Drivers of inter- and intra-annual variability of dissolved organic carbon concentration in the River Thames between 1884 and 2013

Running title

Century-long rise in fluvial DOC variability

Valentina Noacco[1*], Christopher J. Duffy[2], Thorsten Wagener[1,3], Fred Worrall[4], Matteo Fasiolo[5] and Nicholas J. K. Howden[1,3]

[1] Department of Civil Engineering, University of Bristol, Bristol, BS8 1TR, UK,

[2] Department of Civil and Environmental Engineering, Penn State University, PA 16802, USA,

[3] Cabot Institute, University of Bristol, Bristol, BS8 1UJ, UK,

[4] Department of Earth Sciences, Durham University, Durham, DH1 3LE, UK.

[5] School of Mathematics, University of Bristol, BS8 1TW, UK.

[*] valentina.noacco@bristol.ac.uk

Acknowledgments

This work was supported through grants from NERC (1678985), the University of Bristol Cabot Institute, and a University of Bristol doctoral studentship award.

This article has been accepted for publication and undergone full peer review but has not been through the copyediting, typesetting, pagination and proofreading process which may lead to differences between this version and the Version of Record. Please cite this article as doi: 10.1002/hyp.13379

Abstract

The World's longest record of river water quality (River Thames – 130 years) provides a unique opportunity to understand fluvial dissolved organic carbon (DOC) concentrations dynamics. Understanding riverine DOC variability through long-term studies is crucial to capture patterns and drivers influencing sources of DOC at scales relevant for decision making. The Thames basin (UK) has undergone massive land-use change, as well as increased urbanisation and population during the period considered. We aimed to investigate the drivers of intra-annual to interannual DOC variability, assess the variability due to natural and anthropogenic factors, and understand the causes for the increased DOC variability over the period. Two approaches were used to achieve these aims. The first method was singular spectrum analysis, which was used to reconstruct the major oscillatory modes of DOC, hydroclimatic variables and atmospheric circulation patterns, and to visualise the interaction between these variables. The second approach used was generalized additive modelling, which was used to investigate other non-natural drivers of DOC variability. Our study shows that DOC variability increased by 80% over the data period, with the greatest increase occurring from the beginning of World War II onward. The primary driver of the increase in DOC variability was the increase in the average value of fluvial DOC over the period of record, which was itself linked to the increase in basin population and diffuse DOC sources to the river due to land-use and land-management changes. Seasonal DOC variability was linked to streamflow and temperature. Our study allows to identify drivers of fluvial intra-annual and interannual DOC variability, and therefore empowers actions to reduce high DOC concentrations.

Keywords:

Dissolved organic carbon (DOC)

Interannual variability

Singular spectrum analysis (SSA)

Generalized additive model (GAM)

Thames basin

Hydroclimate

Sewage effluents

Land-use change

1. Introduction

The flux of DOC from land to the ocean constitutes an important component of the global carbon cycle (Cole *et al.*, 2007; Battin *et al.*, 2009). Increased DOC in inland waters can be an indication of reduced carbon storage in terrestrial reserves or of increased carbon sources in the form of fertilisers, wastewater and other direct inputs to the landscape (Worrall *et al.*, 2004b; Butman *et al.*, 2014). Once it has reached the river network, fluvial DOC can be degassed to the atmosphere, contributing to carbon dioxide emissions (Moody *et al.*, 2013). Increases in freshwater DOC concentration have been observed throughout the northern hemisphere (Monteith *et al.*, 2007), causing concern for so-called "global browning" of rivers (Roulet & Moore, 2006; Oosthoek, 2016). Moreover increased fluvial DOC constitutes a cost for water companies, as water requires additional pre-treatment before chlorination to avoid the formation of carcinogenic by-product compounds (Hsu *et al.*, 2001; Worrall & Burt, 2005).

Most studies have investigated the drivers of fluvial DOC trends (Worrall and Burt, 2004, 2007a; Monteith *et al.*, 2007; Finstad *et al.*, 2016), rather than its short-term variability. Recent synthesis studies have highlighted the contribution of anthropogenic activities to the increase in fluvial DOC (Bauer *et al.*, 2013; Regnier *et al.*, 2013; Butman *et al.*, 2014; Noacco *et al.*, 2017a). Nonetheless there are still gaps in our understanding as to how fluvial DOC dynamics from seasonal to decadal scales are impacted by anthropogenic activities and by climate variability, as highlighted by Tian *et al.* (2015a). This limitation could be due to the short length of most DOC records. A small number of studies had the possibility of considering records earlier than the 1960s (see references in Filella & Rodríguez-Murillo, 2014), and this hampers the identification and attribution of long-term oscillations.

