



## Soil-to-stream export of dissolved organic carbon and its functional composition can be predicted using only widely available data

Katarzyna Sawicka<sup>1\*</sup>, Edwin C. Rowe<sup>1</sup>, Donald T. Monteith<sup>2</sup>, Amy Pickard<sup>3</sup>, Brian M. Spears<sup>3</sup>, Jennifer Williamson<sup>1</sup>, Annette Burden<sup>1</sup>, Alan Radbourne<sup>1</sup>, Zak Mitchell<sup>1</sup>, Dan J. Lapworth<sup>4</sup>, Christopher A. Yates<sup>5,6</sup>, Penny J. Johnes<sup>5</sup> & Christopher D. Evans<sup>1</sup>

<sup>1</sup> UK Centre for Ecology & Hydrology, Environment Centre Wales, Deiniol Rd, Bangor LL57 2UW, UK.

<sup>2</sup> UK Centre for Ecology & Hydrology, Library Avenue, Lancaster Environment Centre, Lancaster, Bailrigg LA1 4AP, UK.

<sup>3</sup> UK Centre for Ecology & Hydrology, Bush Estate, Penicuik EH26 0QB, UK.

10 <sup>4</sup> British Geological Survey, Environmental Science Centre, Keyworth, Nottingham, NG12 5GG, UK.

<sup>5</sup> School of Geographical Sciences, University of Bristol, University Road, Bristol BS8 1SS, UK.

<sup>6</sup> AtkinsRéalis, The Hub, 500 Park Avenue, Aztec West, Bristol, UK

\*Corresponding author: Katarzyna Sawicka, katwic55@ceh.ac.uk

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### Abstract.

Dissolved organic carbon (DOC) exports from soil to aquatic systems are significant components of the global carbon cycle and are of concern to the water industry owing to the role of DOC in the formation of disinfection byproducts. Modelling the processing of DOC as it flows from soil to the ocean requires distinction between compounds that are relatively more aromatic, coloured, ultraviolet-sorbent and photolabile, but resistant to microbial breakdown ( $T_1$ ), from less photo-reactive but more microbially labile compounds ( $T_2$ ). We assessed whether mean annual DOC concentration and its  $T_1$  fraction ( $pT_1$ ) can be predicted from data that are widely available, without *in-situ* measurements, to enable applications within Earth System Models. Using only spatially resolved data that are available at global scale, we estimated DOC concentration and  $pT_1$  for a range of headwater catchments in the United Kingdom. The best fitted models predicted DOC concentration (Nash-Sutcliffe efficiency,  $NSE = 0.71$ ) and  $pT_1$  ( $NSE = 0.57$ ) from land use (arable and wetland), soil type (peat or mineral), precipitation chemistry (ionic strength) and areal runoff. Application at national scale demonstrated expected spatial patterns in the distribution of DOC concentration and  $pT_1$ , with high concentrations in peatlands in the north of the country, and highest  $pT_1$

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in northern and western areas with high peat cover and surface runoff generation. The approach described here could be applied to other regions, transferring understanding of land-to-water DOC export from data-rich to data-poor areas.

## 30 1 Introduction

Dissolved organic matter (DOM) fluxes from the land to the ocean are a significant component of the global carbon (C) cycle and account for a high proportion of net terrestrial CO<sub>2</sub> uptake (e.g. Drake et al., 2018; Regnier et al., 2013). Most current Earth System Models (ESMs) (e.g. Clark et al., 2011; Friedlingstein et al., 2014 and references therein) only consider vertical exchanges of C between terrestrial and oceanic reservoirs and the atmosphere. Ultimately, lateral land-ocean transport also  
35 needs to be taken into account in order to “close” the C cycle, but the magnitude and fate of this flux remains uncertain since it depends on the amount of DOM decomposition and CO<sub>2</sub> evasion during transport (Cole et al., 2007; Creed et al., 2015; Fabre et al., 2020). Predictive models have been developed for DOM fluxes at the tidal limit of rivers (e.g. Williamson et al., 2021) and for processing within the aquatic system (e.g. Anderson et al., 2019). Process models of soil and DOM production have also been developed (Rowe et al., 2014), but these require detailed parameterisation. The current study aimed to develop  
40 a relatively simple statistical model of DOM quantity, and quality in terms of inherent reactivity, which can predict soil-to-headwater fluxes on the basis of widely available data.

In addition to acting as a significant store and conveyor of reduced carbon, DOM plays a pivotal role in the transport of energy, nutrients and trace metals (Aiken et al., 2011; Christensen et al., 1996), shaping the structure and function of aquatic ecosystems and modulating the impacts and responses to anthropogenic nutrients (Creed et al., 2018; Johnes et al., 2023; Prairie, 2008; Tank et al., 2010). Moreover, discoloration of water by chromophoric DOM and increased disinfection  
45 byproducts loads associated with the chemical treatment of DOM, are undesirable for drinking water (Williamson et al., 2023). In many countries water companies have a legal requirement to produce potable water with no discernible colour (Li and Mitch, 2018; Villanueva et al., 2023); DOM therefore has to be removed from raw water prior to disinfection steps (Ritson et al., 2016).

50 The DOC flux in most upland rivers is dominated by soil-derived material (Aitkenhead and McDowell, 2000; Regnier et al., 2013). However, in catchments with higher agricultural and urban landcover and more mineral soils, including the lower sections of many larger river systems, the chemical characteristics, such as photolability/non-photolability, and amount of DOC are often dominated by DOM from autochthonous production and wastewater inputs. These catchments are further shaped by microbial and photochemical breakdown products of soil-derived DOM (Yates et al., 2023). Headwaters are  
55 therefore likely to provide the best indication of the main factors driving the allochthonous, i.e. land-to-water, DOC flux. In order to contribute to ESMs, the modelling of soil-to-stream DOC export, and the quality of that DOC, must be based solely on explanatory variables that can be derived from large spatial-scale datasets that, for example, quantify soil type, land use,

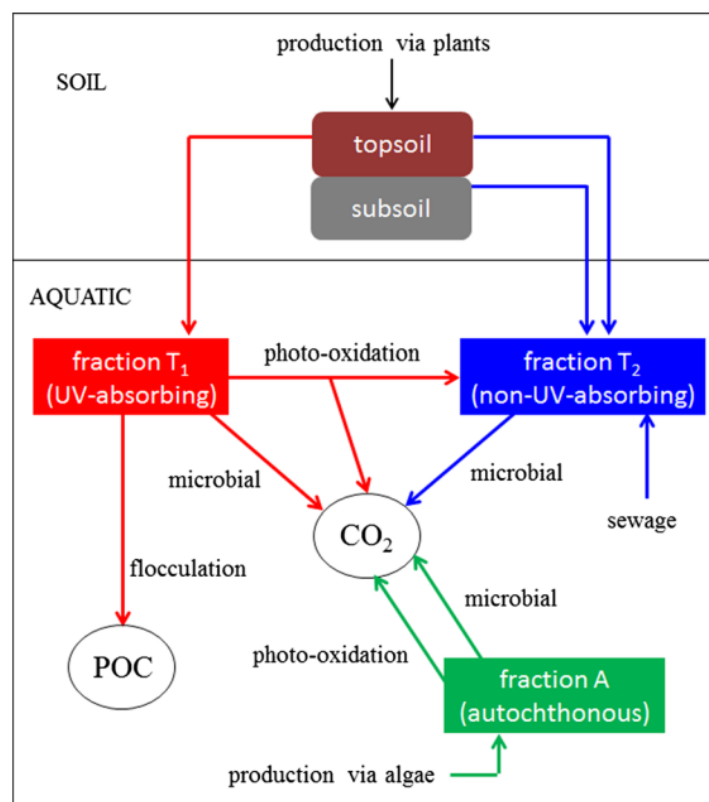


and meteorology at an acceptable spatial resolution. It is also necessary to restrict sites in the calibration dataset to headwater catchments, where water residence time has been limited and autochthonous DOC can be assumed to be negligible.

60 The residence time of DOC in natural systems depends both on chemical characteristics, that for example determine its mobility in soils and susceptibility to physical and biological breakdown, and on ecosystem-level properties such as water residence time, land use, nutrient loading and anthropogenic stressors (Cotner et al., 2022; Kothawala et al., 2021; Soares et al., 2019). The chemical properties of DOC are strongly dependent on source material and previous biogeochemical transformations (Schlesinger and Bernhardt, 2013) and as a result, DOC comprises a plethora of molecules with a broad spectrum of  
65 characteristics and reactivity (Aris, 1989; Maurice et al., 2002).

