Increased dissolved organic carbon concentrations in peat-fed UK water supplies under future climate and sulfate deposition scenarios

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Key Points:

- Mean annual DOC concentrations in nine UK peatland rivers will increase in the future, by as much as 53 % for the highest emissions scenario.
- Large increases in mean DOC concentrations are projected in future autumn and winter, periods when DOC concentrations are already high.
- Large decreases in mean discharge are projected for April to September, periods when discharge is already low.

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Abstract

Peatlands are globally-important terrestrial carbon stores as well as regional sources of potable water supply. Water draining from peatlands is rich in dissolved organic carbon (DOC), which can be problematic for water treatment. However, it is unclear how future climate and sulfate deposition changes may impact DOC in peatland-derived potable water. The United Kingdom (UK) is a global hotspot that consumes 79 % of all potable water derived directly from peatlands. Here, a physically-based hydrological model and a biogeochemical organic carbon model were used to predict discharge and DOC concentration in nine hotspots of peatland-derived potable water use in the UK under a range of 21st-century climate and sulfate-deposition scenarios. These nine catchments supply 72 % of all peatland-derived water consumed in the UK, and 57 % of the global total, equivalent to the total domestic consumption of over 14 million people. Our simulations indicate that annual discharges will decrease, and that mean annual DOC concentrations will increase under all future scenarios (by as much as 53.4 % annually for the highest emissions scenario) in all catchments. Large increases (by as much as a factor of 1.6) in DOC concentration in the 2090s over the baseline period are projected for autumn and winter, seasons when DOC concentrations are already high in the baseline datasets such that water treatment works often reach their capacity to cope. The total DOC flux is largely insensitive to future climate change because the projected increase in DOC concentration is mostly counterbalanced by the projected decrease in discharge.

Plain Language Summary

Peatlands are important sources of potable water in some parts of the world. The UK is a particular hotspot and consumes around 79 % of all drinking water provided by peatlands globally. Water draining from peatlands is rich in dissolved organic carbon (DOC). DOC from peatlands represents an important component of the global carbon cycle and is problematic for water treatment. Using physically-based hydrological and organic carbon models combined with future climate and sulfate deposition scenarios for the UK, we demonstrate that river DOC concentrations are likely to increase under all future scenarios, particularly in autumn and early winter. These changes will create problems for water treatment because many water treatment plants that remove DOC already reach capacity during these seasons. Furthermore, large decreases in river discharge are projected in future summers for these important catchments, creating additional pressure for UK water resources.

Keywords: Dissolved organic carbon (DOC); Peatland; Drinking water; Climate change; Sulfate deposition; United Kingdom

1 Introduction

Peatlands are organic-rich wetlands formed from poorly decomposed plant detritus. They cover approximately 2.84 % of the global land surface (Xu et al., 2018b), yet hold more than 600 gigatons of carbon, at least a sixth of all global soil carbon (Page et al., 2011; Yu, 2012). As large, concentrated stores of carbon, peatlands also are key sources of concentrated dissolved organic carbon (DOC) that can be flushed out of the system into water courses (Freeman et al., 2004). The export of DOC from peatlands is already an important component of the carbon cycle (Holden, 2005; Limpens et al., 2008) and may become more important in the future under environmental change.

DOC is operationally defined as the fraction of total organic carbon that can pass through a 0.45 µm vacuum filter. DOC is a complex mixture of low and high molecular weight compounds that originate from vegetation, litter, soil leachates, plant root exudates, and microbial enzymes and biomass (Guggenberger & Zech, 1994; Thurman, 2012). The removal of DOC is a major component of potable water treatment, and can be particularly important

downstream from peat-dominated catchments (Martin-Ortega et al., 2014; Ritson et al., 2016; Ritson et al., 2014; Whitehead et al., 2006). While DOC colors the water (Worrall et al., 2003), leading to low aesthetic quality, it does not pose a particularly strong health risk in itself. However, potentially carcinogenic trihalomethanes and haloacetic acids are formed as by-products when DOC-rich waters are disinfected by chlorine treatment (Chow et al., 2003; Lavonen et al., 2013; Rook, 1974). The concentrations of these by-products in drinking water are strictly regulated in most countries and so removal of DOC is required before disinfection, usually via an intensive treatment that requires high amounts of energy and chemical dosage.

Changes in climate and atmospheric acid deposition have been shown to be key factors behind increasing DOC concentrations in waters flowing from peatlands in Northern Europe and North America in the past few decades (de Wit et al., 2007; Eimers et al., 2007; Erlandsson et al., 2008; Evans et al., 2006; Freeman et al., 2004; Worrall & Burt, 2004). Biological and physicochemical processes which are affected by temperature, water availability and atmospheric acid deposition together control the production of DOC, while hydrological processes primarily govern export (Evans et al., 2006). In order for DOC to enter water bodies, the organic matter must be first solubilized by physicochemical and biological decomposition processes and then mobilized through subsurface and overland flow (Fraser et al., 2001; Holden, 2005).

Temperature and water availability are key drivers of peat accumulation and decomposition, and are also important for DOC production rates (Charman et al., 2013; Fenner & Freeman, 2011; Ritson et al., 2017). Laboratory experiments and field studies in the years after droughts have shown that *in-situ* soil DOC concentrations are increased by temperature and drier conditions that lead to deeper water tables (Chapman et al., 2005; Clark et al., 2005; Evans et al., 2005; Fenner & Freeman, 2011; Ritson et al., 2017; Scott et al., 1998; Stutter et al., 2007; Watts et al., 2001; Worrall et al., 2006). Despite this, years with larger rainfall totals are often associated with higher total DOC fluxes from peatland streams (Clark et al., 2007; Clark et al., 2008). Thus, interactions between rainfall and temperature variation in the future are likely to be key factors that need to be explored in order to predict both the fluxes and concentrations of DOC from peatlands that supply potable water treatments works. High fluxes of DOC may sometimes be associated with low concentrations of DOC (Clark et al., 2007; Clark et al., 2008) and so this situation would not be a problem for existing DOC treatment plants in the future.

Acid atmospheric deposition affects soil solution chemistry and the solubility of DOC. The mobilization of metal cations in acid-sensitive soils is associated with larger amounts of acid deposition, which will decrease organic matter solubility (Monteith et al., 2007; Vanbreemen et al., 1984). Therefore, sulfate deposition from atmospheric pollution has been suggested as an important factor driving DOC export in peatlands (de Wit et al., 2007; Evans et al., 1988; Hruška et al., 2009; Löfgren et al., 2009; Tipping & Hurley, 1988). Long-term studies from lake and stream monitoring sites in Europe and North America have shown that in many places since the 1970s, DOC concentration has increased in conjunction with a decrease in sulfate deposition (e.g. Evans et al. 2006; Monteith et al. 2007).

Globally, the usage of peatland-supplied drinking water is highly concentrated in important hotspots. The UK consumes approximately 0.60 km^3 yr^{-1} of drinking water directly delivered by peatlands, equivalent to 79% of the global total. Although water supply peatlands cover only 0.31% of the UK, the UK consumes approximately 1.56 km^3 yr^{-1} of mixed-source (includes direct-source) peat-fed potable water, equivalent to supporting 28.25 million people or 43.1% of the UK population (Xu et al., 2018a). Conventional coagulation-flocculation is the most widely used operational method for DOC removal in the water industry (O'Melia et al.,

1999). Although current DOC concentrations do not exceed the capacity of existing water treatment facilities to continue to remove DOC, the removal of DOC from peatland-supplied water represents the largest costs in raw water treatment for water utilities in the UK (Ritson et al., 2014; Whitfield et al., 2011; Xu et al., 2018a). Projections of 21st century climate change for the UK forecast warmer, wetter winters and springs; and warmer, drier summers and autumns (Jenkins et al., 2009). Current estimates indicate decreased sulfate deposition during the same timeframe (IPCC, 2014; Lamarque et al., 2013). These projected changes would appear to indicate changing DOC concentrations and fluxes in the future, but until now there has been no attempt to quantify the degree of any future changes in DOC for the large peatland-derived drinking water provision catchments in the UK, or what they might mean for aquatic carbon loss from these peatlands. If increases in DOC concentration do continue, peaks in concentrations might exceed the capacity of existing water treatment facilities to continue to remove DOC, which may lead to the interruption of drinking water supply. Thus, considerable expenditure in new water treatment plants and increases in operational costs might be needed in areas that are reliant on peatland-derived water (Worrall & Burt, 2009). Therefore, it is important to undertake predictive work in order to ensure that UK water supplies are future-proofed and long-term capital investment planning is informed.

By using the Integrated Catchments model for Carbon (INCA-C) (Futter et al., 2007) and the derivative rainfall-runoff model Precipitation, Evapotranspiration and Runoff Simulator for Solute Transport (PERSiST) (Futter et al., 2014), this study seeks to provide a present-day calibration and the first future simulation of discharge, DOC concentration and DOC flux for several of the most important peatland-derived drinking water supply catchments in the UK under a variety of 21st-century climate and sulfate deposition scenarios. We test the hypothesis that mean DOC concentration and flux, as well as their seasonal variability, will all increase under future changes of climate and atmospheric acid deposition in peat-fed UK water supplies.