There are several reasons why it is important to investigate drivers of DOC variability in aquatic systems. Firstly, high DOC levels can affect aquatic life (Kullberg *et al.*; Karlsson *et al.*, 2009; Woollings *et al.*, 2015) due to light attenuation, and drinking water treatability (Eikebrokk *et al.*, 2004; Ledesma *et al.*, 2012; Zeng and Arnold, 2014). Intra-annual (Winterdahl *et al.*, 2014; Hytteborn *et al.*, 2015) to interannual (Erlandsson *et al.*, 2008) DOC variability can exceed long-term trends in magnitude. Given that rapid and large variations in DOC concentration can lead to high DOC levels for brief periods, short-term changes can have effects as detrimental as long-term DOC increase. Long-term studies such as the present one which investigate interannual as well as intra-annual variability are essential to capture patterns and drivers influencing sources of DOC at the relevant temporal scales (Köhler *et al.*, 2008). In the specific, long-term climate records allow the examination of long-term variations in fluvial DOC, which in turn allow the putting of short-term observations into the right context (Botta, 2002). In fact, parts of long-term oscillations, due for example to teleconnections, could be misinterpreted as short-term trends, or natural variability could mask the effect of human activities (Burt *et al.*, 2008; Burt and Howden, 2013; Hannaford *et al.*, 2013). Our study aims to understand the links between teleconnections and DOC variability, and to separate the stationary signals from the non-stationary ones, which will enable the forecasting of the impact they will have on future water quality (Adrian *et al.*, 2009). Moreover, identifying the natural baseline of DOC variability allows the detection of early warning signs of a deteriorating aquatic environment and to provide evidence for policy-makers to steer towards more effective policy interventions (Burt *et al.*, 2008; Putro *et al.*, 2016), in view of achieving good ecological status under the EU Water Framework Directive (WFD) (European Union, 2000). Finally, gaining insights on the drivers of the variability of carbon exports to the ocean, both natural and anthropogenic, will allow the appraisal of the best management options to limit detrimental impact on the environment and to better understand the future sustainability of catchments exposed to human activities (Tian *et al.*, 2015a).

In this study we investigate the drivers of DOC variability in the Thames basin. The Thames basin (UK) has undergone important historical changes, including the expansion of agricultural practices (e.g. extensive ploughing of grassland into arable land, introduction of widespread mechanization and land drainage (Howden *et al.*, 2010; 2013)) and an increase of urbanisation and population, for over a century. These changes have caused an increase of fluvial DOC concentration throughout the 20th century (Noacco *et al.*, 2017a), while DOC variability has risen. Nonetheless the drivers of increased DOC levels might be different from those of increased DOC variability. The Thames basin offers a unique opportunity to investigate the relationship between hydroclimatic variability and DOC concentrations, as it is the longest fluvial DOC concentration record in the World (1884-2014, (Noacco *et al.*, 2017a)). Furthermore, the length of the record and the observed long-term changes in the basin land use and population make it possible to investigate the influence of hydroclimatic variability in comparison to long-term changes due to anthropogenic forcing.

Large-scale teleconnections (i.e. spatially and temporally large-scale anomalies that influence the variability of the atmospheric circulation, such as El Niño/Southern Oscillation (ENSO), North Atlantic Oscillation (NAO) (NOAA, 2017)) are known to affect regional hydrological regimes (Zanchettin *et al.*, 2008; Burt & Howden, 2013; Kosanic *et al.*, 2014). Therefore the study of the connections between large-scale climate patterns and catchment-scale precipitation and streamflow is essential to furthering our understanding of hydroclimatological processes (Kingston *et al.*, 2009). The subsequent connection to basin carbon dynamics has seldom been considered. Assessing causality between atmospheric circulation patterns and streamflow or precipitation is complicated by the fact that multiple circulation patterns may be influential in the same region (Kingston *et al.*, 2006; Hannaford & Marsh, 2008).

Our hypothesis is that the increase in fluvial DOC variability in the Thames basin in the 20th century was due to hydroclimatic variability, influenced in turn by the variability of atmospheric circulation patterns. The aims of this study were to: (1) test if atmospheric circulation patterns, such as NAO and ENSO, influence the hydroclimatic variability (in the form of temperature, rainfall and streamflow) in the Thames basin; (2) test if the hydroclimatic variability in turn influences the intra-annual to interannual variability of DOC; and (3) estimate the contribution of anthropogenic drivers to DOC variability. A systematic study of the drivers of fluvial DOC variability enables us to assess the magnitude of naturally and anthropogenically driven DOC variability and to investigate the drivers of the century-long increase in DOC variability. Moreover, our study is the first to quantify both the amount of DOC variability that can be predicted with the available data and the amount of DOC variability that cannot be predicted with the available variables. The former allows the forecast of fluvial DOC concentrations in the future, if conditions do not change, while the latter highlights the conditions in which high DOC variability is expected, therefore elucidating the conditions where further measurements are needed to investigate the sources of DOC. This in turn will aid future efforts to detect signs of deteriorating water quality.

2. Review of teleconnections, hydroclimatic factors and human impacts on DOC

A range of drivers can impact fluvial DOC variability, both natural (teleconnections and hydroclimatic factors) and anthropogenic, direct and indirect. Organic carbon concentrations in streams is known to have seasonal and interannual variability, due to climate variability (Köhler *et al.*, 2008). Teleconnections, with their oscillatory components, can influence DOC variability indirectly, by influencing hydroclimatic patterns. Teleconnections, given their long-distance range of influence, provide a useful framework to link carbon fluxes to climate variability, as they include covariability patterns between different climate factors over different time scales (Hallett *et al.*, 2004). In this study, we aim to investigate the effects of intra-annual to interannual variability of the hydroclimate on DOC variability, therefore periodic oscillations such as the atmospheric circulation patterns are considered. A literature review of the main drivers, direct and indirect, of DOC variability is provided.

The North Atlantic Oscillation is the most important mode of climatic variability in the northern hemisphere. It has a decadal-scale variability (Woollings *et al.*, 2015). In the UK the effect of NAOI was found to be weak in the lowlands. Nonetheless in southern Britain a statistically significant negative correlation with precipitation was found in summer (Burt & Howden, 2013), and in winter (Wilby *et al.*, 1997). These weak correlations in southern Britain compared to the western part could be due to catchments in the south being more sheltered from westerly winds and from moisture-laden air flows coming westerly from the North Atlantic, and to the permeable geology of these basins, which dampens the climate signal variability on river flow (Lavers *et al.*, 2010).