Anderson et al. (2019) highlighted the importance of distinguishing between 1) fraction of DOC that is strongly ultraviolet-absorbing (UV-absorbing) and so prone to photo-oxidation as well as flocculation, but relatively resistant to microbial consumption ( $T_1$ ), and 2) fractions that is weakly or not UV-absorbing, is not prone to photooxidation and flocculation and is relatively amenable to biological degradation ( $T_2$ ). We operationally define  $T_1$  as terrigenous DOM that strongly absorbs UV  
70 radiation, whereas  $T_2$  represents compounds that are only weakly or not absorbing for UV, such as many carbohydrates and proteins. The effects of these processes on  $T_1$  and  $T_2$  turnover can thereby be simulated within the aquatic component of Land-to-Ocean (LTO) transport models, such as the UniDOM framework (Figure 1). The UniDOM framework assumes that all DOC deriving from terrestrial decomposition can be functionally assigned to one of these two ‘end member’ pools, so the DOC from soil can be characterised simply by the proportion represented by the  $T_1$  class,  $pT_1$ . A third pool is included in  
75 UniDOM model to represent low molecular weight autochthonous (i.e. largely algal and higher plant derived) and wastewater DOC inputs. These are mainly weakly UV-absorbing, i.e. non-chromophoric, and because they are relatively biologically available have high rates of turnover. Given that autochthonous DOC production in most small headwater catchments is likely to be strongly limited by the relatively low incidence of direct and diffuse inputs of nutrients (Evans et al., 2017b), the current study focused on characterising and predicting the soil derived flux of  $T_1$  and  $T_2$  DOC into headwaters only.

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**Figure 1. The UniDOM conceptual framework for soil to aquatic DOC modelling which distinguishes fractions  $T_1$  (photolabile) and  $T_2$  (non-photolabile), as well as an autochthonous (A) fraction (Anderson et al. 2019).**

85 Various process-based and statistical models have been created to assess factors driving the dynamics of DOC within a range  
of different environments, as reviewed by Di Grazia et al. (2023) and Monteith et al. (2023). Such mechanistic models tend to  
be detailed and require extensive parameterisation with site-specific calibration. Modelling of spatial variation in DOC  
concentrations across catchments, on the other hand, tends to draw primarily on static catchment-scale metrics (Williamson et  
al. (2021). However, few have attempted to predict functional composition of DOC or proxies for this composition such as  
90 specific ultraviolet absorbance at 254 nm per unit DOC concentration ( $SUVA_{254}$ ). Williamson et al. (2021) showed that  
 $SUVA_{254}$  can be modelled as a function of land use, altitude and rainfall, but their study focused on DOC fluxes at the tidal  
limit, and hence once they have been subjected to freshwater processing and autochthonous production. Numerous studies  
have provided insights into controls on DOM composition, linking this to land cover and soil type (e.g. Fellman et al., 2008;  
Han et al., 2021; Hanley et al., 2013; Ma and Li, 2020; Qin et al., 2020), and meteorological events (e.g. Hood et al., 2006;  
95 Wallin et al., 2015; Werner et al., 2019), but none of the resulting models are suitable for predicting the quantity and quality



of DOM entering river systems. The type and amount of DOM entering rivers strongly influence everything from nutrient cycling and light availability to drinking-water treatment costs and the overall health of aquatic ecosystems. It is therefore important to quantify as accurately as possible its functional fractions and total export.

100 The aim of this study, therefore, was to develop new models of the concentrations and functional characteristics of DOC entering headwaters based on widely available data, that can be directly applied to data-poor regions or within ESMs. We focused on SUVA<sub>254</sub> as the metric of DOC quality since this is strongly related to photolability, allowing predictions of headwater DOC fluxes to feed into aquatic processing and transport models.

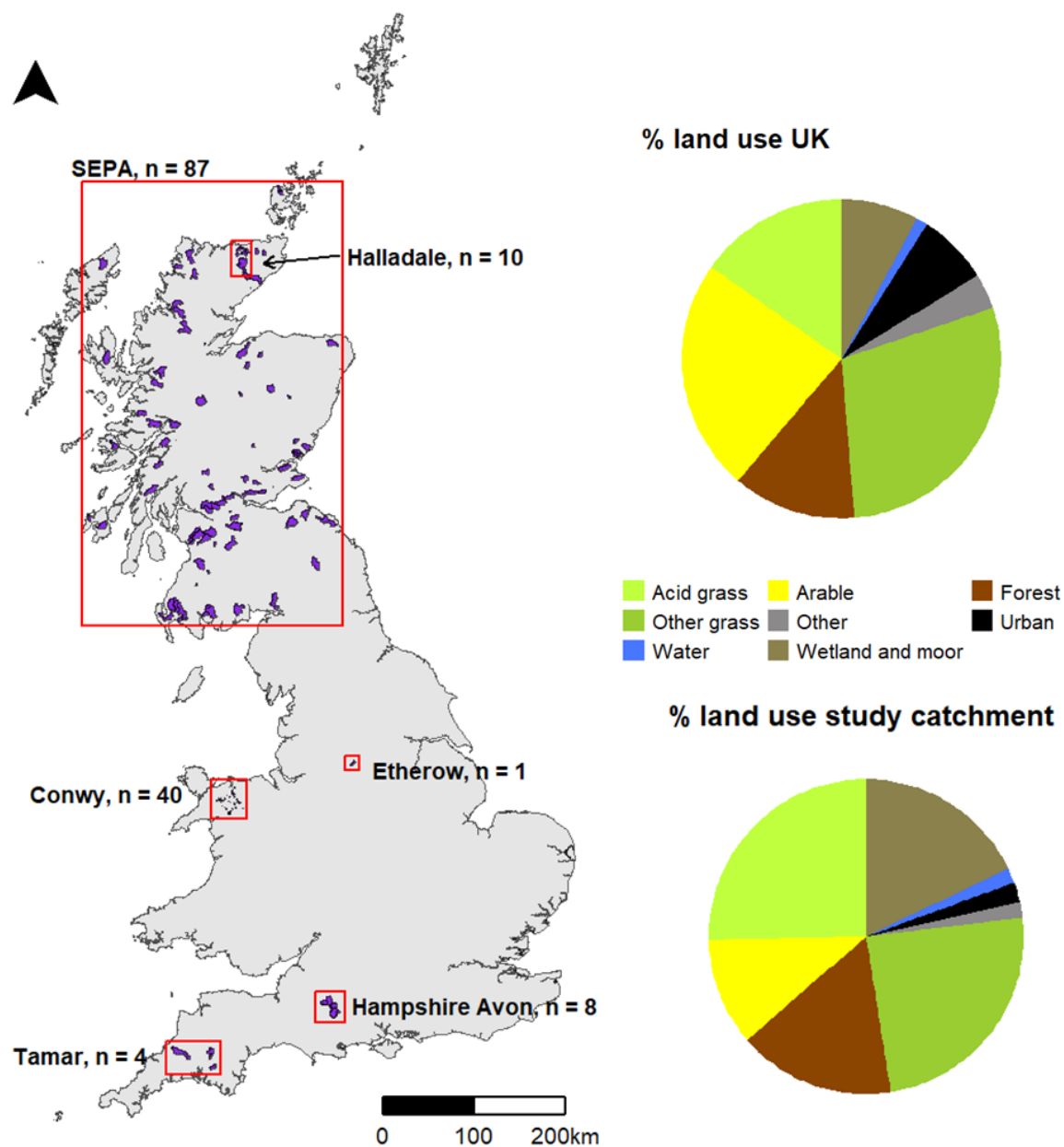
## 2 Methods

105 Data were obtained for 150 headwater catchments across Great Britain (GB) with areas less than 100 km<sup>2</sup> (1st. quartile 1.4 km<sup>2</sup>, median 19.6 km<sup>2</sup>, mean 32.4 km<sup>2</sup>, 3<sup>rd</sup>. quartile 60.3 km<sup>2</sup>), within which aquatic production and processing were considered likely to be small relative to terrestrial production (Bouwman et al., 2013). Dissolved organic carbon concentration [DOC] and SUVA<sub>254</sub> were obtained from a total of six separate regional monthly grab-sampled water chemistry sampling campaigns conducted during various periods between the years of 2007-2020. (Figure 2, Table 1).

