2020-2100) of mean annual temperature and precipitation surplus, of a range of modelled chemical variables: a) pH; b) dissolved organic carbon (DOC); c) dissolved organic nitrogen; and d) net primary production. Outputs shown here were simulated by the MADOC model for the Migneint Podzol site (control treatment), in 2021 (top row) and in 2100 (bottom row).

Figure 9. UK peat bogs: spatial distributions in 2007 of: a) S deposition; b) N deposition, and of predictions by the MADOC model of: c) pH; and d) dissolved organic carbon flux, g C m\(^{-2}\) yr\(^{-1}\).

Figure 10. Alternative future trajectories of DOC flux following an increase in response to a rise in pH, assuming that turnover of the PDOC pool is rapid (solid line) medium (dashed line) or slow (dotted line), as a result of differences in the proportion of decomposition that becomes PDOC ($k_{inpdc}$) and in the proportion of PDOC mineralised per year ($k_{minpd}$).
Figures

Figure 1.

Organic matter sorption (DyDOC_lite)
Figure 2.
Figure 3.

- **Migneint peat**
- **Migneint podzol**
- **Peak District peat**
- **Peak District podzol**

<table>
<thead>
<tr>
<th>pH</th>
<th>DOC g m⁻² y⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>▲</td>
<td>▲</td>
</tr>
</tbody>
</table>

Legend:
- Acid
- Alkaline
- Control

2000 - 2020
Figure 4.

(a) Predicted pH vs. Measured pH

(b) Predicted DOC g m\(^{-2}\) y\(^{-1}\) vs. Measured DOC g m\(^{-2}\) y\(^{-1}\)

- **Peat Con**
- **Peat Acid**
- **Peat Alk**
- **Pod Con**
- **Pod Acid**
- **Pod Alk**
Figure 5.

(a) pH over time from 1980 to 2020.

(b) DOC concentration in g m⁻² y⁻¹ from 1980 to 2020.
Figure 6.

(a) Simulated pH vs Observed pH

(b) Simulated DOC vs Observed DOC g m⁻² y⁻¹

(c) Simulated pH (slope of change 88-10) vs Observed pH (slope of change 88-10)

(d) Simulated DOC (slope of change 88-10) vs Observed DOC (slope of change 88-10)
Figure 7.

a) pH

2021

b) DOC

2100

NPP
Figure 8.

2021

a) pH

b) DOC

c) NPP

2100

Precipitation surplus m\(^{-1}\)

Mean temperature °C
Figure 9.
Figure 10.

![Graph showing DOC g m⁻² y⁻¹ over time with different curves labeled with values for k_{input} and k_{min}]

- k_{input} = 0.89, k_{min} = 0.62
- k_{input} = 0.49, k_{min} = 0.43
- k_{input} = 0.19, k_{min} = 0.05

X-axis: Year (1990 to 2050)
Y-axis: DOC g m⁻² y⁻¹