El Niño/Southern Oscillation (ENSO) is the most prominent global mode of climate variability (Tsai *et al.*, 2015; Bonan, 2016; Zhu *et al.*, 2017). ENSO has a low-frequency oscillatory component of around 5-7 years, and a near two-year component (Ghil & Vautard, 1991). ENSO has been found to positively influence precipitation in the UK, especially during winter (Mariotti *et al.*, 2002). In winter and spring, a warm event causes anomalous moisture from the subtropical Atlantic to be channelled away from western Europe toward higher latitudes, where positive rainfall anomalies are found (Mariotti *et al.*, 2002). Most studies have found that ENSO does not influence the hydroclimate in the UK (Pozo-Vázquez *et al.*, 2005; Davey *et al.*, 2014), therefore strong effects on DOC are unlikely. Nonetheless, this study aims to investigate how the intra-annual to interannual variability of the hydroclimate influences DOC variability, therefore understanding how periodic oscillations, such as the atmospheric circulation patterns, affect hydroclimatic variability will allow to elucidate the effect on DOC as well.

Hydroclimatic factors are known to influence the production, transport and transformation of DOC (Tian *et al.*, 2015b), even though a mechanistic description of DOC production and transport in the landscape is incomplete (Winterdahl *et al.*, 2016). Temperature influences DOC production, as higher temperatures affect the metabolism of trees and microbes, and increase the activity of soil microorganisms which decompose organic matter, which in turn increases the production of DOC in leachate (Gillooly, 2001; Wallenstein and Weintraub, 2008; Winterdahl *et al.*, 2016). DOC mobilization is influenced by temperature (Christ & David, 1996; Neff & Hooper, 2002; Winterdahl *et al.*, 2011), as well as by precipitation (Clark *et al.*, 2009; Laudon *et al.*, 2012). Temperature influences the production and decay of potentially mobile organic matter between rainfall events by controlling microbial activity. Temperature also regulates dissolved organic matter (DOM) dissolution and desorption, although the sensitivity of these physiochemical processes to temperature changes is poorly known. Quantities of DOM mobilised in response to rainfall increase with temperature and decrease with rainfall intensity and frequency (Xu and Saiers, 2010). The hydrology of a catchment impacts DOC both directly and indirectly. It has a direct influence on the soil residence time and on the transport of DOC from soil to river (Clark *et al.*, 2010). DOC is further influenced indirectly by the soil water content, which affects the biological production and/or biogeochemical cycling and chemical controls on solubility (Clark *et al.*, 2010). Both seasonal and interannual variations in DOC concentrations are typically dominated by variations in temperature and precipitation (Clark *et al.*, 2010). Erlandsson *et al.* (2008) investigated the interannual variability of organic matter in 28 Scandinavian basins with mainly agricultural, forest and alpine land cover over 35 years and found the variability of streamflow and sulphate to be the most important drivers. Tian *et al.* (2015a) found interannual climate variability to dominate variability of C export from eastern North America to the Atlantic Ocean over the 20th century. Correlation between river discharge and river carbon fluxes indicated that carbon export is mainly limited by water availability, instead of DOC production and export. Tian *et al.* (2015b) considered the drivers for C variability in the Mississippi River basin in the 2000s and found climate variability as well as floods and droughts to be most influential for interannual variability. Leach *et al.* (2016) found annual precipitation to account for most of the variability of C export in a Swedish catchment over a 12-year period.

In addition to hydroclimatic factors, changes in land use, land management, anthropogenic atmospheric CO_2 concentration (Tian et al., 2015b), and sulphur deposition (Clark *et al.*, 2005; Monteith *et al.*, 2007) can also influence fluvial DOC variability. Land use changes, including the increase in urban area, can impact DOC export directly and indirectly. The direct effect occurs by increasing DOC production (e.g. by increasing sewage effluents and combined sewer overflows), and indirectly by altering the hydrological regime of a catchment, through changes in the hydrological properties of the soil and vegetation (Farley et al., 2005; Piao et al., 2007). Changes in land management practices, due to ploughing, fertilisation and irrigation can also greatly impact fluvial carbon exports as well (Raymond, 2003; Oh and Raymond, 2006).

3. Methodology

3.1 Study area

The River Thames basin is a temperate lowland catchment located in southeast England. It drains a 9,948 km^2 mineral soil dominated catchment, from its source in the Cotswold Hills to its tidal limit at Teddington Lock upstream of London (Marsh & Hannaford, 2008; Bowes *et al.*, 2016). It has a large urban population, that has grown four-fold since the 1880s (rising from less than 1 to 3.7 million in 2007). It also provides two-thirds of London's drinking water, with an urban area of just over 1,700 km^2 (Environment Agency, 2009). Moreover it has many sewage treatment works (STW), related to its high population density (ca. 960 people km^{-2}) (Merrett, 2007). Tertiary wastewater treatment has been installed at the 36 largest STW (serving approximately 2.7 million people) upstream of the tidal limit since 2003 (Kinniburgh & Barnett, 2009). In spite of the high population density, the Thames basin upstream of London is predominantly rural, especially in the upland part (Environment Agency, 2009). The Thames basin is mostly underlain by Cretaceous Chalk, with areas of limestone, mudstones, sandstones, and Oxford clay (Howden *et al.*, 2011).