110 **Table 1 Water sample datasets used to derive statistical models.**

| Campaign name  | Sampling duration   | Sampling frequency             | Number of sampling sites | Number of samples |
|----------------|---------------------|--------------------------------|--------------------------|-------------------|
| SEPA           | Feb 2007 - Oct 2018 | Varying (Weekly – Two-monthly) | 87                       | 22478             |
| Halladale      | Apr 2018 – Mar 2019 | Monthly                        | 10                       | 155               |
| Etherow        | Apr 2018 – Feb 2020 | Monthly                        | 1                        | 24                |
| Conwy          | Jun 2007 – May 2016 | Monthly                        | 40                       | 602               |
| Hampshire Avon | Nov 2015 - Oct 2016 | Varying (Weekly – Monthly)     | 8                        | 316               |
| Tamar          | Apr 2019 - Mar 2020 | Monthly                        | 4                        | 132               |

Collectively, samples spanned a wide range of land uses that is broadly representative of the UK, although the distribution was skewed towards higher proportions of acid grassland, wetland and moorland relative to arable land (Figure 2).



115 Figure 2. Location of study headwater catchments (purple insets) and percent land cover in Great Britain (GB), as assessed from the Land Cover Map (LCM) 2015 and the percentage of land cover within all study catchments. Land cover types grouped as shown in Table 2. SEPA on the GB map denotes Scottish Environment Protection Agency.



## 2.1 DOC and SUVA measurements and chemical analysis

120 Dissolved organic carbon and absorbance analyses were conducted across multiple accredited laboratories (UKCEH Lancaster,  
University of Bristol, British Geological Survey, and Bangor University). Comparability of data was ensured through the use  
of standard analytical protocols. All laboratories used a 0.45  $\mu\text{m}$  filtration pore size, a 1 cm fixed optical path length for  
measuring absorbance, routine blank correction using ultrapure water, identical DOC determination methodology (Pt-catalysed  
combustion NPOC on Shimadzu TOC-L platforms) and DOC comparable UV–Vis instrumentation. All laboratories followed  
125 established quality assurance and quality control procedures, including instrument calibration with certified standards, routine  
analysis of blanks and reference materials, and internal performance checks (information provided by data providers).  
Laboratory-specific details are summarised in Table A3.

The collated dataset benefits from methodological consistency across sites and use of widely adopted DOC and UV–  
absorbance analytical standards supporting cross-catchment comparability. Potential sources of uncertainty include minor  
inter-laboratory instrument variability, differences in filter material (cellulose nitrate vs. cellulose acetate), and the use of  
130 different spectrophotometer models, which may introduce small systematic offsets in absorbance. However, these effects are  
expected to be minor relative to spatial and temporal variability in DOM composition and concentration, and do not  
compromise the interpretation of large-scale patterns and partitioning outcomes.

## 2.2 Catchment characteristics

135 Sampling locations were rounded to the nearest 50 m, and catchment boundaries were calculated using a Digital Elevation  
Model with 50 m lateral and 10 cm vertical resolution (Morris and Flavin, 1990). For each of the derived catchments, data on  
climate, land-cover, and deposition of anthropogenic and marine salts were collated. Area-weighted mean annual precipitation,  
near-surface air temperature and potential evapotranspiration were derived from the CHESSE meteorological data for the dates  
matching the DOC and SUVA data (Robinson et al., 2016; Robinson et al., 2017). Annual average deposition data  
140 corresponding to the campaign years were obtained from the Concentration Based Estimated Deposition (CBED) model (Levy  
et al., 2020a; Levy et al., 2020b; Smith et al., 2017, 2018).

Land use data were obtained from the UKCEH Land Cover Map 2015 (Rowland et al., 2017). Peat areas were derived from  
the UK Peatland Map (Evans et al., 2017a). The 21 LCM habitat types were aggregated to reduce the number of potential  
explanatory variables, as set out in Table 2. Livestock will affect DOC export to waters, with the extent of this impact varying  
according to landscape character, stocking density and farming practices, however obtaining this data was beyond the scope  
145 of the funding for this project. The area of “improved, calcareous and neutral grassland” is a proxy for grazing intensity in  
both upland and lowland catchments, since this class is dominated by improved (i.e. fertilised) agricultural grassland. Selected  
potential explanatory variables used in statistical modelling are presented in Table 2 and Figure 3. Runoff was estimated by



150 subtracting estimated evaporative loss (ET) from precipitation. Concentrations of ions in precipitation were derived by dividing deposition by precipitation. The sum of concentrations of the major acid anions ( $\text{SO}_4^{2-} + \text{Cl}^- + \text{NO}_3^-$ ), expressed in equivalents, includes both marine and anthropogenic anions and was used as a proxy for variation in the total ionic strength of precipitation.

**Table 2. Summary of mean and standard deviation (SD) of annual response variables (in bold) and selected potential explanatory variables (n = 150).**

| Abbreviation              | Description                                      | Unit                         | Mean (SD)          |
|---------------------------|--|------------------------------|--------------------|
| <b>[DOC]</b>              | <b>Median annual DOC concentration</b>           | <b>mg L<sup>-1</sup></b>     | <b>6.36 (4.12)</b> |
| <b>SUVA<sub>254</sub></b> | <b>Median annual mass specific UV absorbance</b> | <b>L (mg C)<sup>-1</sup></b> | <b>3.86 (0.94)</b> |
| MAT                       | Mean annual air temperature                      | deg C                        | 8.06 (1.02)        |
| MAP                       | Mean annual precipitation                        | m year <sup>-1</sup>         | 1.71 (0.77)        |
| MAR                       | Mean annual runoff                               | m year <sup>-1</sup>         | 1.30 (0.76)        |
| H <sup>+</sup>            | Hydrogen ion deposition                          | keq ha <sup>-1</sup>         | 0.16 (0.08)        |
| NH <sub>x</sub>           | Ammonium deposition                              | keq ha <sup>-1</sup>         | 0.61 (0.32)        |
| nmS                       | Non-marine sulphur deposition                    | keq ha <sup>-1</sup>         | 0.24 (0.12)        |
| BC <sub>tot</sub>         | Base cations deposition                          | keq ha <sup>-1</sup>         | 0.86 (0.47)        |
| Cl <sub>tot</sub>         | Chloride deposition                              | keq ha <sup>-1</sup>         | 3.40 (1.96)        |
| S <sub>tot</sub>          | Sulphur deposition                               | keq ha <sup>-1</sup>         | 0.61 (0.30)        |
| N <sub>tot</sub>          | Nitrogen deposition                              | keq ha <sup>-1</sup>         | 0.97 (0.46)        |
| IS <sub>precip</sub>      | Ionic strength of precipitation                  | meq L <sup>-1</sup>          | 0.25 (0.06)        |
| pPeat                     | Catchment peat area proportion                   | Proportio                    | 0.30 (0.32)        |
| pArable                   | Arable and horticultural land use cover          | Proportio                    | 0.08 (0.18)        |
| pForest                   | Coniferous and broadleaf woodland land use       | Proportio                    | 0.17 (0.24)        |
| pWetMoor                  | Wetland, moorland and heathland land use cover   | Proportio                    | 0.21 (0.30)        |
| pAcid grass               | Acid grassland land use cover proportion         | Proportio                    | 0.28 (0.33)        |
| pOther grass              | Improved, calcareous and neutral grassland land  | Proportio                    | 0.21 (0.27)        |
| pCalcareous grass         | Calcareous grassland land use cover proportion   | Proportio                    | 0.002 (0.015)      |
| pUrbanSuburb              | Urban and suburban land use cover proportion     | Proportio                    | 0.02 (0.07)        |
| pWater                    | Freshwater land use cover proportion             | Proportio                    | 0.02 (0.04)        |
| pOther                    | Supralittoral sediment, Saltmarsh and inland     | Proportio                    | 0.01 (0.05)        |
|                           | rock   | n                            |                    |



## 2.3 Statistical modelling

155 Two main response variables were modelled: annual median DOC concentration and  $SUVA_{254}$ . Fitted  $SUVA_{254}$  values were subsequently used to derive  $pT_1$  according to Anderson et al. (2019) (Eq. 1).

$$pT_1 = \begin{cases} 0, & \text{if } SUVA_{254} < 1.8 \\ 0.1695 SUVA_{254} - 0.3051, & \text{if } 1.8 \leq SUVA_{254} \leq 7.7 \\ 1, & \text{if } SUVA_{254} > 7.7 \end{cases} \quad (1)$$