2 Materials and Methods

2.1 Study sites

In this paper, we studied nine hotspots catchments (Figurer 1), which, between them, deliver 72 % of all potable water directly sourced from peatlands consumed in the UK. We identified these hotspots catchments using the Peat Population Index (PPI) and Peat Reservoir Index (PRI) derived by Xu et al. (2018a). The PPI identifies catchments in which high population density coincides with high proportional peat coverage; while the PRI identifies those catchments in which potable water supply reservoirs are supplied by a high proportion of peat cover. Xu et al. (2018a) demonstrated that between them, PPI and PRI are useful in identifying those catchments that supply large volumes of peat-derived drinking water to large human populations. The peatlands in these catchments are therefore important to the maintenance of potable water supply. Dozens of water treatment plants distributed throughout the nine study catchments supply 72 % of all potable water directly sourced from peatlands consumed in the UK, equivalent to 57 % of the global total (Xu et al., 2018a). Peatland extent was derived from PEATMAP (Xu et al., 2018b). The distribution and characteristics of the nine study catchments across the UK are shown in Figure 1 and Table 1. Characteristic climate data for each catchment were derived from 'UK daily climate data sets (http://data.ceda.ac.uk/badc/ukcp09/data)'. Land cover and daily river flow discharge were derived from 'UK National River Flow Archive dataset (http://nrfa.ceh.ac.uk/data/)'. Annual volumes of potable water directly supplied by peatlands were derived from (Xu et al., 2018a).

2.2 INCA-C model setup

INCA-C is a dynamic, semi-distributed, process-based organic carbon cycling model which is used to simulate DOC concentration and flux under present and future climate and sulfate conditions in this paper. INCA-C is designed to be applied to natural and semi-natural forested and peat-dominated catchments in boreal and temperate regions (Futter et al., 2007). INCA-C generates daily time series of simulated soil carbon stocks and fluxes including soil organic carbon (SOC) and DOC in a number of user-specified land-cover types. There are two interconnected sub-models within INCA-C: a hydrological sub-model that simulates fluxes between water pools; and a biogeochemical carbon sub-model that simulates transformations between different carbon pools (Figure S1). The required input data for INCA-C includes daily time series of soil moisture deficit (SMD), hydrologically effective rainfall (HER), temperature (in °C), and precipitation (in mm) for the simulation period. HER is the depth of precipitation or snowmelt, net of evaporation that can enter the upper soil horizon while SMD is an estimate of the difference between the amount of water in the soil and the amount of water it can hold. HER and SMD can be derived from a separate hydrological model, i.e. PERSiST (Futter et al., 2014; Lupon et al., 2018). As input data, PERSiST requires daily time series of air temperature and precipitation. More details about INCA-C and PERSiST can be found in Futter et al. (2007, 2009, 2014).

2.2.1 Required input and model calibration data sources in baseline periods

Daily data of precipitation and temperature for the study catchments were derived from UKCP09 daily climate data sets (1960s-2016). Basic information and land cover data for the catchments were derived from the UK National River Flow Archive dataset; sulfate deposition data - both marine and non-marine loads (1990s-2016) - were derived from United Kingdom Eutrophying & Acidifying Pollutants: Precip-Net. Gaps in the data of UKEAP (<0.1 %) have been filled by linear interpolation between known values. Daily river discharge at outlets (1970s-2016) of the catchments was derived from the UK National River Flow Archive dataset. DOC concentration at the catchment outlet was derived from the Water Quality Archive developed by the Environment Agency. The archive provides DOC concentration at the outlets for 2005-2016 for all sites except that there was a shorter data duration available for the Tyne (2006-2015), Tees (2006-2016) and the Wye (2005-2013) catchments. Sampling frequencies varied between the nine catchments, ranging from sub-weekly to monthly.

2.2.2 Model calibration, evaluation and sensitivity analyses

INCA-C model fit was assessed based on the values of R^2 coefficients and Nash-Sutcliffe (N-S) coefficients relating measured and simulated DOC concentration, as well as measured and simulated stream discharge. The period of available datasets was divided into two parts: the first part (2005-2010) was used for calibration and the second part (2011-2016) was used for evaluation. Shorter periods were available for the Tyne (2006-2010), Tees (2006-2010) and Wye catchments (2005-2009) for calibration; and for Tyne (2011-2015) and Wye (2010-2013) catchments for evaluation. The calibration strategy for PERSiST and INCA-C followed the steps described by Futter et al. (2014) and Ledesma et al. (2012). Firstly, PERSiST was calibrated and then used to generate a time series of SMD and HER for running INCA-C. The best-performing parameter set in terms of R^2 and N-S coefficients was determined using the Monte Carlo procedure that included (100 loops of 300 runs each). In the evaluation periods, the best-performing parameter sets obtained during calibration for PERSiST and INCA-C were employed for modelling the flow and DOC in each case. This process aims to examine if the best-performing parameter sets selected in the calibration periods were able to be used for projection by evaluating the R^2 and N-S statistics of the evaluation period.

Sensitivity analysis of discharge and DOC-related parameters was performed to assess the effects of the hydrological, catchment, and in-stream variability of concentrations of DOC in surface water by varying the best performing parameter sets by ± 30 % in an analogous Monte Carlo procedure (de Wit et al., 2016). For each parameter, the ensemble of values from the 100 parameter sets was compared to a rectangular distribution using a Kolmogorov-Smirnov (KS) test. A significant KS statistic ($p < 0.05$) implied that the posterior distribution was not rectangular and thus that streamflow or DOC simulations were sensitive to the specific parameter (Futter et al., 2014).

2.3 Future climate and sulfate deposition scenarios

Future projections were separated into two time periods: 2030-2039 (termed here 2030s) and 2090-2099 (termed here 2090s). Future daily climate projections over the 21st century were derived from the United Kingdom Climate Projection 2009 (UKCP09) (Jenkins et al., 2009) which were produced based on Met Office Hadley Centre's climate model (Pope et al., 2000) and Intergovernmental Panel on Climate Change (IPCC) Special Report on Emission Scenarios (Nakicenovic et al., 2000). There are three scenarios in UKCP09: high emission (A1F1), medium emission (A1B) and low emission (B1). At the time of writing, the UKCP09 data are the most up-to-date, publically-available, downscaled climate projections for the UK. Temperature and precipitation changes with respect to baseline periods (Figure S2 and S3) were calculated based on UKCP09 outputs. In order to capture the likely change of each variable, the precipitation and temperature scenarios were composed of climate variables corresponding to a UKCP09 model realization, of which the average precipitation and temperature were at the 50th position for the 100 model realizations for each time period. In this study, climatic variables take values of central estimates (50 % probability level) because such scenario establishment is capable of capturing the likely change of each variable with time.

Future sulfate deposition dynamics were derived from the estimations from the Atmospheric Chemistry and Climate Model Intercomparison Project (Lamarque et al., 2013). In Europe, the sulfate deposition for the 2030s will decrease to 36 % of the baseline period, and for 2090s will decrease to 18 % of the baseline period. Although these scenarios represent inter-annual change, they do not represent intra-annual (seasonal) variability.

Thus, six future scenarios were considered: (1) 2030s B1: combinations of future precipitation and temperature under the lowest emission (or UKCP09 B1) with projected sulfate deposition in the 2030s; (2) 2030s A1B: combinations of future precipitation and temperature under medium emission (or UKCP09 A1B) with projected sulfate deposition in the 2030s; (3) 2030s A1F1: combinations of future precipitation and temperature under the highest emission (or UKCP09 A1F1) with projected sulfate deposition in the 2030s; (4) 2090s B1: combinations of future precipitation and temperature under the lowest emission (or UKCP09 B1) with projected sulfate deposition in the 2090s; (5) 2090s A1B: combinations of future precipitation and temperature under medium emission (or UKCP09 A1B) with projected sulfate deposition in the 2090s; and (6) 2090s A1F1: combinations of future precipitation and temperature under the highest emission (or UKCP09 A1F1) with projected sulfate deposition in the 2090s. All six scenarios were run through PERSiST using the best parameter set obtained during calibration in each catchment in order to generate necessary INCA-C inputs. Subsequently, the six scenarios were run through INCA-C using the best parameter set obtained during calibration in each catchment in order to generate future stream discharge, DOC concentration, and DOC flux to be compared with baseline periods.

3 Results

3.1 Mean discharge and DOC projections

Simulations for all future scenarios agree on reduced mean discharge in the 2030s and 2090s compared to the baseline period (Figure 2). Projected changes in mean discharge ranged from -27.4 % to -2.9 % in the 2030s, with a mean of -12.1 % across all nine catchments; and -40.1 % to -2.8 % in the 2090s, with a mean of -15.6 % across the nine catchments. All scenarios indicated projected increases in mean DOC concentrations in all nine catchments between the baseline period and the 2030s, and that these increases would continue into the 2090s (Figure 3). Between the baseline period and the 2030s, mean DOC concentration is projected to increase by between 0.3 % under the lowest greenhouse gas (GHG) emissions scenario (in the Derwent (Derbyshire) catchment) and by as much as 31.9 % under the highest emissions scenario (Severn catchment), with an average increase of 14.8 % across all catchments and future scenarios. By the 2090s, projected mean DOC concentrations based on mean daily data will have increased compared to the baseline period by between 5.4 % (Derwent (Derbyshire) catchment, lowest GHG emissions scenario) and 53.4 % (Severn catchment, highest GHG emissions scenario), with a mean average increase of 26.5 % across all catchments and future scenarios. Mean average DOC concentrations are highest in the Tyne catchment and lowest in the Derwent (Cumbria) catchment during both the observational baseline period and under all future scenarios. The Tyne catchment delivered 91 million m^3 of directly-sourced peat-fed potable water per year during the baseline period, more than any other peat-fed drinking water supply catchment in the world (Xu et al., 2018a).