3.2 Data used

3.2.1 Hydroclimatic and teleconnections

Average monthly temperature (°C) and total monthly rainfall (mm) data were available for Oxford (Figure 1), which is centrally located within the basin, from 1853 (UK Meteorological Office – https://www.metoffice.gov.uk/public/weather/climate-historic/#?tab=climateHistoric). The mean annual temperature and rainfall is 10.1 °C and 652.7 mm (1884-2013, standard deviation 0.7 °C and 114.1 mm), respectively. Continuous gauged mean daily river flow records (m^3 s^{-1}) were available at the basin outlet at Teddington Weir from 1883, with mean annual flow of 65.5 m^3 s^{-1} (1884-2013, standard deviation 26.7 m^3 s^{-1}) (National River Flow Archive – https://nrfa.ceh.ac.uk/data/station/meanflow/39001- Figure 1). The NAOI was obtained as monthly indices from the NOAA Earth System Research Laboratory (https://www.esrl.noaa.gov/psd/gcos_wgsp/Timeseries/NAO/ - Figure 1). In this study the Bivariate EnSo Timeseries ("BEST" ENSO index) 1-month running mean was used (Figure 1), which combines an atmospheric component of the ENSO phenomenon (the Southern Oscillation Index or "SOI") and an oceanic component (Nino 3.4 sea surface temperature (SST), which is defined as the SST averaged over the region 5N-5S and 170W to 120W). The inclusion of the SOI, which is better measured historically, reduces the effect of biases due to the reconstruction of the SST data (Smith and Sardeshmukh, 2000). This index was obtained from NOAA Earth System Research Laboratory (http://www.esrl.noaa.gov/psd/people/cathy.smith/best/#values).

3.2.2 DOC concentration data

Water colour data and DOC concentration (mg l^{-1}) measurements (> 20,000 samples) (Figure 1 in Noacco *et al.* (2017)) were made for the Thames at Hampton (51.42°N, 0.37°W) and at Teddington (51.43° N, 0.33° W). DOC measurements were not available throughout the period, but for some periods both DOC and colour were available, therefore calibration curve between DOC and water colour was constructed, as in Worrall & Burt, (2007b). A review of the methods for measuring colour (1883 to 1990) and DOC (1990 to 2013) and the calibration of DOC from colour measurements is provided in Appendix A and Noacco *et al.* (2017), while information on water colour and DOC sources is provided in Table 2 in Noacco *et al.* (2017). The monthly DOC data are available at https://doi.org/10.5285/57943561-4587-4eb6-b14c-7adb90dc1dc8 (Noacco *et al.*, 2017b). A statistical analysis of the impact of the change in analytical techniques is provided in Noacco *et al.* (2017).

3.3 Singular Spectrum Analysis (SSA)

SSA was used to extract the dominant frequency oscillations from the time series and to estimate the variability associated with each frequency component (Vautard *et al.*, 1992). SSA is closely related to Empirical Orthogonal Function (EOF) (Kumar & Duffy, 2009) and to principal component analysis in the lag time domain (Hanson *et al.*, 2006). SSA is a data-driven, model-free method, and does not require stationarity (Vautard *et al.*, 1992; Golyandina & Zhigljavsky, 2013) or normality of the time series, and requires minimal statistical or data structure assumptions (Marques *et al.*, 2006; Wang *et al.*, 2015). Moreover SSA can reconstruct the original data with a minimum of independent oscillatory modes (Priestley & Priestley, 1981). SSA is based on the idea of sliding window over a time series to search for patterns, in order to extract the maximum variance with the minimum number of independent components (Kumar & Duffy, 2009). A detailed description of SSA can be found in Vautard *et al.*, (1992), but a brief description is provided in Appendix B.

SSA has been applied in a range of disciplines, including digital signal processing, nonlinear dynamics, climate, oceanography, medicine and mathematical statistics (Vautard *et al.*, 1992; Marques *et al.*, 2006), as well as hydrology (Lisi *et al.*, 1995; Sivapragasam *et al.*, 2001; Marques *et al.*, 2006). SSA can also be applied to detrend data to remove anthropogenic influences.

The reconstructed mean monthly DOC (mg l^{-1}), mean monthly streamflow (Q) (m^3s^{-1}), total monthly precipitation (P), mean monthly temperature (T) (°C), monthly ENSO and monthly NAO indices, were plotted in Figure 2 (details in Appendix B). The reconstructed data was then plotted as a "hydro-geo-climatic" phase plane, where time series triplets were plotted together in a 3-D parametric plot with time implicit trajectories. Before plotting, each reconstructed time series was normalized by subtracting the mean and rescaling by its respective range (Kumar & Duffy, 2009) to facilitate comparison

$$\hat{X}(t) = \frac{\hat{x}(t) - \hat{x}_{min}}{\hat{x}_{max} - \hat{x}_{min}} \quad (1)$$

$\hat{X}(t)$ represents the normalized variables $\widehat{DOC}, \hat{Q}, \hat{P}, \hat{T}, \widehat{ENSO}\ or\ \widehat{NAO}'s$ at time t; $\hat{x}_{max}$ and $\hat{x}_{min}$ are the maximum and minimum of the time series over their record length (1884-2013).

Phase plane plots (Figures 3-6) help to visualise whether the modes of oscillation of DOC interact or co-vary with those of hydroclimatic variables, and if the oscillatory components in atmospheric circulation patterns interact with those of hydroclimatic variables, which could then influence DOC indirectly (Figures S1-3 show a simplified version, where only three years are plotted). These graphs also provide an index of the dynamic behaviour of the atmosphere-terrestrial-climatic system.

The planar projections of the phase plane plots in the ENSO-Q and DOC-Q planes were analysed for two time periods: 1884 to 1937 and 1938 to 1989, to elucidate the behaviour of DOC and ENSO, and to understand their relationships with streamflow pre- and post-1938 (Figure 5). The variability in two seasons is highlighted as an example through histograms: in winter (December-February), when the catchment experiences peak flows, and in summer (June-August), characterised by the lowest flows.