160 The response variables were screened for outliers, and values beyond six times the standard deviation were excluded from the dataset. Explanatory variables (Table 2) and response variables were checked for normality using Shapiro tests and transformations applied where appropriate. Models for annual median DOC concentration and  $pT_1$  were fitted using forward and backward multivariate linear regression to identify the best predictor suites. Models were tested for multicollinearity using analysis of the variance inflation factor (VIF). The best models were assessed mainly using minimal Akaike Information Criterion (AIC), although process understanding was applied to choose from models with similar AIC. The accuracy of model  
165 predictions of DOC concentration and  $pT_1$  was also assessed in relation to observations using Nash-Sutcliffe efficiency (NSE) (Nash and Sutcliffe, 1970, Eq. 2). In Eq. 2,  $m_i$  and  $o_i$  are  $i$ th of  $n$  simulated and observed values and  $\bar{o}$  denotes mean of observed values. Values of NSE fall into the range of  $-\infty$  and 1, where 1 is a perfect fit, and any positive value suggests the model is a better predictor than the mean of the observations.

$$NSE = 1 - \frac{\sum_{i=1}^n (o_i - m_i)^2}{\sum_{i=1}^n (o_i - \bar{o})^2} \quad (2)$$

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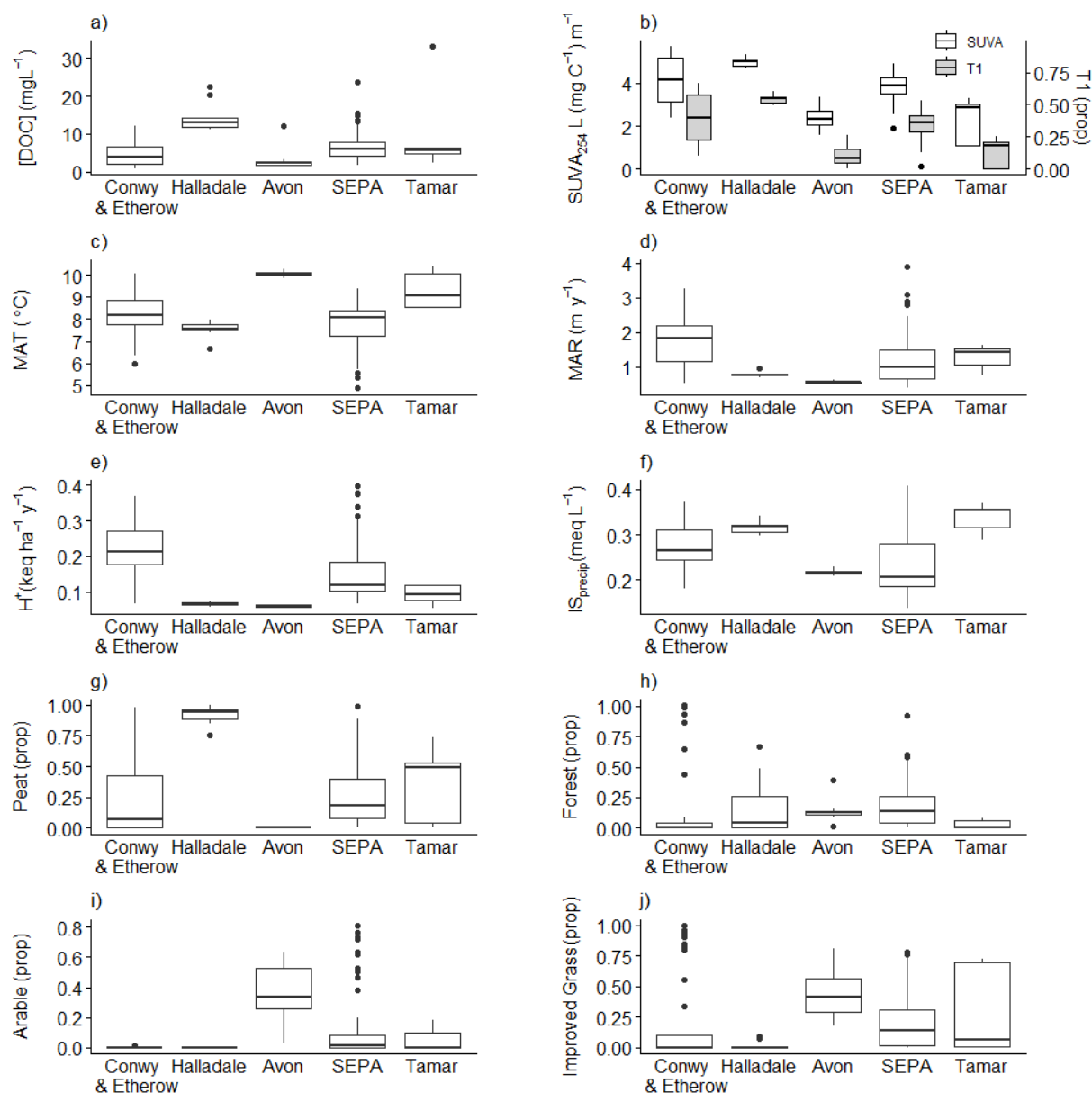
Models of annual medians were applied on a 1 km x 1 km grid for GB using available spatial data for 2017, as described in section 2.2. All analyses were performed in R v. 4.0.3 (R Core Team, 2021).



### 3 Results

#### 175 3.1 Patterns in response and explanatory variables

Variation among sites in annual means for DOC concentration,  $SUVA_{254}$ ,  $pT_1$  and selected explanatory variables shows the broad differences among sites in the different sampling campaigns (Table 2 and Figure 3). In these results, River Etherow data (single catchment) were grouped with data from the Conwy locations, since these exhibited comparable ranges of DOC concentration and  $SUVA_{254}$ . Halladale is a peat-dominated catchment, Avon is dominated by arable, and the other campaigns had more variable land-use compositions. The annual median DOC concentration spanned a range of 0.8 – 23.6 mg L<sup>-1</sup> with the greatest values mainly in the highly peaty Halladale headwaters. The annual median  $SUVA_{254}$  ranged from 1.0 - 5.7 L mg C<sup>-1</sup> m<sup>-1</sup>, resulting in a  $T_1$  fraction between 0 and 0.66 following Equation 1. The greatest  $SUVA_{254}$  values were observed in relatively peaty catchments in the Conwy, SEPA and Halladale sites.



185 **Figure 3** Ranges of response and explanatory variables: a) annual median DOC concentration (mg L<sup>-1</sup>); b) annual  
 190 annual median SUVA<sub>254</sub> (L mg C<sup>-1</sup> m<sup>-1</sup>); c) mean annual temperature, °C; d) mean annual runoff, m y<sup>-1</sup>; e) H<sup>+</sup> ion deposition,  
 keq ha<sup>-1</sup> yr<sup>-1</sup>; f) ionic strength of precipitation, meq L<sup>-1</sup>; g) peat area proportion of the catchment; h) forest area  
 proportion of the catchment; i) arable area proportion of the catchment (-); j) Improved Grassland area proportion of  
 the catchment (-). The boxplots show inter-quartile range (IQR) of the 25th and 75th percentiles and the whiskers  
 extend to the 1.5 \* IQR in each direction.



### 3.2 Model performance for DOC concentration and SUVA<sub>254</sub>

The best model for predicting annual median log(DOC concentration) (Eq. 3) included the effects of: peat area proportion (positive effect); mean annual runoff (negative effect), arable and horticulture area proportion (negative effect), wetland and moorland area proportion (negative effect) and ionic strength of precipitation (negative effect). This model explained 63% of the variance with a NSE of 0.71 but underestimated log(DOC concentration) for some campaigns (Figure 4a). An assessment of t-values showed that the factor that most affected log(DOC concentration) was peat area proportion, followed by MAR and arable land area proportion. The wetland and moorland area proportion contributed least to the variance explained (Table 3). Peatland and wetland-moorland variables were strongly correlated ( $\rho = 0.77$ , Appendix A Table A1), however multicollinearity analysis using the variance inflation factor (VIF) suggested only moderate multicollinearity (all VIF values < 3), providing no evidence that wetland and moorland areas must be excluded from the model.

$$\log([DOC]_a) = 1.12 + 1.66 p_{Peat} - 0.46 MAR - 1.19 p_{Arable} - 0.59 \log(IS_{precip}) - 0.57 p_{WetMoor} \quad (3)$$

**Table 3 Best linear regression model for natural log annual median DOC concentrations (Eq. 3,  $R^2 = 0.63$ ).**

| Parameter            | Coefficient | SE   | 95% CI         | t(144) | p-value | Reduction in variance explained if variable removed |
|----------------------|-------------|------|----------------|--------|---------|---|
| (Intercept)          | 1.12        | 0.24 | [ 0.65, 1.60]  | 4.67   | < .001  | -   |
| pPeat                | 1.66        | 0.17 | [ 1.32, 2.00]  | 9.63   | < .001  | 23%   |
| MAR                  | -0.46       | 0.05 | [-0.56, -0.36] | -9.05  | < .001  | 20%   |
| pArable              | -1.19       | 0.25 | [-1.70, -0.69] | -4.72  | < .001  | 5%  |
| log( $IS_{precip}$ ) | -0.59       | 0.16 | [-0.91, -0.27] | -3.69  | < .001  | 3%  |
| pWetMoor             | -0.57       | 0.18 | [-0.93, -0.21] | -3.15  | 0.002   | 2%  |