Except for the Derwent (Derbyshire) and Severn catchments, where the greatest DOC concentrations are projected under the intermediate emission scenario (A1B), average DOC concentrations are projected to rise monotonically in the direction of increasing emissions. However, in the 2090s, the differences between the average DOC concentrations under the A1F1 scenario and the A1B scenario for Derwent (Derbyshire) and Severn catchments are quite small. The difference is 0.71 % for Derwent (Derbyshire) and 0.94 % for Severn catchment, while for the other catchments studied, the equivalent mean increase of DOC concentration is 3.19 % under A1F1 scenario compared to those under A1B scenario. By the 2090s, the mean DOC concentrations under the A1F1 scenario are projected to be larger than those under the A1B scenario in the Derwent (Derbyshire) and Severn catchments from January to July. However, these increases would be counterbalanced between August and November, since the mean DOC concentrations under the A1F1 scenario are projected to be smaller than those under the A1B scenario in this period (Figure 3). The behaviour of the Derwent (Derbyshire) and Severn catchments could be because of differences in precipitation (negatively correlated to DOC concentration). The increase above the baseline of monthly precipitation is larger in the latter part of the year (November), compared to mid-summer (July) under A1F1 by 12 % for both the Derwent (Derbyshire) and the Severn catchment. For the other catchments studied the equivalent mean difference is 10.84 % (Figure S3). Therefore, DOC in the Derwent (Derbyshire) and Severn catchments may be more diluted under A1F1 than that under the A1B scenario between August and November. The mean annual precipitation and standard deviations of daily precipitation for the Derwent (Derbyshire) catchment are the lowest of all the catchments studied (Table 1). These factors may contribute to a narrow range of DOC concentration change under the different climate and sulfate deposition scenarios for the Derwent (Derbyshire) except for the period when future precipitation is projected to have the largest increase (December to February, Figure S3).

3.2 Projected seasonal variability of discharge and DOC

Projected changes in the seasonal patterns of DOC concentrations are of more significance than the annual means, with likely important consequences for both water treatment costs and aquatic ecology. We find increasing seasonal variability in DOC concentrations in all nine catchments under future scenarios, with large peaks in DOC concentration when high-flow (wet) months follow a sequence of low flow (dry) months. The projected changes in future sulfate deposition for the 2030s and 2090s contain inter-annual variability, but contain no intra-annual (seasonal) variability (see Methods, above). The temperature and precipitation scenarios we used to drive our models, on the other hand, contain both inter- and intra-annual variability. Our projections that DOC concentrations in the 2090s will have greater seasonal variability than in either the 2030s or the baseline period (Figure 4) are therefore attributable to the increasing seasonality of precipitation and temperature (Figure S2 and S3). Therefore, we propose that the large projected decrease in sulfate deposition (36 % of the baseline average during 2030s; 18 % during 2090s) will be an important driver of the overall change in mean annual DOC concentrations, but that the changes in precipitation and temperature will drive altered seasonality of DOC concentrations. This is consistent with previous studies suggesting that the majority of the increase in DOC concentrations over the past two to three decades was associated with the decline in atmospheric sulfate deposition while climate change was likely to result in only modest increases in DOC concentrations in similar catchments in the UK and Norway (Futter et al., 2009; Laudon et al., 2012).

Our simulations project a wide and seasonally variable range of future discharge regimes (Figure 5). Most of the highest monthly discharges are projected to occur between October and March, while discharge between April and September is projected to be the lowest and the least variable. With respect to the baseline period, April to September will be the annual period with the largest projected reduction in discharge (26.91 % of the baseline average during 2030s; 41.00 % during 2090s) as compared with October to March, in which only small changes (4.03 % of the baseline average during 2030s; 7.17 % during 2090s) are projected. As with discharge, our simulations project increased seasonal variability of total DOC flux from all nine catchments from the baseline period to the 2030s, and further increases in seasonality to the 2090s (Figure 6). Most of the greatest increases in monthly DOC flux are projected to occur between October and March (13.36 % of the baseline average during 2030s; 24.34 % during 2090s), while these increases seem likely to be largely counterbalanced by the significant decreases between April to September (19.36 % of the baseline average during 2030s; 34.46 % during 2090s). Therefore, the simulated effects of future climate change upon annual DOC fluxes are more modest than those for DOC concentrations.

4. Discussions

4.1 Model performance during observational baseline period

The PERSiST simulated values fitted observations of discharge well (Table 2). Normally, applications of hydrological models resulting in model performances of at least N-S > 0.5 for flow simulations are considered good (Moriasi et al. 2007). Modelled discharge captured the seasonal variations, and the timing of the rising and falling limbs (Figures 7 and 8) with R^2 ranging from 0.47 to 0.79 and N-S values ranging from 0.46 to 0.73 in the calibration periods, and with R^2 ranging from 0.44 to 0.78 and N-S values ranging from 0.42 to 0.75 in the evaluation periods. Large decreases in mean discharge are projected for April to September, with smaller changes between October and March (Table 2). Between April and September in all nine catchments, the mean difference in the mean values between simulated discharge and discharge is only 5.71 $m^3 s^{-1}$, 3.13 $m^3 s^{-1}$ for standard deviation values and 5.91 $m^3 s^{-1}$ for

median values. Between October and March in all nine catchments, the mean difference in the mean values between simulated discharge and discharge is only 5.02 $m^3 s^{-1}$, 7.07 $m^3 s^{-1}$ for standard deviation values and and 3.95 $m^3 s^{-1}$ for median values. We deemed these differences to be acceptable considering the mean of 37.07 mg L^{-1} across all nine catchments.

Overall, the INCA-C model was able to reproduce the intra- and interannual variation in DOC concentration during the baseline simulation period, resulting in R^2 ranging from 0.38 to 0.62 and N-S values ranging from 0.37 to 0.59 in the calibration periods, and R^2 ranging from 0.29 to 0.69 and N-S values ranging from 0.20 to 0.65 in the evaluation periods (Figure 9, 10). Except for the best INCA-C modelling performance (R^2 is 0.85 and N-S is 0.84) by de Wit et al. (2016), most previous INCA-C modelling studies showed the R^2 ranging from 0.12 to 0.76 and N-S values ranging from 0.25 to 0.65 (Futter and de Wit, 2008; Futter et al., 2009, 2011; Ledesma et al., 2012; Oni et al., 2012, 2014). INCA-C is a multi-parameter process-based model which simulates complex, interdependent processes in soil and stream systems across large catchments. The performance of INCA-C will be synthetically affected by the characters of research sites (e.g. area, discharge, retention volume and carbon content in the soil boxes of different land cover types), data quality of driving factors (e.g. climate data, atmospheric data), and the calibration strategy (e.g. loops of running, adjustment of parameters).

On the whole, we deemed the performance of INCA-C to be acceptable for the purposes of broad-scale comparisons between catchments and between contrasting climate scenarios. The model's good performance in six out of the nine catchments likely indicates its reasonable representation of a number of underlining biogeochemical processes, but its performance is poor in three catchments (i.e. Severn, Derwent (Derbyshire) and Eamont catchments). In these three catchments, the model failed to capture some of the high peaks occuring in periods when the DOC concentrations are normally low (i.e. Spring and Summer) - this is the main factor decreasing the overall R^2 and N-S during the study period. For example, in the Severn catchment, during the year 2011 there was an extremely high peak in measured DOC concentration of 6.61 mg L^{-1} on 7th April, while the average measured DOC concentration in April during the baseline period is only 3.43 mg L^{-1}. One factor that likely plays a role here is calibration strategy. Since the calibration strategy used involves attempts to minimize the sum of squares between modeled and observed values (Futter et al., 2007, 2008), all observations are weighted equally. Thus, the calibration may be biased toward fitting high-frequency, low-magnitude DOC fluxes, which may lead in some cases to low-frequency, high-magnitude DOC flux events (i.e., autumn peaks) being poorly represented, as seems to be the case in these three catchments (Ledesma et al., 2012). The driver for the high peak in concentration on 7th April appears to be rainfall immediately after a warm, dry period. There was a continuous half month of drought (the total rainfall is only 0.41 mm) since mid-March, followed by a wet week of rainfall until 7th April 2011. Furthermore, the mean daily temperature on 6th April 2011 was 16.2 ºC, the highest in April for the whole baseline period, whereas the average temperature in April was 9.1 ºC. The increase of temperature together with wet conditions after a dry period could dramatically increase the DOC production and release (Clark et al., 2007, 2008), leading to the high peak in concentration on 7th April 2011. A similar situation also occurred in November 2015 and February 2016 in Derwent (Derbyshire) catchment, and October 2011 and March 2016 in Eamont catchment. Due to the limited nature of publicly available data, in this project we applied INCA-C to several large catchments rather than to their sub-catchments. It may be difficult for the model to capture all conditions that vary across a large catchment when it is simulated as a single, lumped box. For example, the precipitation data were collected from a station close to the outlet of the catchment, which can summarize general rainfall patterns but

the extreme local events occurring upstream might not be captured (e.g. summer-autumn storms occurring upstream which might influence total discharge, leading to the dramatic changes of DOC concentration). All of this may render the model calibrations more difficult and affect the overall performance of INCA-C model.