3.4 Generalised Additive Models

GAM is a semi-parametric additive modelling technique where the impact of the covariates on the predicted variable is captured through smooth functions, which can be nonlinear. GAM is a generalization of multiple regression, which is also additive, but the linear responses are replaced by nonparametric functions with multiple parameters (i.e. the effects are not assumed to have a predetermined shape, such as linear, quadratic, etc., and it is not important to interpret the coefficients of the effects). GAMs are different from linear models because they are data-driven, and the shape of the response curves are determined by the data, instead of choosing an *a priori* parametric model (Hwang *et al.*, 2016). GAM has various advantages, which include that it is easy to interpret; it can uncover hidden patterns in the data (relationships between independent and dependent variable are not assumed to be linear) since it uses flexible predictor functions; it avoids over-fitting since the predictor functions are regularized (i.e. it imposes a penalty to control the "wiggliness" of the smooth effects (Wood, 2004)); and it strikes a balance between the interpretable (but biased) linear model, and the extremely flexible, "black box" learning algorithms (Larsen, 2015). GAMs have been widely used in a variety of fields, such as species distribution (Friedlaender *et al.*, 2006; Meynard and Quinn, 2007; Murase *et al.*, 2009), plant ecology (Albert & Schmidt, 2010; Salmaso *et al.*, 2012), hydrological processes (Chebana *et al.*, 2014), and water quality (Morton & Henderson, 2008; Ryder *et al.*, 2014; Harding *et al.*, 2016; Hwang *et al.*, 2016).

We used an additive model to determine the effects of several covariates on the mean and variance of the detrended DOC. The model was built from two sub-models. The explanatory variables statistically significant at a probability of not being zero less than 0.05 were included. The first model explains the expected value of the detrended DOC (i.e. explained DOC standard deviation (SD) or the proportion of the DOC variability which is predictable, given the variables used). DOC was detrended given that we were interested in the variability of DOC, and not its long-term trend. For this model monthly average streamflow (Q_t) (m^3 s^{-1}), total monthly rainfall (P_t) (mm), temperature (T_t) (°C), monthly ENSO ($ENSO_t$), the interaction between streamflow and time (t), the interaction between rainfall and time were used:

$$E(DOC_t) = s_1(Q_t) + s_2(P_t) + s_3(ENSO_t) + s_4(T_t) + I(Q_t\mathrm{t}) + I(P_t\mathrm{t}) \qquad (2)$$

where $s_1, \ldots, s_4$ are the smooth effects and I is an interaction term (Wood, 2004). The second model sought to explain the log of the standard deviation of the detrended DOC (i.e.

unexplained DOC SD or the proportion of the DOC variability not predictable with the variables used), and for this model streamflow (Q_t), temperature (T_t), ENSO ($ENSO_t$), the effect of the smoothed average value of DOC ($mean_{DOC_t}$), and the effect of the change over time in sampling frequency ($Freq\_Sampl_t$) and analytical technique (An_Techn_t) were used:

$$\log\sqrt{Var}(DOC_t) = Q_t + T_t + mean_{DOC_t} + Freq\_Sampl_t + An\_Techn_t \qquad (3)$$

where $mean_{DOC_t}$ is the smoothed value of the monthly DOC (mg l^{-1}) and it represents the impact of anthropogenic drivers, given that it has been previously shown that the main drivers for the increase in mean DOC over the same period were increase in urbanisation, hence of wastewater, and land use change (Noacco *et al.*, 2017a). Urbanisation increase and land-use change could not be included directly in the GAM model, as the available data are at the annual scale and typically operate over longer time scales, which would not have allowed to detect their impact on DOC intra-annual variability. Different methods for measuring water colour and DOC have been used over the period: DOC calibrated from Burgess units of colour (Burgess, 1902) (1884-1974), DOC calibrated from Hazen units of colour (1975-1990), and DOC concentration measured directly (1991-2005). Furthermore, water colour and DOC were measured at different sampling frequencies over the period: daily (1884-1952), weekly (1952-1985), monthly (1985-2013). The different analytical techniques and sampling frequencies are described at length in Appendix A and in Noacco *et al.* (2017) and are summarised in Table 2. Therefore the effect of these changes on DOC variability is included in Equation 3 through $Freq\_Sampl_t$, a dummy variable to account for the periods with different sampling frequency, and through An_Techn_t, a dummy variable to account for the periods with different analytical technique. By combining Equations 2 and 3 the total variance of DOC within a year can then be obtained by the following variance decomposition:

$$Var(DOC|year) = Var[E(DOC_t)|t \in year] + E[Var(DOC_t)|t \in year]. \qquad (4)$$

Where the first term on the right-hand side is the variance of the expected value of DOC in a given year (from Equation 2), while the second term is the variance of DOC around its expected value (from Equation 3) averaged over a year. These two terms are defined as explained and unexplained variance, respectively. The explained variance quantifies the model's ability to predict the observed DOC, and it approximates the variability of the expected DOC around its mean over the whole period. The unexplained variance quantifies the remaining part of the observed DOC variance, and it is an estimate of the variability of DOC around its expected or conditional mean value. Hence, the predictability of DOC is directly proportional to the ratio of explained to unexplained variance. The second term is called unexplained variance because it is the variance coming from exogenous sources, not directly explained by the variables considered. Nonetheless, by considering the DOC variance as a function of the variables used, we can estimate how the uncertainty in DOC varies with these variables. Therefore, if the coefficient of a variable in Equation 3 is positive, the variability of DOC will increase as that variable increases, but this does not say whether the expected value of DOC will increase or decrease, hence the term unexplained.

Analyses were carried out with the mgcv package (Wood, 2004) in R (R Core Development Team), where the distribution chosen was a Gaussian location scale additive model with a log of the standard deviation of 0.01.