We have also explored increasing complexity of the model by including an interaction term between peatland area proportion and MAT, on the basis that the rate of microbial decomposition of organic matter is known to be temperature dependent, and



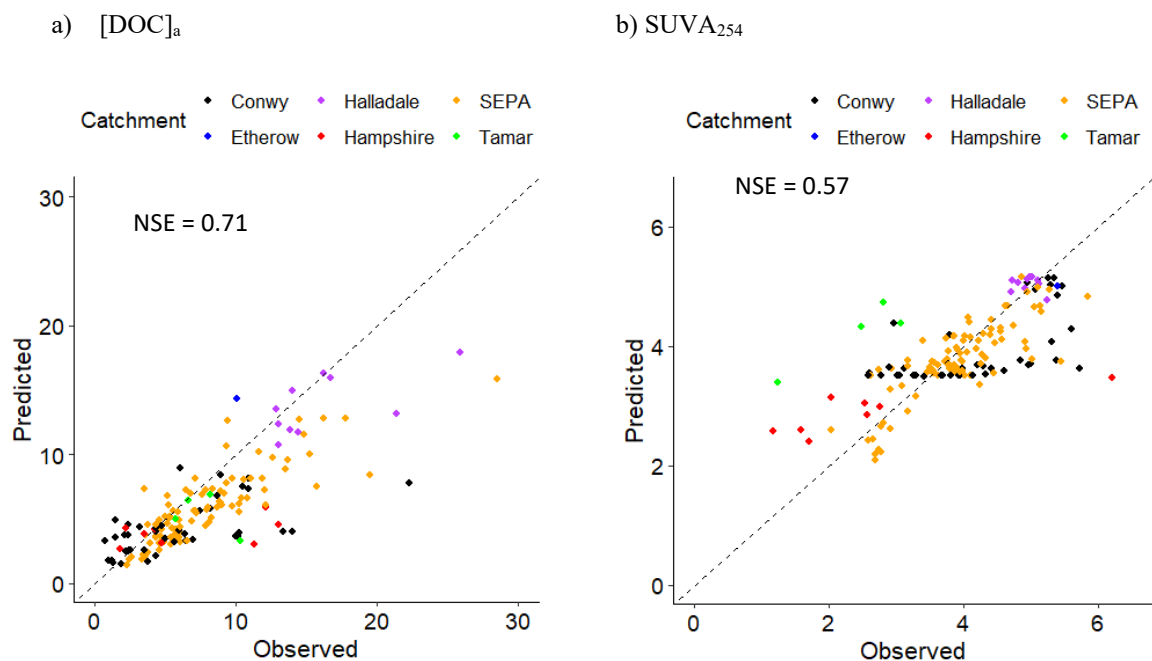
evidence this dependence is more sensitive in peats than in other soil types (Davidson and Janssens, 2006). This yielded an alternative model with an AIC value differing only fractionally from the selected model (Appendix A, Table A2).

210 The best model for predicting annual median  $SUVA_{254}$  (Eq. 4) included the effects of peatland area proportion (positive effect) and arable land (negative effect). This model explained 57% of the variance with NSE of 0.57 (Figure 4b). However, this model overestimated  $SUVA_{254}$  for the Tamar, and most of the Hampshire catchments. Peatland area proportion had the strongest effect on  $SUVA_{254}$ , followed by the arable land proportion (Table 4).

$$SUVA_{254} = 3.51 + 1.67 pPeat - 1.74 pArable \quad (4)$$

215 **Table 4 Best linear regression model for annual median  $SUVA_{254}$  (Eq. 4,  $R^2 = 0.57$ ).**

| Parameter   | Coefficient | SE   | 95% CI         | t(147) | p      | Loss of variance explained if term removed |
|-------------|-------------|------|----------------|--------|--------|--|
| (Intercept) | 3.51        | 0.08 | [ 3.35, 3.67]  | 43.80  | < .001 | -  |
| pPeat       | 1.67        | 0.17 | [ 1.34, 2.00]  | 9.97   | < .001 | 29%  |
| pArable     | -1.74       | 0.30 | [-2.33, -1.15] | -5.80  | < .001 | 10%  |

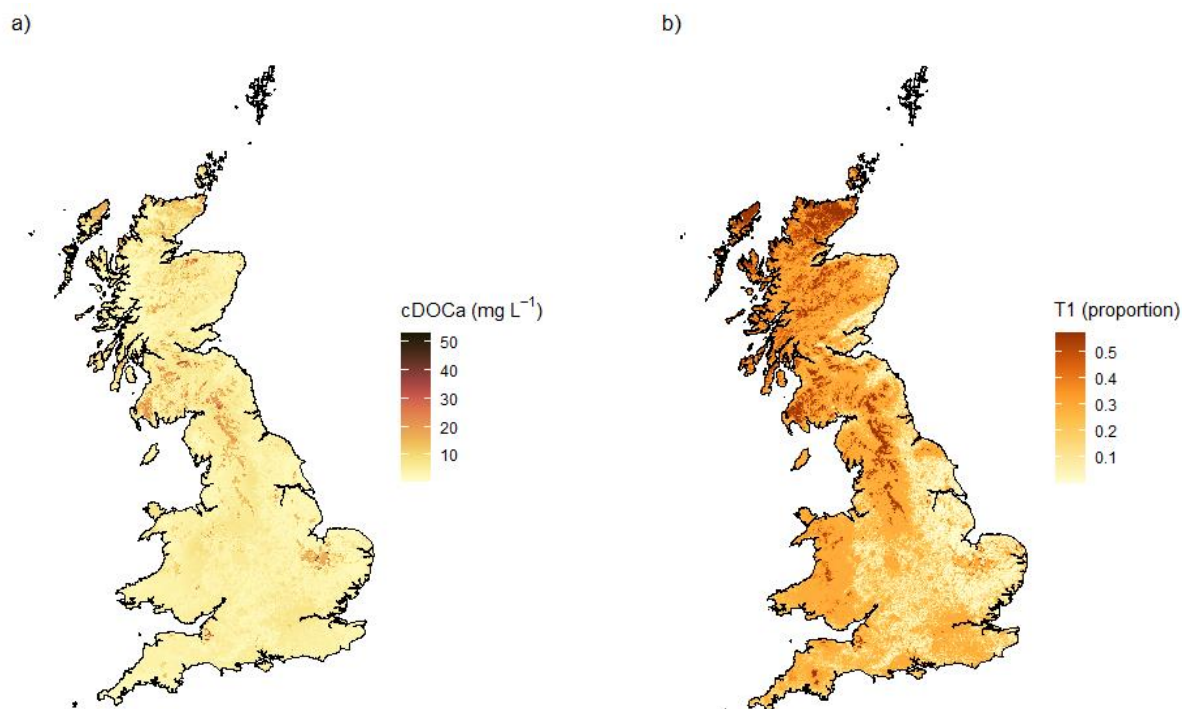


220 **Figure 4. Comparisons of observed and predicted transformed values: a) annual median [DOC] (mg/L); b) annual**  
**median SUVA<sub>254</sub> (L mg C<sup>-1</sup> m<sup>-1</sup>). NSE denotes Nash-Sutcliffe coefficient.**

### 3.3 Wider-scale calculation of DOC and its quality predictions

225 Application of the models using widely available data to a 1km x 1km GB grid indicated clear spatial patterns in the  
 concentrations and quality of DOC exported from the land to headwaters (Figure 5a). The highest DOC concentrations were  
 found in Southern Scotland, Northern England, and East Anglia. These are areas with high proportions of peat cover, but less  
 rainfall compared to areas further west and north, and hence less dilution of DOC. The relatively low predicted concentrations  
 in North-West Scotland and West Wales, despite extensive peatlands in these areas, most likely relate to high rainfall, although  
 high rates of sea-salt deposition is also likely to depress DOC release. By contrast, simulations suggest high DOC  
 230 concentrations in the peatland areas of East Anglia and the Somerset levels, where a low runoff rate limits dilution, and a low  
 sea-salt load results in comparatively more dissolution of DOC.

The highest proportion of the photolabile T<sub>1</sub> fraction was simulated in the North-West of Scotland, North England, central  
 Wales and locally in Dartmoor National Park in the south-west, which are all areas with a high peat area proportion in the  
 catchment and predominantly surface runoff generation (Figure 5b).