For the baseline periods, mean simulated daily DOC concentration ranged, respectively, from 1.69 mg L^{-1} (Derwent (Cumbria) catchment) to 9.49 mg L^{-1} (Tyne catchment), similar to the calibration period (Table 2). Large increases in mean DOC concentrations are projected for October to March compared to relatively small changes between April and September (Table 2). Between October and March for all the nine catchments, the mean difference in the mean, standard deviation and median values between simulated DOC concentrations and observed DOC concentrations is only 0.26 mg L^{-1}, 0.32 mg L^{-1}, and 0.15 mg L^{-1}, respectively. Between April and September for all the nine catchments, the mean difference in the mean, standard deviation and median values between simulated DOC concentrations and observed DOC concentrations is only 0.28 mg L^{-1}, 0.66 mg L^{-1}, and 0.25 mg L^{-1}, respectively. These differences are acceptable considering the mean of 5.07 mg L^{-1} across all nine catchments. Therefore, the INCA-C model reproduces the intra-annual (seasonal) dynamics of DOC at the study sites, indicating that it is able to handle variations in soil moisture, temperature control and sulfate deposition. In addition, the 20 best performing INCA-C parameter sets were retained for estimation of uncertainty bands for daily concentration. Figure 10 shows that more than 93% of observed DOC concentration observations were captured by the 95% confidence intervals of the DOC concentration simulations based on the 20 best parameter sets for the nine study catchments. Thus, the calibrated models have the potential to be used for long-term and future scenario analysis.

4.2 Statistical analysis

The data points that comprise each climatic "treatment" (i.e. baseline, 2030s B1, 2030s A1B, 2030s A1F1, 2100s B1, 2100s A1B and 2100s A1F1) are in fact a time series and therefore represent non-independent measurements. In this study, a repeated measures analysis of variance (ANOVA) with a Greenhouse-Geisser correction was conducted to compare the effect of different treatments on discharge, DOC concentration and DOC flux for each site. Table S1 shows that mean discharges and DOC concentrations for all the nine catchments differed significantly between all future scenarios. Seven paired samples t-test were used to make *post hoc* comparisons between different treatments. The paired samples t-test for different conditions indicated that the discharge and DOC concentration under different treatments are significantly different from each other (Table S2-S19). Overall, all the studied catchments are projected to experience statistically significant decreased mean dischages and increased DOC concentration. However, the simulated effects of future climate change upon annual DOC fluxes are more modest than those for DOC concentrations. The Severn and Ribble catchments are projected to experience statistically significant ($p < 0.05$) increased DOC flux, while the Derwent (Derbyshire) and Eamont catchments are projected to experience statistically significant ($p < 0.05$) reduced DOC flux, despite increased DOC concentrations. The simulations indicate no significant change (less than 5 % or $p > 0.05$) in DOC flux for the other catchments compared to the baseline period (Figure S4, Table S1, and Tables S20-S28). Therefore, our results indicate that future climate and sulfate deposition scenarios are likely to have a significant effect on DOC concentrations, but with more modest implications for DOC flux.

The list of statistically sensitive PERSiST hydrological and INCA-C model parameters for simulation of discharge and DOC concentrations in the calibration period, identified with the Monte Carlo analysis, is presented in Table S29 and S30. At least two of the four

precipitation-related parameters (flow velocity modifier *b*, adjustment factors *RainMultiplier*, *SnowMultiplier*, and *ResidenceTime*) were the most sensitive to perturbations in discharge modelling (Table S29). The parameter *b* is used to define flow velocity (as $V = a \times Q^b$, where V is equal to streamflow velocity, and Q is stream discharge) which impacts the stream flashiness. The *RainMultiplier* and *SnowMultiplier* are the adjustment factors relating measured precipitation to estimated rainfall and snowfall, respectively. *ResidenceTime* represents the residence time of water in a soil box as a proxy for the hydraulic conductivity of that particular soil box. In addition, the temperature-related parameters *GrowingDegreeThreshold* and *DegreeDayEvapotranspiration* were among the sensitive parameters for discharge modelling. The *GrowingDegreeThreshold* is the temperature threshold above which evapotranspiration can occur (°C), and *DegreeDayEvapotranspiration* is the depth of water lost due to evapotranspiration per degree per day when the temperature exceeds the limit at which evapotranspiration occurs. Therefore, discharge modelling is highly affected by the precipitation and temperature for the baseline period, which is consistent with findings in previous studies (Jin et al., 2012; McIntyre et al., 2005; Oni et al., 2012).

Sensitivity analyses of DOC modelling (Table S30) indicate that simulated DOC concentration was highly dependent on soil hydrological (*flow_b* and *base flow index*), thermal (*COUP_10DegreeResponse*), and chemical properties (*OrganicLayerB2* and *MineralLayerB2*). The definition of the *flow_b* parameter is the same as the *b* parameter in PERSiST. The *base flow index* parameter represents the fraction of water that is transferred from upper to lower model storage, which can affect the response time of subsurface water, and therefore controlling streamflow from precipitation and snowmelt. The *COUP_10DegreeResponse* parameter is the thermal conductivity of the soil and a parameter controlling process-rate responses to a 10°C change in soil temperature. It represents the increase in biological production with soil temperature, which is a very sensitive temperature-related parameter. The *OrganicLayerB2* and *MineralLayerB2* are the parameters that determine the DOC desorption rate in the upper (organic) and lower (mineral) soil layers to changes in chemistry and were also sensitive in most cases. This is not surprising since the biological processes that control the production of DOC are all governed in turn by temperature and pH, while DOC export is controlled by hydrological processes. A combination of higher temperatures, reduced precipitation and reduced sulfate deposition in the future thus seems likely to lead to considerably higher DOC concentrations at peak times of year.

4.3 Implications for water security and carbon budgets

Climate and sulfate deposition-induced changes to DOC dynamics are likely to threaten regional water security in the UK without increased operational and capital investments to improve DOC removal capacity. Large increases (by as much as a factor of 1.6) in DOC concentration in the 2090s compared to the baseline period are projected in the autumn and winter, a time when DOC concentrations are already high in the baseline datasets. It is at this time of year that water treatment works are already operating at peak DOC removal capacity due to high DOC concentrations. Moreover, there will not only be an increase in DOC concentrations, but also an increasing range and variability of DOC concentrations, which relate to the consequent increase in organic matter solubility (Evans et al., 2006; Hytteborn et al., 2015; Ledesma et al., 2016). The cost of treating DOC in potable water is composed of operational and capital investments. The operational costs include chemical costs of coagulants, increased energy use, staffing and sludge removal. When water DOC-related color peaks become too severe, the capacity of water treatment facilities is exceeded, new technologies are required, and therefore water companies have to invest in capital for every new treatment plant. The large increases in DOC concentrations in the coming decades in these

and other peatland-derived drinking water supply catchments will have important consequences for water treatment infrastructure and would likely require large capital investment to maintain safe drinking water.

Future river discharge in key UK peat-fed drinking water supply catchments is projected to decrease under climate change, which is likely to contribute to increased risk to the water supply. Large decreases in discharges are projected for April to September in the future, periods when discharges are already relatively low. This could also result in water security problems, especially since climate change is likely to drive up the demand for water alongside population growth.

Furthermore, in contrast to increased DOC concentrations, median values of total DOC flux are projected to have decreased in the 2090s compared to the baseline. This may have implications for aquatic ecosystems that process DOC. The declining DOC flux in some catchments also suggests that, relative to DOC losses via surface water runoff, gas losses from the terrestrial compartment may become an even more important component of the UK peatland carbon balance in the future. However, peat erosion in the UK has previously been predicted to increase under future climate change, with enhanced losses of particulate organic carbon to the fluvial system (Li et al., 2017). The fate of this particulate carbon is unclear, but work to date suggests around half is trapped in reservoirs or is transported to estuaries, and the rest may be processed to DOC or gas en route (Palmer et al., 2016). Thus, sediment loads, driven by peatland degradation under climate change, may present both a costly treatment problem related to sediment removal, and provide an in-stream DOC source that will compound our projected future increases in DOC concentrations.

5 Conclusions

Our study is the first to model DOC in the UK's significant peatland-derived drinking water supply catchments under future climate and sulfate deposition changes. In summary, taken across all scenarios, we project that annual mean DOC concentrations in peatland-derived potable water will increase and that annual mean discharge will decrease. Projected changes in the seasonality of DOC dynamics are important, and projected variability of discharge, DOC concentration and DOC flux are higher in the 2090s than in the 2030s in all catchments, and greater in high GHG emission scenarios than in low GHG scenarios.