4. Results

4.1 SSA results

SSA was used to extract the dominant oscillations of the time series considered (i.e. temperature, rainfall, streamflow, ENSO, NAO and DOC) Table 1. The annual oscillation is the leading pair of eigenvalues for temperature, rainfall, streamflow and NAO, which shows that the seasonal cycle explains most of the variability for these variables. By contrast, a 4.6-year cycle is the dominant oscillation for DOC and ENSO. The annual cycle explains a higher proportion of the total variance of streamflow (40.4%), and especially of temperature (91%), compared to the other variables. Rainfall is mainly dominated by noise as only 10% of its variance is explained by its dominant oscillations, i.e. the annual and interannual oscillations (1, 2 and 2.8 years time periods) (Table 1). Interannual oscillations (> 1 year) explain 5% of the variance of rainfall, while they are amplified in streamflow, which explain 8.6% of its variance, and even more in DOC, where they explain 18%. As expected ENSO is dominated by interannual oscillations, which explain 62.7% of its variance, while NAO is dominated by harmonics of the annual cycle (< 1 year), explaining 7.9%. The weak climate forcing modes (e.g. interannual oscillations in precipitation) are amplified in streamflow and DOC.

The noise-free $\hat{Q} - \hat{T} - \widehat{DOC}$ trajectory plot (i.e. with the dominant oscillatory components of the variables reconstructed from Equation B.2 and with the noise and trend components removed) shows a consistent pattern (Figure 3a) (as a banana shape) throughout the period (except in the last two decades), which suggests that the same oscillatory modes are present throughout (video S1). The $\hat{Q} - \hat{T} - \widehat{DOC}$ trajectories move along the DOC axes, indicating that DOC is dominated by interannual oscillations. The noise-free $\hat{Q} - \hat{P} - \widehat{DOC}$ trajectory plot does not show a consistent pattern throughout the period (Figure 3b, and video S2), which could be because the precipitation time series is dominated by noise and possibly very weak oscillatory modes not resolved by SSA. The noise-free $\hat{Q} - \hat{T} - \widehat{ENSO}$ trajectories on the other hand have a consistent pattern (Figure 3c) (again as a banana shape) throughout the record considered (video S3). ENSO, like DOC, has a strong interannual component, which is shown by the $\hat{Q} - \hat{T} - \widehat{ENSO}$ trajectories moving along the ENSO axes. The pattern of the $\hat{Q} - \hat{P} - \widehat{ENSO}$ trajectories (Figure not shown) is less clear, again due to the nature of the rainfall time series. There is no consistent pattern for the $\hat{Q} - \hat{T} - \widehat{NAO}$ trajectories for the whole period (Figure 3d and S1d), which changes over time, and is dominated by intra-annual to annual oscillations. There are no strong correlations between DOC and ENSO or NAO, which are statistically significant. There is a weak positive correlation of 0.1 ($p < 0.05$) between DOC and ENSO in spring.

The phase plane plots also help in identifying points in time when the dynamics of the system have changed, for example due to forcing factors. The variability of DOC increases after 1938, and its interannual oscillations are amplified especially during the period of WWII (Figure 4a-b). After 1990, the interannual and especially intra-annual components of DOC are amplified (Figure 4c). The interannual variability of ENSO does not change over this period, and it is relatively high compared to the one of DOC between 1884 and 1989 (Figure 4d-f and video S3). The relationship between NAO and streamflow and temperature changes over the period (Figure 4g-i and S1d). Between 1884 and 1937 and between 1938 and 1989 $\hat{Q} - \hat{T} - \widehat{NAO}$ plots show a multi-lobed and bi-lobe structure, respectively (Figure S2), which indicates the presence of important intra-annual frequencies, and harmonics of the annual cycle (Kumar & Duffy, 2009).

ENSO has the same interannual oscillations before and after 1938, and its relationship with streamflow and temperature is also consistent throughout the period (Figures 5 and S3). Only the variability of DOC has an increase after 1938 (Figure 5 and Table 3). This behaviour suggests that the increase in the intra-annual to interannual variability of DOC is not related to changes in the ENSO signal, or to hydroclimatic forcing in general, even though DOC shares the same modes of oscillations as streamflow and temperature before 1989 (Figure 4a-b). The time averaged $\hat{Q} - \hat{T} - \widehat{DOC}$ trajectories, and the pairwise planar projections Q-T, DOC-Q and DOC-T were examined for three time periods: 1884-1938, 1939-1989, 1990-2013 (Figure 6). The shape of the Q-T trajectory does not change over time, which indicates that the hydroclimatic dynamics are not subject to changes over the periods considered. The phase plane shape of the trajectories of the dominant frequencies of DOC-Q and DOC-T expands over time, suggesting that there are changes in the amplitude of the dominant oscillations of DOC. Moreover, the increase in DOC variability is higher for higher flows and lower temperature, i.e. in the winter months (Figure 6).

4.2 GAM results

In the previous section it was shown that the variability of the hydrological variables and teleconnections does not play a role in the increase in DOC variability, although they are linked to the intra-annual to interannual variability of DOC. Observed fluvial DOC variability increases by 80% over the period and by 230% until the 1994, after which it decreases by 46% (Figure 7a). By regressing the observed SD of DOC on the predicted SD an R^2 of 0.60 was obtained. This relationship means that the variables considered (in Equations 2 and 3) explain 60% of the total observed DOC variability. The effect of streamflow was to increase the variance of DOC, while increases in temperature decreased DOC variance. Depending on the sources, higher flows could increase or dilute DOC, while higher temperatures are associated with lower DOC variability. NAO was not found to have a statistically significant effect on the variance of DOC, while ENSO was found to influence the expected value of the detrended DOC, but not its variance (Equation 2). GAM allows to capture non-linear relationships, and the relationships found were indeed non-linear (Equation 2), therefore simpler approaches would have required strong assumptions regarding these relationships.