235 **Figure 5 National scale estimates of a) annual median DOC (mg L<sup>-1</sup>), b) T<sub>1</sub> fraction of DOC in 2017.**

## 4 Discussion

### 4.1 Controls on DOC quantity

240 The model selected to simulate annual DOC concentration pointed towards soil type, land use, hydrology and ionic strength of precipitation as the main controls on DOC entering streams from soils. Application of the model at national scale shows DOC concentrations that relate strongly to the geographical distribution of peatland cover and precipitation pattern (e.g. Williamson et al., 2021), while the effect of greater ionic strength implies that exposure to sea-salt deposition also plays a role (e.g. Sawicka et al., 2021). In this study, annual median concentrations of DOC were also influenced (negatively) by the occurrence of arable land.

245 Catchment peat area proportion is a particularly strong predictor for DOC concentrations in surface waters where peat soils occur (e.g. Creed et al., 2003; Hope et al., 1994; Larsen et al., 2011; Monteith et al., 2015; Weyhenmeyer and Karlsson, 2009).



This relationship could, intuitively, be considered to reflect the influence of the large stock of soil organic matter within these systems. However,  $^{14}\text{C}$  measurements suggest that DOC entering these waters is mainly derived directly from relatively recently produced organic matter, i.e. from recent primary production rather than from stored carbon in the organic soils (e.g. Tipping et al., 2012). In peat soils, much of the organic matter is situated within the hypoxic catotelm and there is little interaction of soil solution with the mineral subsoil. Therefore, high DOC concentrations, possibly reflect restricted opportunities for sorption and mineralisation of dissolved organic matter leached from roots and litter. Despite the focus on climatic impacts on DOC as a future driver of DOC trends (e.g. de Wit et al., 2021; Herreid et al., 2024; Monteith et al., 2023), we found no effect of MAT on DOC concentration and only a weak effect of the interaction term between peatland area proportion and MAT. The standard deviation in MAT in this dataset is considerably low ( $1.02^\circ\text{C}$ ) which could have effect on the “best” model selection not featuring MAT. The selection of a MAT x pPeat interaction in the alternative model hints that a thermal effect may have been more apparent if the dataset had spanned a wider temperature gradient.

Although the peatland and broader wet-moorland variables were derived from separate datasets, the peat class effectively represents a subset of the wider wet-moor category. This overlap means the model separates their influences even though wetlands are generally expected to enhance DOC export (Wei et al., 2021). Because peatland extent exerts a particularly strong positive effect on DOC, the model assigns most of the expected DOC-enhancing signal to peatlands. Once this dominant contribution is accounted for, the remaining wet-moor area—representing other wetland types—shows a negative association with DOC. This pattern likely reflects the contrasting characteristics of non-peat wetlands such as floodplains or mineral-soil wetland, which may be less oxygen-depleted and/or support more readily decomposable vegetation, leading to greater carbon retention or processing rather than export (Wang et al., 2024). Thus, the negative coefficient for the broader wet-moor class should be interpreted as the influence of these non-peat wetland environments, not as evidence that wetlands generally reduce DOC.

The arable area proportion of the catchment was negatively correlated with DOC concentration in our study, presumably because arable production in the UK is mainly located on well-drained soils with low organic matter content and leachate flow pathways through mineral subsoil (Yates et al., 2023), rather than this reflecting a direct relationship between crop type and DOC concentration. Yates et al. (2019) found low DOC:DON (dissolved organic nitrogen) and DOC:DOP (dissolved organic phosphorus) ratios in catchments dominated by arable farming, which is consistent with the wider literature (Aitkenhead-Peterson et al., 2009; Graeber et al., 2015; Heinz et al., 2015; Williams et al., 2016). Field drainage in many arable systems reduces contact time between water and soil organic material, and the removal of crop residues reduces the amount of such material, which both reduce organic matter dissolution rates (Mattsson et al., 2005; Palviainen et al., 2016).

Hydrological processes influence DOC in headwater systems through both direct and indirect pathways. Direct influences arise from changes in how long water remains in soils and from shifts in the pathways that transport DOC from soils to streams. In organo-mineral soils, DOC concentrations commonly rise with increasing discharge because flow paths transition from



baseflow moving through deeper mineral layers to stormflow traveling through surface organic horizons (McDowell and  
280 Likens, 1988). In peat soils, which typically contain higher DOC levels, the opposing effects of enhanced DOC mobilization  
and dilution during storm events can result in little or no overall change in DOC concentration (Clark et al., 2007; Eimers et  
al., 2008; Laudon et al., 2004). Hydrology also affects DOC indirectly by regulating soil moisture conditions that control  
biological production, biogeochemical processes, and chemical factors governing DOC solubility. For example, elevated DOC  
concentrations in peat pore waters have been observed following extended dry periods (Watts et al., 2001). In contrast, short-  
285 term lowering of the water table during droughts has been linked to reduced DOC concentrations, likely due to sulphide  
oxidation, increased acidity, and the resulting decrease in DOC solubility (Clark et al., 2005). Livestock grazing in the UK  
typically takes place on heavier and/or wetter soils than are used for arable, with lower inherent permeability. Intensive grazing  
generates soil compaction, promoting overland flow and near-surface flow pathways which rapidly deliver excreta to adjacent  
streams, meaning that DON and DOP flows predominate over mineral nutrient flows in catchments dominated by pasture  
290 (Lloyd et al., 2019). This is true of sites in the lower Conwy catchment, and in the Tamar and Sem sub-catchments of the  
Hampshire Avon and accounts for the patterns reported here.

The negative effect of runoff in the model was probably mainly due to a dilution effect, even though precipitation events  
facilitate the movement of DOC from organic horizons into the hydrological system, particularly in upland catchments such  
as the upper Conwy, Halladale and Etherow. Indeed, the organic-rich topsoils and peatlands typical of these upland catchments  
295 directly contribute to an increase in surface water DOC through overland and near surface interflow responses (Williamson et  
al., 2023). The overall effect of runoff in the model is presumably a combination of simple dilution (negative effect);  
dissolution of DOC concentration (positive effect); dilution of inorganic ions, decreasing dissolution of DOC concentration  
(negative effect); and increased proportion of flow from topsoil (positive effect). All these effects could usefully be  
incorporated in process-based ESMs.

The negative effect of ionic strength of precipitation represents a solubility control on DOC. Rising concentrations of DOC in  
300 surface waters have been consistently attributed to enhanced solubility of soil organic matter associated with post-acidification  
recovery, which is the only proposed mechanism showing consistent monotonic change across affected regions (de Wit et al.,  
2007; Erlandsson et al., 2011; Erlandsson et al., 2010; Evans et al., 2006; Futter et al., 2014; Monteith et al., 2014; Oulehle  
and Hruška, 2009; Sawicka et al., 2016). Long-term trends in DOC concentrations are inversely related to changes in acid  
deposition indicators, including sulphate and chloride levels in soils and surface waters (de Wit et al., 2021; Sawicka et al.,  
305 2021), as well as bulk acidity inputs (de Wit et al., 2007). These relationships are strongest in low-base cation systems  
(Monteith et al., 2007), such as the upland catchments examined in this study. In coastal regions previously affected by  
atmospheric contamination, such as western parts of the United Kingdom and southern and western Scandinavia, reductions  
in air pollution have shifted precipitation chemistry toward increasing dominance of ionic strength by sea salts (Tso et al.,  
310 2022). As a result, DOC solubility in upland drinking-water catchments in these areas is likely to become more responsive to

storm-driven variability in soil-water ionic strength linked to marine aerosol inputs (de Wit and Wright, 2008; Evans et al., 2005).

315 The solubility of higher molecular weight organic compounds is generally increased by complexation with protons and metal ions (Tipping and Hurley, 1988) and so the solubility of DOC is increasing in response to a reduction in soil acidity and/or soil water ionic strength (Monteith et al., 2023). These effects will be damped in alkaline to circumneutral catchments with higher buffering capacity (Edmunds W and Kinniburgh D, 1986) such as the Hampshire Avon and Tamar in this study, and overridden by direct fluxes of DOC to waters from anthropogenic sources such as livestock excreta, sewage effluent discharges and septic tank seepage (Lloyd et al., 2019; Yates et al., 2023; Yates et al., 2019; Yates et al., 2016). To improve predictions of DOC in lowland catchments, anthropogenic sources, such as biosolids, need to be taken into account explicitly, but a relatively simple model is sufficient to capture effects at broad scale.