Some of our estimates of increasing future DOC concentration and decreasing discharge may be conservative since peatlands are potentially sensitive to human management interventions, but we did not simulate their effect. Most commonly, interventions such as drainage, overgrazing, afforestation, and prescribed burning change the structural and biological environment of peatlands, and damage peat-forming vegetation, potentially leading to increased DOC concentrations and decreased overland flow (Holden & Burt, 2003; Holden et al., 2006, 2007). Conservation management and ecological restoration of peatlands to make them more resilient to climate change (e.g. by blocking drainage ditches to maintain shallow water tables (Armstrong et al., 2010)) may be a relatively low cost approach to reducing DOC concentrations in the aquatic compartment as compared with capital investment in DOC treatment and removal in drinking water facilities (Martin-Ortega et al., 2014). However, this cannot be relied upon given the large-scale increases in DOC concentrations suggested by our simulations, particularly in autumn and winter months. Thus, a dual approach will be required to ensure the future security of peatland-derived drinking water in the UK and other similar areas worldwide, involving both more efficient water treatment technology and responsible stewardship of peatlands.

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Supporting Information

Figures S1−S4, Tables S1−S30.

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Table 1. Characteristics of the nine study catchments across the UK between 2005 and 2016.

Catchment	Area (km^2)	Land Cover	Average temperature (°C)	Annual precipitation (mm)	Annual potable water directly supplied by peatlands (million m^3)
Tyne	2,176	Grassland (62%), agriculture (4%), peatland (12%) and forest (22%)	9.4	755	90.71
Wye	4,010	Grassland (62%), agriculture (17%), peatland (5%), forest (14%) and urban (2%)	10.2	1041	73.66
Tees	818	Grassland (59%), agriculture (13%), peatland (24%) and forest (4%)	9.7	700	63.82
Derwent (Derbyshire)	1,178	Grassland (60%), agriculture (12%), peatland (9%), forest (10%) and urban (9%)	10.8	635	62.26
Ouse	3,315	Grassland (44%), agriculture (32%), peatland (13%), forest (7%) and urban (4%)	10.3	695	43.49
Severn	2,025	Grassland (70%), agriculture (6.5%), peatland (5%), forest (17%) and urban (1.5%)	10.2	659	39.94
Ribble	1,145	Grassland (71%), agriculture (3%), peatland (9%), forest (10%) and urban (7%)	10.1	1102	28.79
Derwent (Cumbria)	235	Grassland (73%), agriculture (2%), peatland (13%), forest (11%) and urban (1%)	9.1	1016	23.19
Eamont	396	Grassland (78%), agriculture (4%), peatland (7%), forest (9%) and urban (2%)	9.4	855	17.69

Table 2. Descriptive statistics (mean, standard deviation and median) for the baseline periods for all the nine catchments.

			Discharge ($m^3 s^{-1}$)			DOC concentration ($mg L^{-1}$)		
Catchment	**Period**		**Mean**	**Standard Deviation**	**Median**	**Mean**	**Standard Deviation**	**Median**
Tyne	**April to September**	**Simulated**	30.60	41.41	20.59	9.33	2.92	8.88
		Observed	31.21	44.85	17.20	9.90	4.35	8.51
	October to March	**Simulated**	62.22	50.87	47.4	9.57	2.99	8.93
		Observed	66.62	63.18	43.7	9.68	3.02	9.03
	Annual	**Simulated**	46.53	46.08	32.88	9.49	2.96	8.92
		Observed	48.46	57.35	29.70	9.79	3.71	9.02
Wye	**April to September**	**Simulated**	58.02	59.88	40.41	3.27	0.82	3.18
		Observed	46.55	53.17	29.90	3.16	1.36	2.89
	October to March	**Simulated**	106.93	106.75	68.97	3.14	1.12	2.91
		Observed	103.27	91.55	70.70	3.18	1.66	2.75
	Annual	**Simulated**	82.91	89.87	50.76	3.17	0.98	3.05
		Observed	73.34	79.89	44.80	3.21	1.52	2.81
Tees	**April to September**	**Simulated**	16.45	28.60	9.24	8.37	2.83	8.00
		Observed	13.56	19.70	8.03	8.78	3.92	7.69
	October to March	**Simulated**	26.49	34.65	14.96	7.10	3.17	6.53
		Observed	30.66	34.04	18.12	8.09	3.94	7.04
	Annual	**Simulated**	21.99	32.12	11.49	7.77	3.07	7.26
		Observed	21.52	29.00	12.40	8.45	3.93	7.18
Derwent (Derbyshire)	**April to September**	**Simulated**	20.47	13.92	16.29	3.54	0.84	3.46
		Observed	15.39	13.40	11.77	3.36	0.97	3.03
	October to March	**Simulated**	29.59	19.21	25.76	3.08	0.74	2.99
		Observed	25.37	21.72	19.07	3.29	0.88	3.10
	Annual	**Simulated**	25.11	17.33	19.97	3.30	0.82	3.25
		Observed	18.75	19.10	12.80	3.32	0.92	3.06
Ouse	**April to September**	**Simulated**	44.83	41.54	31.18	6.21	2.32	5.95
		Observed	36.03	42.17	21.94	6.75	3.81	5.54
	October to March	**Simulated**	72.99	58.85	53.98	5.70	2.15	5.24
		Observed	82.13	74.18	52.66	5.86	2.47	5.35
	Annual	**Simulated**	59.01	52.66	40.38	5.94	2.25	5.59
		Observed	57.35	65.00	33.43	6.28	3.19	5.41
Severn	**April to September**	**Simulated**	36.11	31.71	25.73	4.28	1.02	4.23
		Observed	28.11	28.21	17.51	4.61	2.02	4.04
	October to March	**Simulated**	62.80	47.92	48.06	4.17	1.02	4.00
		Observed	68.67	62.19	44.85	4.31	1.52	4.02
	Annual	**Simulated**	49.52	42.72	34.92	4.22	1.02	4.12
		Observed	45.76	53.30	23.88	4.46	1.78	4.02
Ribble	**April to September**	**Simulated**	31.64	36.21	21.86	6.33	2.73	5.93
		Observed	22.23	35.42	10.30	6.61	2.61	5.81
	October to March	**Simulated**	57.94	59.14	38.78	5.12	1.79	4.88
		Observed	50.14	58.55	28.10	5.55	1.91	4.96
	Annual	**Simulated**	44.74	50.73	27.11	5.71	2.39	5.23
		Observed	36.14	50.32	17.10	6.01	2.30	5.29
Derwent (Cumbria)	**April to September**	**Simulated**	11.04	8.13	8.29	1.81	0.55	1.73
		Observed	9.29	8.67	6.40	1.88	0.54	1.87
	October to March	**Simulated**	21.80	21.12	14.69	1.59	0.45	1.47
		Observed	18.35	17.04	13.30	1.60	0.64	1.46
	Annual	**Simulated**	16.39	16.81	10.59	1.69	0.51	3.57
		Observed	13.75	14.21	9.25	1.75	0.61	4.44
Eamont	**April to September**	**Simulated**	15.65	14.76	10.70	2.37	0.71	2.25
		Observed	12.25	11.64	8.00	2.44	0.88	2.27
	October to March	**Simulated**	29.56	20.74	27.00	1.99	0.47	1.87
		Observed	27.12	16.30	30.64	2.22	0.70	2.08
	Annual	**Simulated**	22.59	22.74	14.01	2.17	0.63	2.00
		Observed	18.53	24.07	10.20	2.33	0.80	2.17

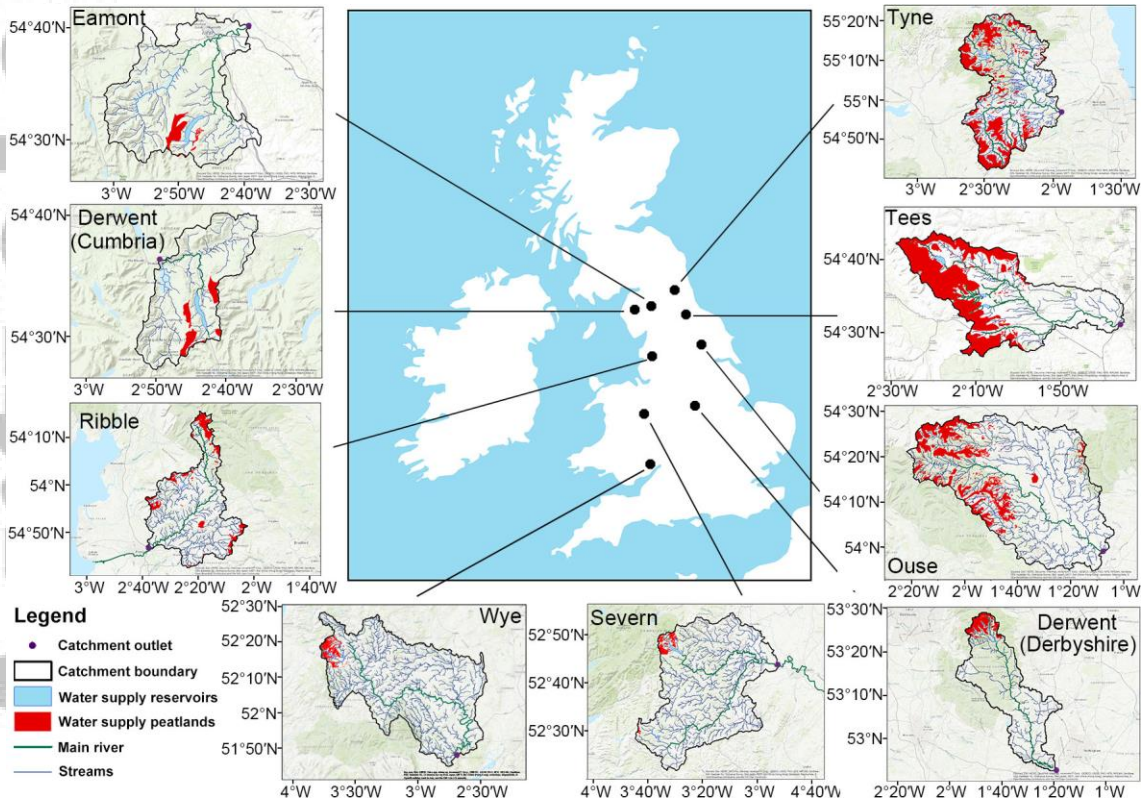

Figure 1 Distribution of the nine study catchments across the UK.