Most of the variability is unexplained (Equation 4 and Figure 7b), which means that the variables considered could explain whether the variance of DOC increases or decreases, but not if the expected value of DOC increases or decreases (i.e. they cannot predict the mean value of DOC). The model shows that the hydroclimatic variables are not able to explain the increase in the variability of DOC over time. In particular the explained SD estimated with hydroclimatic and teleconnections variables is roughly constant over time and much lower than the unexplained SD. Therefore, the increase in DOC variability must be due to other causes. The predictability of DOC decreases with time (Figure 7b), as the ratio of explained to unexplained decreases over time. Finally, the contribution of the variables to the unexplained variability of DOC (Equation 3) is visually quantified (Figure 8). The baseline DOC SD is 0.4 mg l^{-1}, which includes the variability due to hydroclimatic drivers (i.e. streamflow and temperature) and other unknown sources of DOC variability at the beginning of the period, when the anthropogenic impact on fluvial DOC was minimal. Therefore, the natural variability of DOC is around 0.4 mg l^{-1}, and long-term changes over 0.4 mg l^{-1} might be attributable to anthropogenic drivers. The change in analytical technique from Burgess units (1884-1974) to Hazen units of colour (1974-1990) is related to a slight increase in the variability of DOC by 0.1 mg l^{-1}. The change of sampling frequency from weekly (1952-1985) to monthly (1985-2013) is related to a larger increase in the variability of DOC by 0.4 mg l^{-1}. But the variable that is related to most of the increase in the unexplained SD is the moving average value of DOC. Higher DOC average values are related to an increase in the SD of DOC. This effect is stronger during WWII when DOC variability increased by 0.7 mg l^{-1} and is coincident with a substantial conversion of grassland into arable land, which increased the release of DOC from soils to river discharge (Noacco *et al.*, 2017a). In the

1990s the maximum increase in DOC variability, which was not due to changes in how DOC was measured, was by 1.5 mg l^{-1}. In this period considerable areas of grassland were converted for arable production (Noacco *et al.*, 2017a), and average DOC concentrations were at their highest. Since the late 1990s the average value of DOC decreased, and so did its SD, which decreased by 46% (0.6 mg l^{-1}). Average DOC concentration increased by 80% over the whole period, by 196% over the period 1884-1994, increasing by 3.2 mg l^{-1}. In the same period annual SD of DOC increased by 230%, increasing by 1.3 mg l^{-1}. The maximum SD observed over the period of study was 3.3 mg l^{-1}, and it is comparable to the long-term trend in DOC concentration, which highlights the importance of studying DOC variability to put DOC trends into the right perspective. The result obtained with the GAM analysis, that the mean DOC is the variable related to most of the increase in DOC variability, might seem a simple conclusion, but by having included other variables in the analysis its credibility is enhanced (Equations 2 and 3). In fact, in the case where these variables would not have been considered, the method would have been simpler, but the conclusions more dubious.

To summarise, the unexplained SD of DOC is higher for high streamflow and low temperature. Moreover its increase over time is proportional to the average value of DOC. Higher values of DOC in the river were shown to be related to increased sewage effluents and land-use change (Noacco *et al.*, 2017a). Spurious causes of DOC variability, likely from changes in analytical techniques and sampling frequency are higher after 1975, although they are not major contributors to DOC variability.

5. Discussion

In section 5.1 the hypothesis formulated in Section 1 (increased fluvial DOC variability is driven by hydroclimatic variability, driven in turn by atmospheric circulation patterns) is explored. In section 5.2 other possible drivers for the increase in DOC variability over the past 130 years are discussed. In section 5.3 the importance of studying DOC variability is highlighted in an international context.

5.1 Hydroclimatic influence on DOC variability

We tested whether NAO and ENSO were influencing the variability of temperature, precipitation and streamflow in the Thames basin. We found that NAO has intra-annual to annual modes of oscillation, which do not seem to be closely related to those of streamflow, temperature or precipitation. NAO is known to have a decadal scale variability (Woollings *et al.*, 2015), but no dominant decadal oscillation was found through SSA. The effect of NAO on rainfall has been found to be stronger for higher elevations in the UK (Burt & Howden, 2013), which could explain why no strong relation was found between NAO and rainfall for a lowland catchment such as the Thames. ENSO has strong interannual oscillatory components, which were related to those of streamflow and temperature, but no direct effect of ENSO on the hydroclimate was found here. This lack of interaction could be due to the permeable geology of the Thames basin, which dampens changes in precipitation, and because of its easterly location, that it is sheltered from westerly airflows. In fact, Lavers *et al.* (2010) found westerly airflows to explain the weak correlations between teleconnections and precipitation or streamflow in the south of the UK. The study of Wang *et al.* (2015) found, for several basins in the southeast US with minimal anthropogenic impact, low-frequency oscillations in streamflow and precipitation to be significantly correlated with ENSO. In this study the weak interannual oscillations in precipitation were found to be amplified in streamflow time series, which is likely due to subsurface storage. In fact, the basin storage can act as a “low-pass” filter and reduce relatively higher frequency oscillations (Kumar & Duffy, 2009), while low-frequency modes of ENSO pass through the system unaltered. Moreover, the variability of ENSO was found to be high over the whole period and not to increase after 1938, which suggests that the DOC variability increase is likely not driven by ENSO.