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#### 4.2 Controls on DOC quality

The model selected as the best predictor of  $SUVA_{254}$  suggests that DOC quality depends predominantly on land cover, a finding also reported in rivers in North America (Hanley et al., 2013; Wollheim et al., 2015), the Arctic (O'Donnell et al., 2016) and Africa (Lambert et al., 2015). A model including only peatland and arable area proportions proved sufficient to explain most of the variation in DOC quality.

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Peat cover showed a strong positive relationship with  $SUVA_{254}$ , indicating that most DOC exported from peat-dominated catchments falls into the more aromatic category. Dissolved organic matter originating from histosols generally exhibits a high DOC:DON ratio and comprises complex molecules with high molecular weight, resulting in higher  $SUVA_{254}$  values (Weishaar et al., 2003). In the upper Conwy catchment, where blanket bog predominates, DOC:DON ratio, DOC:DOP ratio and  $SUVA_{254}$  values were shown to be positively correlated (Yates et al. (2019)). A large aromatic component and low nitrogen and phosphorus contents in DOM are typical where leachate from peat prevails (Lloyd et al., 2023; Yates et al., 2023). Comparable findings were shown in numerous studies into DOM composition draining peatlands across Europe (e.g. Broder et al., 2017; Mattsson et al., 2005).

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In contrast, arable land cover was negatively associated with  $SUVA_{254}$ . This suggests that DOC in waters draining arable systems tends to be less aromatic and more enriched in aliphatic or microbially derived compounds. Mineralisation rates are often greater in fertilised soils since decomposition is less limited by nutrient availability, promoting microbial processing and generating DOM with lower aromaticity (Graeber et al., 2012; Williams et al., 2010). As discussed above, arable soils also typically lack the slow-decomposing litter inputs that contribute to the accumulation of humic substances in forest and peat soils, further reducing the potential for aromatic DOC export. Similar effects of intensive land use on DOM aromaticity have been reported in temperate and boreal catchments (e.g. Lambert et al., 2015).

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The photolability of compounds is related to their optical properties (Hu et al., 2002). The  $T_1$  fraction consists of compounds that are typically strongly UV absorbing, aromatic, and relatively resistant to microbial decomposition, but are prone to removal from solution via sorption and co-precipitation. Conversely, the  $T_2$  fraction consists of compounds that are typically weakly absorbent or transparent to UV, non-aromatic, and not strongly subject to photo-oxidation, sorption or coprecipitation.

345 However, the molecular composition of DOM within UV absorbency classes is variable (Her et al., 2003) and the derivation of  $pT_1$  from  $SUVA_{254}$  data must be seen as an approximation, albeit a necessary one for earth-system modelling. Within the UniDOM framework (Anderson et al., 2019), water flows from topsoil are considered to export both  $T_1$  and  $T_2$ , while subsoil horizons are considered to export only  $T_2$  because aromatic compounds tend to be sorbed as they pass through soils. The  $SUVA_{254}$  model performed weakly for the Conwy subset where SUVAs are largely predicted to fall within a narrow range.

350 This suggests that the analysis is missing at least one important control on DOC quality. The relationship between  $T_1$  and  $SUVA_{254}$  is not precise and universal, and more studies are needed to quantify uncertainty associated with this relationship.

## 5 Conclusions

This study shows that both the magnitude and functional composition of DOC exported from soils to headwater streams can be predicted from widely available spatial datasets. Using simple statistical models based on land cover, soil type, hydrology and precipitation chemistry, we explained a substantial proportion of observed variation in DOC concentration (NSE = 0.71) and DOC quality, expressed via  $SUVA_{254}$  and the derived photoreactive fraction  $pT_1$  (NSE = 0.57). These results demonstrate that key controls on DOC operate consistently across a wide range of UK headwater catchments and can be captured without site-specific calibration.

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Across both models, peatland extent emerged as the dominant control on DOC dynamics. Catchments with higher peat coverage exported higher DOC concentrations and a greater proportion of  $T_1$ , confirming the central role of peat soils as sources of terrestrially derived organic matter. In contrast, arable land cover was consistently associated with lower DOC concentrations and less aromaticity, reflecting lower soil organic matter content and enhanced sorption and mineralisation in these systems. Hydrological factors, represented by runoff, and precipitation chemistry, represented by ionic strength, exerted additional controls, primarily through dilution and solubility mechanisms. Together, these findings highlight that soil type (particularly peat presence), land use, hydrology and atmospheric inputs jointly regulate both the quantity and quality of DOC exported from land to water.

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Application of the models at national scale reproduced realistic spatial patterns in DOC concentration and composition across Great Britain. High DOC concentrations and high proportions of the  $T_1$  fraction were predicted in peat-dominated regions, particularly in northern and western areas, while lower concentrations and less aromatic DOC were associated with mineral



370 soils and more intensively managed landscapes. These results support the robustness of the modelling framework and demonstrate its suitability for spatial extrapolation using gridded datasets.

The approach developed here has direct relevance for improving representation of lateral carbon fluxes in Earth System Models, which currently underrepresent land-to-ocean DOC transport. Given that DOC constitutes a substantial component of riverine carbon export, incorporating both DOC quantity and its functional composition into modelling frameworks is  
375 important for constraining carbon budgets and understanding downstream processing. In addition, the ability to predict DOC concentration and composition from widely available data provides a practical tool for applications such as assessing spatial variation in drinking water treatment challenges, where DOC concentration and aromaticity are key determinants of treatment cost and by-product formation.

While the primary aim of this study was to develop a simple, transferable modelling framework, the results also indicate  
380 potential directions for further refinement. For example, improved representation of anthropogenic influences (e.g. agricultural inputs or wastewater sources) and additional controls on DOC quality could enhance model performance in some catchments. However, any such extensions must balance increased complexity with the requirement for globally available input data if models are to remain applicable at large spatial scales.

Overall, this study demonstrates that the key features of soil-to-stream DOC export, including both quantity and functional  
385 composition, can be estimated using simple models driven by widely available data. In particular, it emphasises the dominant role of peatlands in controlling DOC fluxes and composition, and provides a practical pathway for incorporating these processes into regional to global assessments of carbon cycling.

#### **Code availability**

All R scripts used for this analysis are available on request.

#### **390 Data availability**

The dataset underpinning models fitting have been submitted for publication on Zenodo data repository (DOI:10.5281/zenodo.18701474).



### Author contributions

395 All authors contributed to the study conception and design. Data collation was performed by KS, ZM and AR. Material preparation and analysis were performed by KS. The first draft of the manuscript was written by KS and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

### Competing interests

The authors have no relevant financial or non-financial interests to disclose.