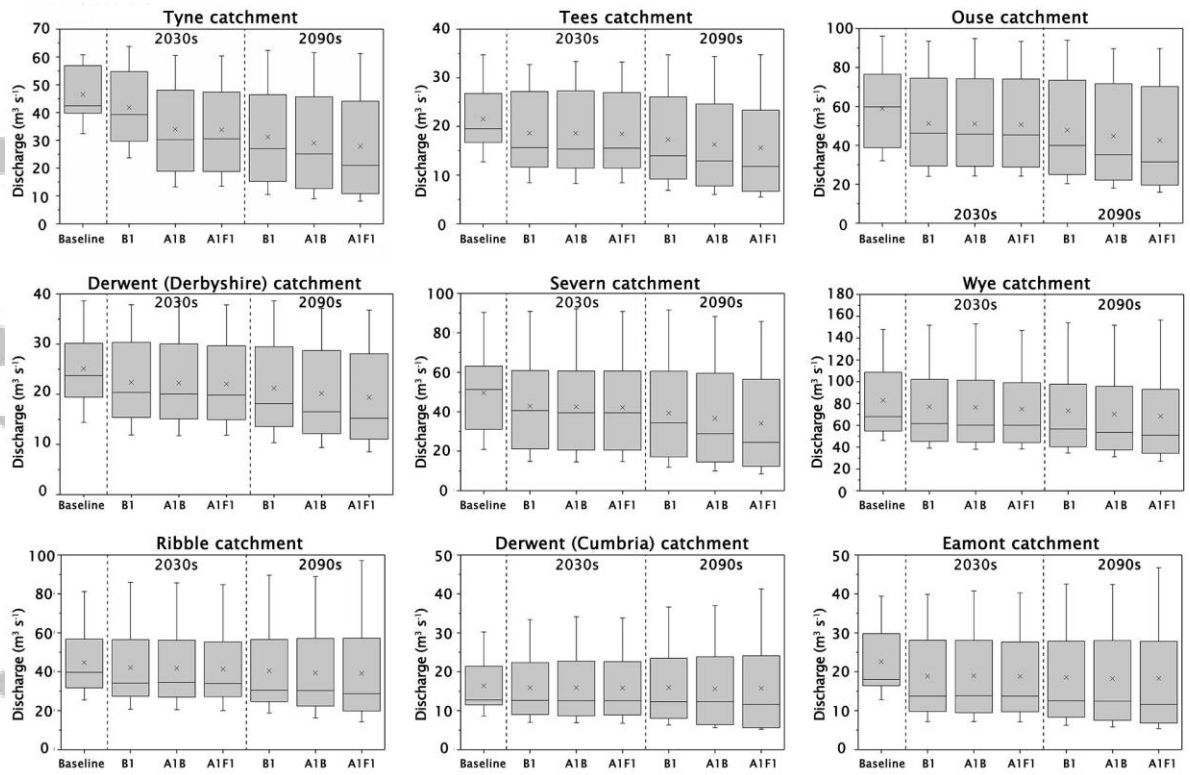

Figure 2 Distributions of mean monthly discharge for each site, during the baseline observational period and under UKCP09 B1 (lowest emissions), A1B (medium emissions), and A1F1 (highest emissions) scenarios for the decades 2030s and 2090s. Box heights represent upper and lower quartiles of discharge; centerlines represent medians; crosses represent means; whiskers show the maximum and minimum values.

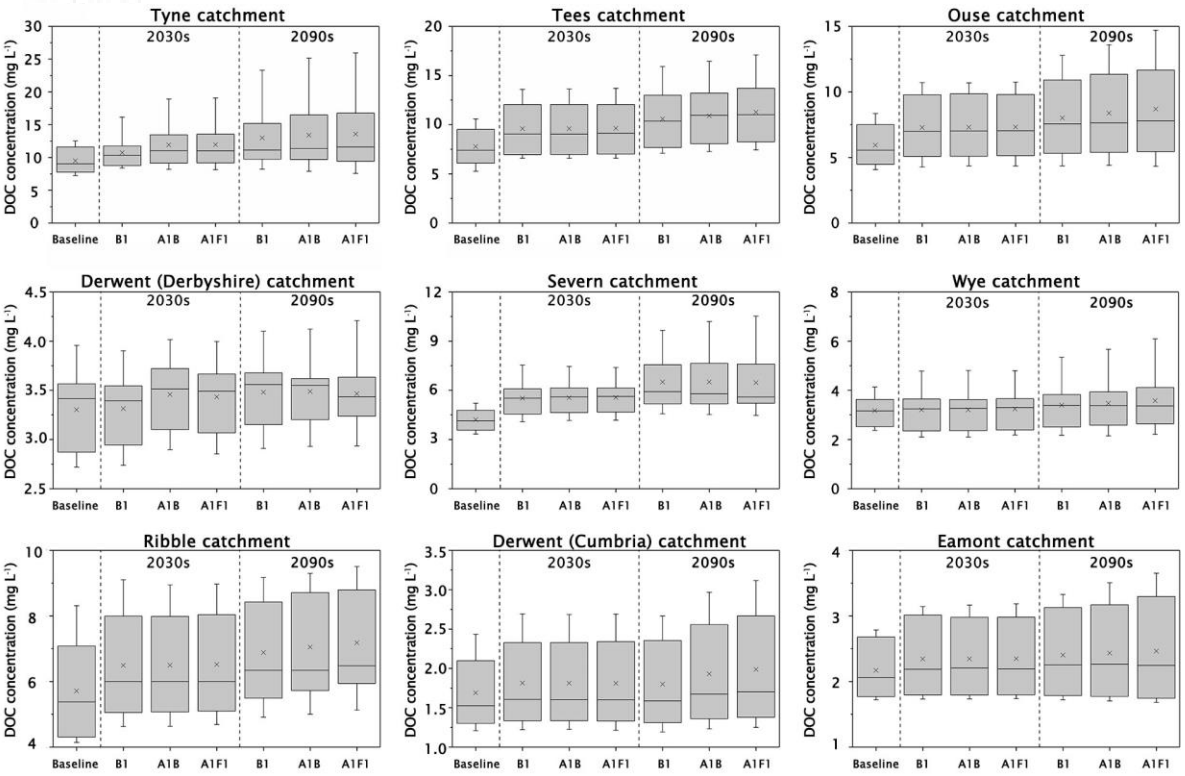

Figure 3 Distributions of mean monthly DOC concentrations for each site, during the baseline observational period and under UKCP09 B1 (lowest emissions), A1B (medium emissions), and A1F1 (highest emissions) scenarios for the decades 2030s and 2090s. Box heights represent upper and lower quartiles of DOC concentration; centerlines represent medians; crosses represent means; whiskers show the maximum and minimum values.

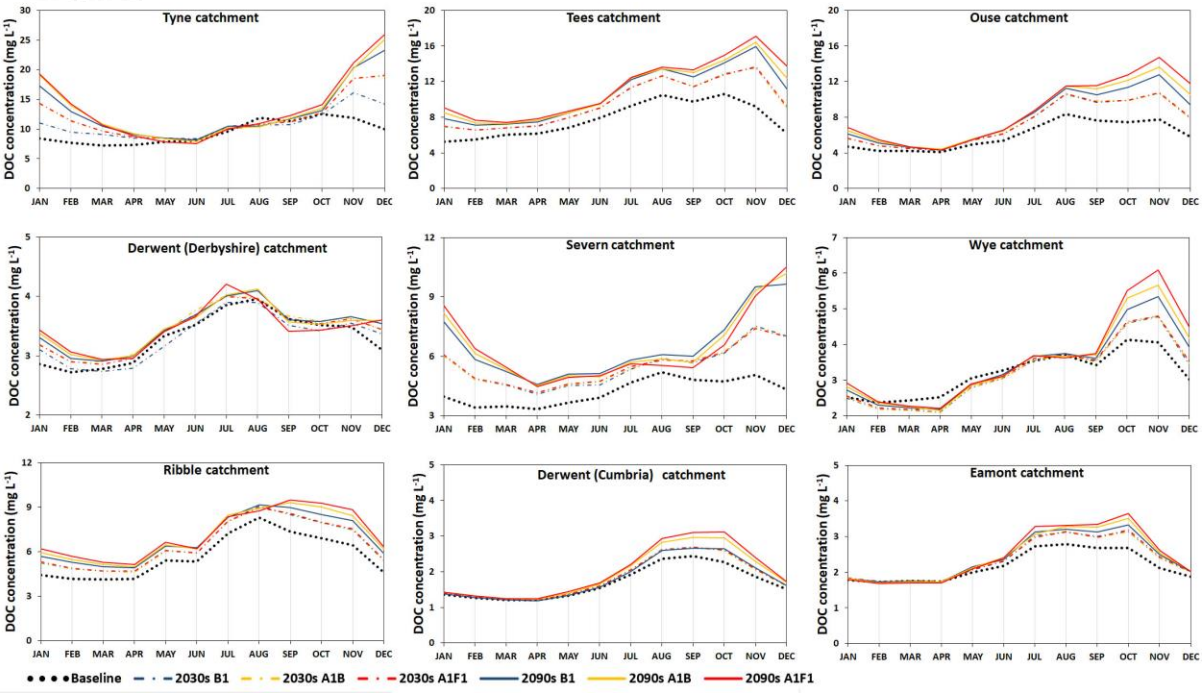

Figure 4 Average monthly DOC concentration during the observational baseline period; and under UKCP09 B1 (lowest emissions), A1B (medium emissions), and A1F1 (highest emissions) SRES scenarios for the decades 2030s and 2090s.