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## Appendix A

**Table A1 Pearson’s correlations coefficients between annual variables used in linear regression modelling.**

|                      | [DOC]    | SUVA <sub>254</sub> | MAT      | MAP      | MAR      | H <sup>+</sup> | NH <sub>4</sub> | nmS     | BC <sub>tot</sub> | CL <sub>tot</sub> | S <sub>tot</sub> | N <sub>tot</sub> | IS <sub>precip</sub> | pPeat    | pArable  | pForest  | pWetMoor | pAcid grass | pOther grass | pUrbanSuburb | pWater |  |
|----------------------|----------|---------------------|----------|----------|----------|----------------|-----------------|---------|-------------------|-------------------|------------------|------------------|----------------------|----------|----------|----------|----------|-------------|--------------|--------------|--------|--|
| [DOC]                |          |                     |          |          |          |                |                 |         |                   |                   |                  |                  |                      |          |          |          |          |             |              |              |        |  |
| SUVA <sub>254</sub>  | 0.60***  |                     |          |          |          |                |                 |         |                   |                   |                  |                  |                      |          |          |          |          |             |              |              |        |  |
| MAT                  | 0.01     | -0.34***            |          |          |          |                |                 |         |                   |                   |                  |                  |                      |          |          |          |          |             |              |              |        |  |
| MAP                  | -0.32*** | 0.15                | -0.40*** |          |          |                |                 |         |                   |                   |                  |                  |                      |          |          |          |          |             |              |              |        |  |
| MAR                  | -0.32*** | 0.15                | -0.42*** | 1.00***  |          |                |                 |         |                   |                   |                  |                  |                      |          |          |          |          |             |              |              |        |  |
| H <sup>+</sup>       | -0.45*** | 0.11                | -0.50*** | 0.90***  | 0.90***  |                |                 |         |                   |                   |                  |                  |                      |          |          |          |          |             |              |              |        |  |
| NH <sub>4</sub>      | -0.31*** | 0.08                | 0.11     | 0.59***  | 0.57***  | 0.56***        |                 |         |                   |                   |                  |                  |                      |          |          |          |          |             |              |              |        |  |
| nmS                  | -0.42*** | 0.08                | -0.1     | 0.71***  | 0.69***  | 0.76***        | 0.93***         |         |                   |                   |                  |                  |                      |          |          |          |          |             |              |              |        |  |
| BC <sub>tot</sub>    | -0.26**  | 0.19*               | -0.45*** | 0.89***  | 0.90***  | 0.84***        | 0.39***         | 0.52*** |                   |                   |                  |                  |                      |          |          |          |          |             |              |              |        |  |
| CL <sub>tot</sub>    | -0.25**  | 0.18*               | -0.45*** | 0.88***  | 0.89***  | 0.82***        | 0.36***         | 0.50*** | 1.00***           |                   |                  |                  |                      |          |          |          |          |             |              |              |        |  |
| S <sub>tot</sub>     | -0.38*** | 0.15                | -0.35*** | 0.93***  | 0.93***  | 0.93***        | 0.68***         | 0.81*** | 0.92***           | 0.91***           |                  |                  |                      |          |          |          |          |             |              |              |        |  |
| N <sub>tot</sub>     | -0.36*** | 0.06                | 0.06     | 0.62***  | 0.60***  | 0.61***        | 1.00***         | 0.95*** | 0.42***           | 0.39***           | 0.71***          |                  |                      |          |          |          |          |             |              |              |        |  |
| IS <sub>precip</sub> | 0.05     | 0.21**              | -0.21**  | 0.16*    | 0.17*    | 0.21*          | -0.04           | 0.02    | 0.55***           | 0.57***           | 0.38***          | -0.03            |                      |          |          |          |          |             |              |              |        |  |
| pPeat                | 0.68***  | 0.69***             | -0.22**  | 0.04     | 0.04     | -0.15          | -0.13           | -0.19*  | 0.13              | 0.13              | -0.02            | -0.16            | 0.26**               |          |          |          |          |             |              |              |        |  |
| pArable              | -0.22**  | -0.54***            | 0.33***  | -0.43*** | -0.43*** | -0.38***       | -0.26**         | -0.27** | -0.49***          | -0.50***          | -0.46***         | -0.25**          | -0.48***             | -0.35*** |          |          |          |             |              |              |        |  |
| pForest              | 0.09     | 0.04                | 0.17*    | 0.03     | 0.03     | 0.02           | 0.13            | 0.07    | -0.08             | -0.08             | -0.02            | 0.13             | -0.18*               | -0.12    | -0.09    |          |          |             |              |              |        |  |
| pWetMoor             | 0.42***  | 0.59***             | -0.30*** | 0.04     | 0.04     | -0.05          | -0.04           | -0.04   | 0.1               | 0.1               | 0.03             | -0.04            | 0.20*                | 0.77***  | -0.29*** | -0.24**  |          |             |              |              |        |  |
| pAcid grass          | -0.24**  | 0.13                | -0.45*** | 0.54***  | 0.54***  | 0.54***        | 0.22**          | 0.32*** | 0.63***           | 0.63***           | 0.58***          | 0.23**           | 0.39***              | -0.02    | -0.33*** | -0.34*** | -0.21*   |             |              |              |        |  |
| pOther grass         | -0.07    | -0.39***            | 0.56***  | -0.43*** | -0.44*** | -0.38***       | -0.1            | -0.19*  | -0.46***          | -0.45***          | -0.39***         | -0.12            | -0.16*               | -0.41*** | 0.13     | -0.13    | -0.38*** | -0.44***    |              |              |        |  |
| pUrbanSuburb         | -0.04    | -0.20*              | 0.11     | -0.20*   | -0.20*   | -0.14          | -0.12           | -0.09   | -0.26**           | -0.26**           | -0.21**          | -0.12            | -0.26**              | -0.17*   | 0.11     | 0        | -0.16    | -0.19*      | 0.08         |              |        |  |
| pWater               | 0.05     | -0.06               | -0.08    | -0.05    | -0.05    | -0.06          | -0.28***        | -0.24** | 0.02              | 0.02              | -0.1             | -0.28***         | 0.11                 | 0.02     | -0.1     | 0.08     | -0.06    | 0.03        | -0.1         | -0.06        |        |  |
| pOther               | -0.25**  | -0.13               | -0.49*** | 0.36***  | 0.37***  | 0.40***        | 0.1             | 0.20*   | 0.34***           | 0.35***           | 0.34***          | 0.13             | 0.07                 | -0.15    | -0.09    | -0.14    | -0.03    | 0.20*       | -0.17*       | -0.05        | -0.07  |  |



**Table A2 Alternative linear regression model for natural log annual median DOC concentrations ( $R^2 = 0.63$ ).**

| Parameter   | Coefficient | SE   | 95% CI         | t(142) | p-value |
|-------------|-------------|------|----------------|--------|---------|
| (Intercept) | 2.79        | 0.45 | [ 1.90, 3.67]  | 6.22   | < .001  |
| pPeat       | -2.22       | 1.24 | [-4.66, 0.23]  | -1.79  | 0.075   |
| MAT         | -0.18       | 0.05 | [-0.29, -0.08] | -3.47  | < .001  |
| MAR         | -0.45       | 0.06 | [-0.56, -0.33] | -7.64  | < .001  |
| Forest      | 0.91        | 0.18 | [ 0.55, 1.27]  | 5.03   | < .001  |
| Acid grass  | 0.4         | 0.16 | [ 0.09, 0.71]  | 2.54   | 0.012   |
| Other Grass | 0.84        | 0.2  | [ 0.45, 1.23]  | 4.26   | < .001  |
| pPeat × MAT | 0.49        | 0.16 | [ 0.18, 0.80]  | 3.15   | 0.002   |



**Table A3 Comparison of laboratory methods used to derive dissolved organic carbon (DOC) and absorbance data across the campaigns.**

|  | <b>SEPA</b> | <b>Conwy</b>   | <b>Etherow</b>                        | <b>Halladale</b>                      | <b>Tamar</b>                          | <b>Hampshire Avon</b>                 |
|--|-------------|--|---------------------------------------|---------------------------------------|---------------------------------------|---------------------------------------|
| <b>DOC laboratory</b>  | *           | UKCEH<br>Lancaster   | UKCEH<br>Lancaster                    | UKCEH<br>Lancaster                    | UKCEH<br>Lancaster                    | University of<br>Bristol              |
| <b>Absorbance laboratory</b>   | *           | Wolfson<br>Carbon<br>Capture Lab,<br>Bangor<br>University  | UKCEH<br>Lancaster                    | British<br>Geological<br>Survey       | British<br>Geological<br>Survey       | University of<br>Bristol              |
| <b>Filtration - filter material</b>                                  | *           | cellulose<br>nitrate filters   | cellulose<br>acetate filters          | cellulose<br>acetate<br>filters       | cellulose<br>acetate filters          | cellulose<br>nitrate filter           |
| <b>Filtration - pore size</b>  | *           | 0.45 µm  | 0.45 µm                               | 0.45 µm                               | 0.45 µm                               | 0.45 µm                               |
| <b>DOC - analysis method,<br/>DOC determined as non-purgeable OC</b> | *           | Pt-catalysed<br>combustion at<br>720°  | Pt-catalysed<br>combustion at<br>720° | Pt-catalysed<br>combustion<br>at 720° | Pt-catalysed<br>combustion at<br>720° | Pt-catalysed<br>combustion at<br>720° |
| <b>DOC - instrument name</b>   | *           | Shimadzu<br>TOC-L  | Shimadzu<br>TOC-L                     | Shimadzu<br>TOC-L                     | Shimadzu<br>TOC-L                     | Shimadzu<br>TOC-L                     |
| <b>Absorbance - cuvette path length</b>                              | *           | UVIKON<br>943 - 1cm<br>(2007-2009)<br>Molecular<br>device<br>Spectramax<br>M2e (2010-<br>2016) - | 1cm                                   | 1cm                                   | 1cm                                   | 1cm                                   |



|                                     |   |   |                                   |                                     |                                     |                                     |
|-------------------------------------|---|---|-----------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|
|                                     |   | microplate reader   |                                   |                                     |                                     |                                     |
| <b>Absorbance - instrument name</b> | * | UVIKON 943 (2007-2009)<br>Molecular device Spectramax M2e (2010-2016) | Agilent Cary 60 spectrophotometer | Cary Eclipse 60 UV-Vis spectrometer | Cary Eclipse 60 UV-Vis spectrometer | Cary Eclipse 60 UV-Vis spectrometer |

\* SEPA has suffered a cyber-attack in 2020 during which they lost all their data and documentation (SEPA, 2026)