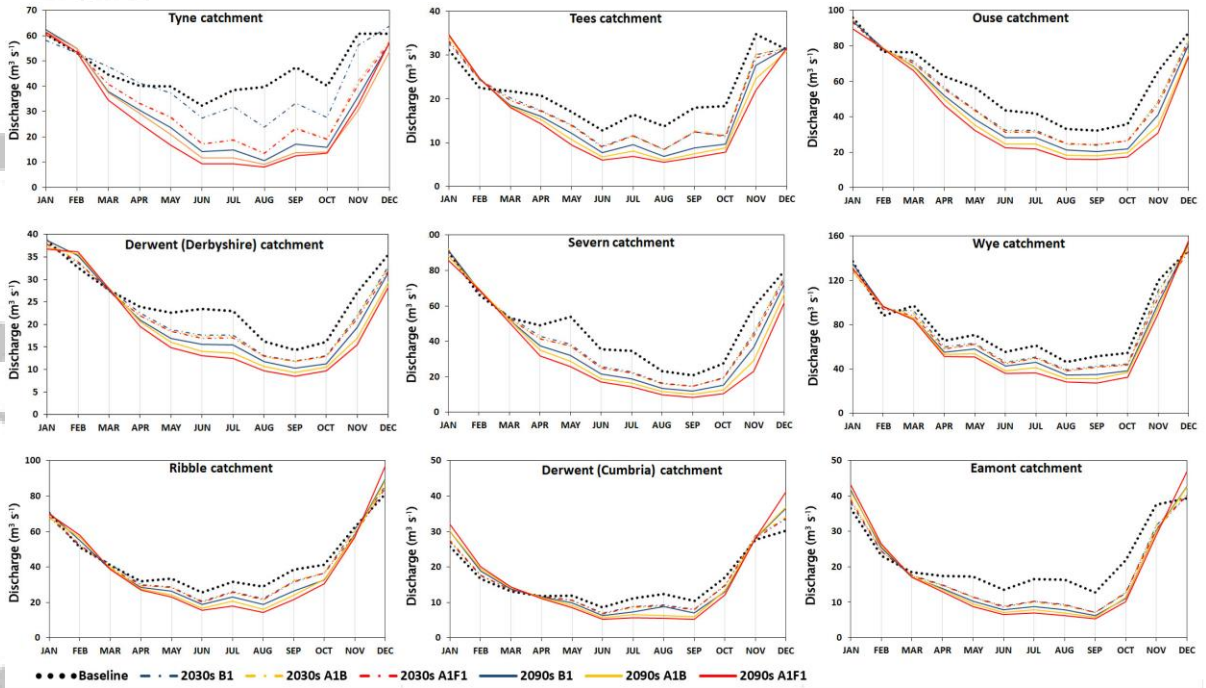

Figure 5 Average monthly discharge during the observational baseline period; and under UKCP09 B1 (lowest emissions), A1B (medium emissions), and A1F1 (highest emissions) SRES scenarios for the decades 2030s and 2090s.

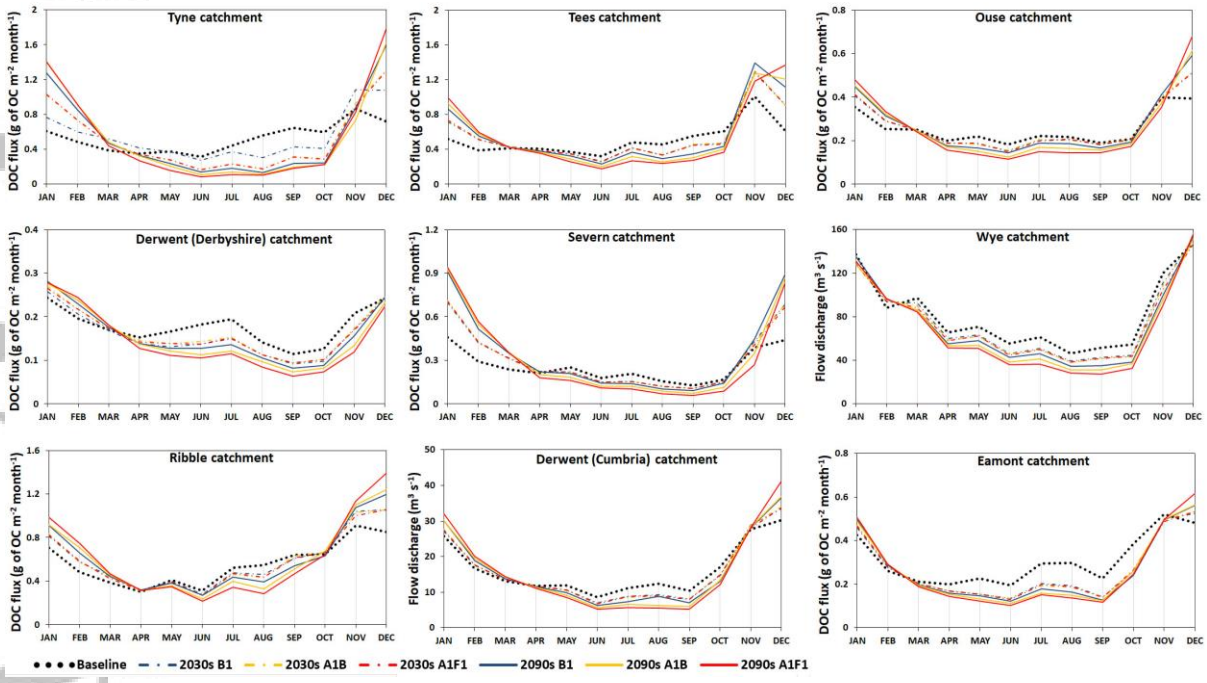

Figure 6 Average monthly DOC flux during the observational baseline period; and under UKCP09 B1 (lowest emissions), A1B (medium emissions), and A1F1 (highest emissions) SRES scenarios for the decades 2030s and 2090s.

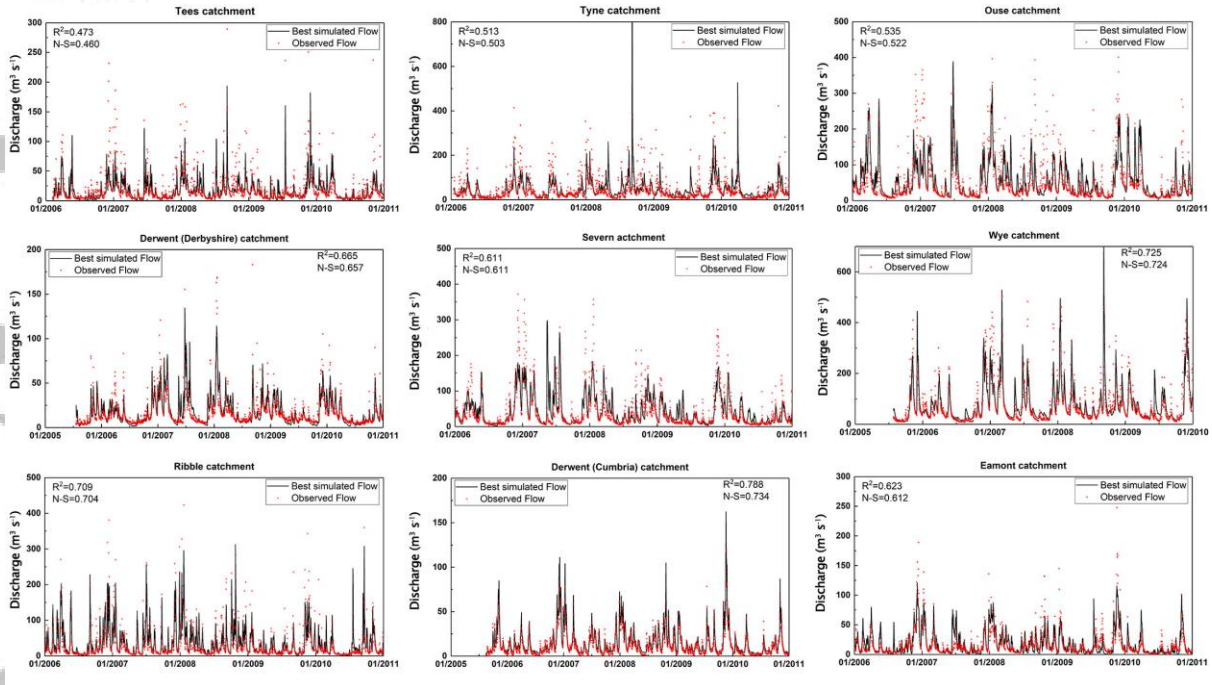

Figure 7. Comparison of observed and simulated discharge for the Tyne, Tees, Wye, Derwent (Derbyshire), Ouse, Severn, Ribble, Derwent (Cumbria) and Eamont catchments for the calibration periods.

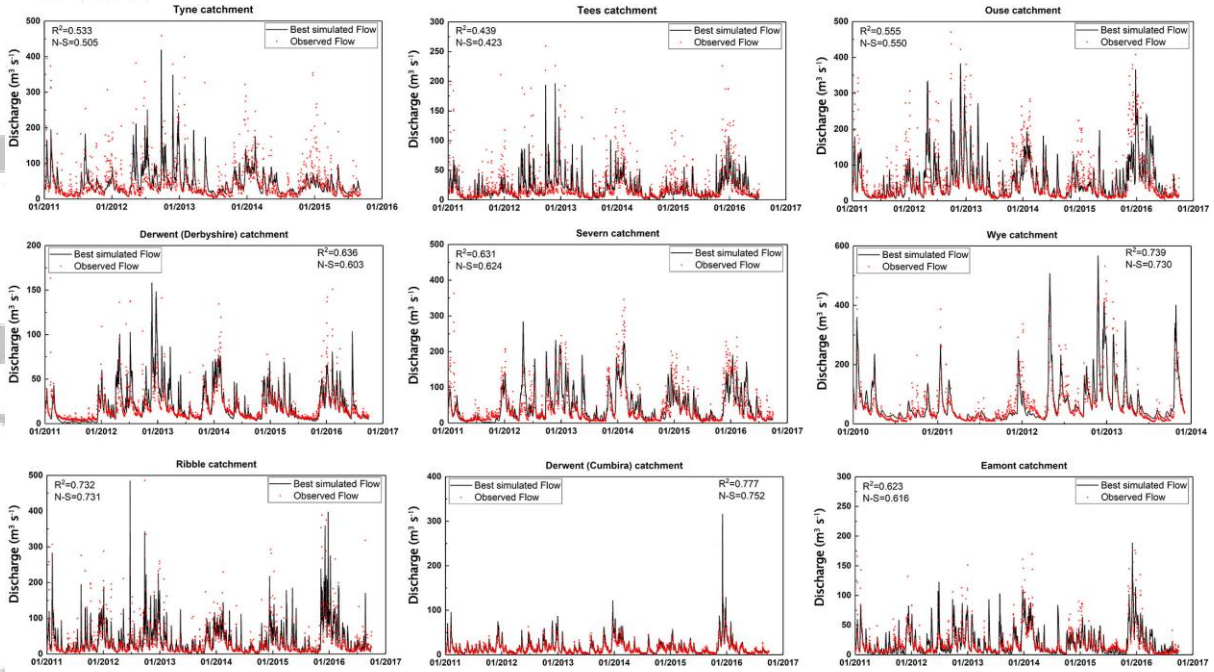

Figure 8. Comparison of observed and simulated discharge for the Tyne, Tees, Wye, Derwent (Derbyshire), Ouse, Severn, Ribble, Derwent (Cumbria) and Eamont catchments for the evaluation periods.

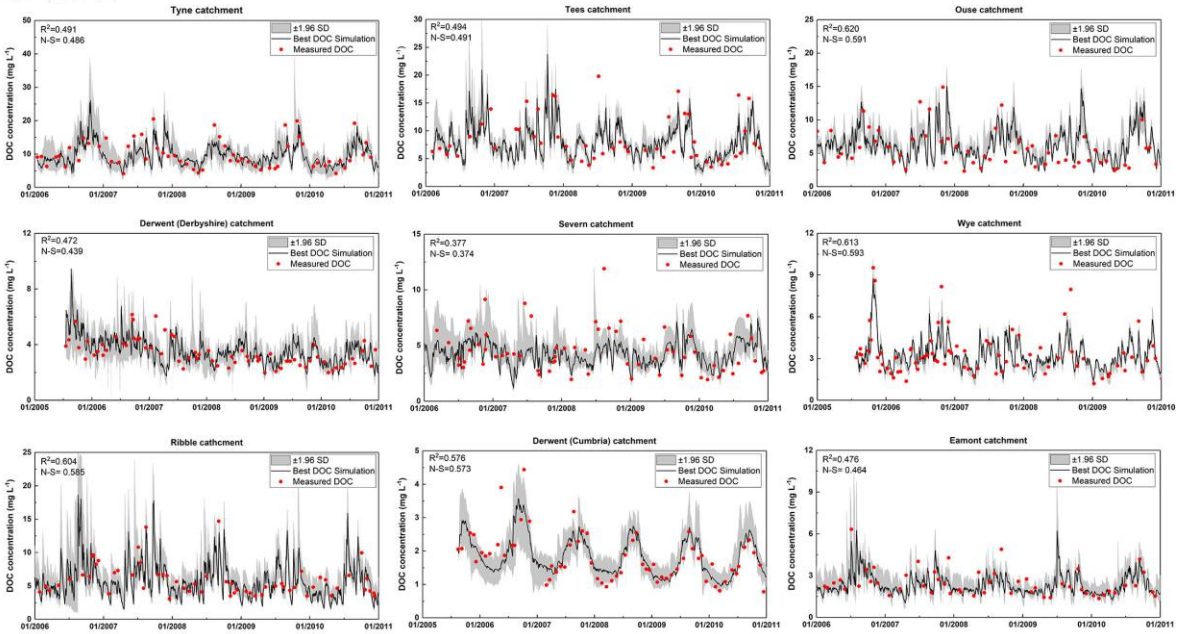

Figure 9. Comparison of observed and simulated stream water DOC concentrations at the Tyne, Tees, Wye, Derwent (Derbyshire), Ouse, Severn, Ribble, Derwent (Cumbria) and Eamont catchments for the calibration periods. The line shows simulated DOC concentrations from the best-performing parameter set. The shaded area shows the 95 % confidence interval of the DOC simulations based on the 20 best-performing parameter sets.

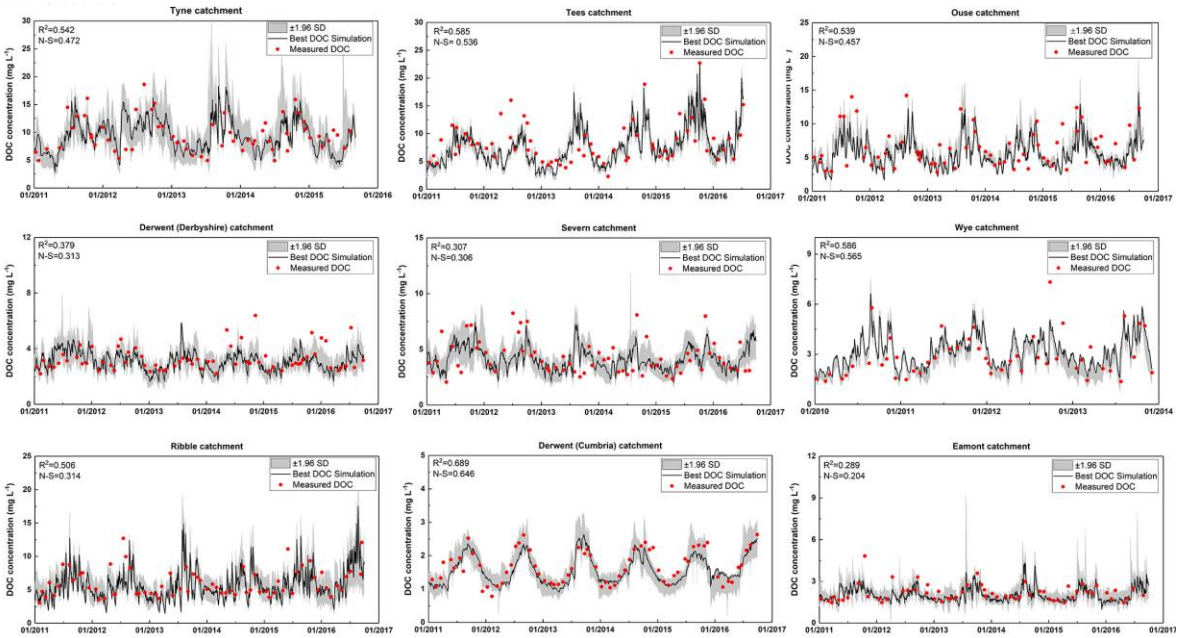

Figure 10. Comparison of observed and simulated stream water DOC concentrations at the Tyne, Tees, Wye, Derwent (Derbyshire), Ouse, Severn, Ribble, Derwent (Cumbria) and Eamont catchments for the evaluation periods. The line shows simulated DOC concentrations from the best-performing parameter set. The shaded area shows the 95 % confidence interval of the DOC simulations based on the 20 best-performing parameter sets.