We also tested whether the hydroclimate was directly influencing DOC variability in the Thames basin. Hydroclimatic factors were found to influence the short-term (e.g. seasonal) variability of DOC, but the increase in DOC variability is not due to hydroclimatic drivers, as the variability of temperature and streamflow does not increase over the period considered. Nonetheless, the variability of DOC was higher for high flows and low temperatures, i.e. during the winter season. This result indicates which conditions to consider in future efforts aimed at investigating sources of DOC during periods of high fluvial DOC variability.

Tian *et al.*, (2015b) found that climate variability (change in temperature and precipitation) was responsible for most interannual variability in carbon export for eastern North America, an area which has also seen a marked increase in population and urban area since the 19th century. In the study of Tian *et al.*, (2015b) the climate changed substantially over the period of record (increase in both temperature and precipitation), which is not the case in this study (temperature increased by 1.3 °C over the period of study). In a small boreal river basin inter-annual DOC concentration was found to be mainly driven by climate, while seasonal DOC patterns were driven by temperature and soil moisture (Futter and Dewit, 2008). In a study of 215 catchments in Sweden intra-annual variability of total organic carbon concentration was found to be mainly influenced by seasonal patterns (used as a proxy variable for soil temperature) (driving an absolute change of 4.2 mg l^{-1}), followed by discharge (3.3 mg l^{-1}), while the long-term trend had an influence one order of magnitude lower (0.17 mg l^{-1}) (Hytteborn *et al.*, 2015). Similar results were obtained in a study of 136 streams in Sweden where the main drivers of DOC intra-annual variability were discharge, month of the year and temperature (Winterdahl *et al.*, 2014). It was further found that in colder northern areas, DOC and discharge had a positive correlation, while in warmer southern areas DOC concentration was positively correlated with discharge while negatively correlated with temperature. Other studies also showed that hydroclimatic factors were good explanatory variables for carbon export variability (Grieve, 1984; Botta, 2002; Ågren *et al.*, 2008; Eimers *et al.*, 2008; Köhler *et al.*, 2008; Alvarez-Cobelas *et al.*, 2012). In the Thames basin, the hydroclimate (streamflow and temperature) influences the short-term (seasonal) variability of DOC, but it is not responsible for the long-term secular increase in DOC variability over the period of record.

5.2 Non-natural drivers for DOC variability increase

There is a dearth of information in the literature about the role of anthropogenic drivers in controlling the temporal variability of riverine DOC, given that hydroclimatic drivers are mainly assumed to affect DOC variability. Possible other causes for riverine DOC variability could be changes in land use (Farley *et al.*, 2005; Piao *et al.*, 2007), in land management (Raymond, 2003; Oh and Raymond, 2006), in atmospheric CO_2 concentrations (Schlesinger and Lichter, 2001), and artificial changes in the DOC record (i.e. not due to actual physical changes in fluvial DOC concentration, but due to changes in analytical techniques and in the frequency of sampling over the period).

Spurious drivers, such as the analytical technique and the sampling frequency, which inevitably changed over a period of 130 years, could increase the variability in the DOC record. The effect of these changes has been considered in the GAM analysis, and including these factors improved the prediction of the observed variance of DOC. The sampling frequency of DOC has become more infrequent over the study period – after 1985 only one or two samples per month were measured, compared to the daily measurements pre-1952. This can have caused an increase in the variability of the record due to the discontinuity of the samples, which are not true monthly averages anymore, and are more prone to day-to-day variability. Nonetheless these factors are not the major source of DOC variability, and they do not explain the increase in variability during WWII and pre-1974.

Land-use change can influence carbon export by altering the hydrology and DOC leachate production. Moreover soil respiration, soil carbon storage, and resistance to erosion are also altered by changing the land cover, which will impact carbon loads (Hope *et al.*, 1994; Kindler *et al.*, 2011). The Thames basin has undergone extensive land-use change, with massive land conversions of permanent pasture into arable production during WWII and in the 1990s (Figure 2c in Noacco *et al.* (2017)) (Howden *et al.*, 2011). Moreover, the catchment has seen an increase in urbanisation, which rose by a factor of 2.5 over the same period. Urbanisation can influence the variability of DOC directly and indirectly. Due to lack of data at the relevant temporal scale on human drivers, we used the mean of DOC concentration to represents the impact of anthropogenic drivers, which had been previously shown to be due to land use change and increase in urbanisation (Noacco *et al.*, 2017a). The use of aquatic organic carbon trend to explain its intra-annual and interannual behaviour has also been used in Hytteborn *et al.*, (2015).

The indirect effect of urbanisation on DOC could be due to changes in the hydrology of the catchment. In fact, urbanisation and the associated increase in impervious surfaces can alter the rate of water infiltration in the soil to recharge groundwater (Lerner, 2002), modify evapotranspiration regimes (Zhang *et al.*, 2011), or increase the flashiness of the basin and possibly the frequency of flooding (Konrad & Booth, 2005). Urbanisation can result in changing flow paths and more overland flow (Gremillion *et al.*, 2000) relative to subsurface flow (Pitt *et al.*, 2002), which could decrease DOC. In this study streamflow variability has not increased over the period due to increased urbanisation, as would be expected from other studies, which showed that streamflow is affected only if a significant portion (i.e. more than

13%) of the catchment is urban (Martin *et al.*, 2012), which it is not the case here. Therefore, the indirect effect of urbanisation on the increase in DOC variability is ruled out.

But urbanisation can also have a direct impact on DOC variability. In fact, sewage effluents to the river are themselves a source of DOM and of particulate organic matter (POM), and increased POM turnover within the stream increases DOC (Worrall & Moody, 2014; Worrall *et al.*, 2018). Sewage effluents are also a nutrient source which could enhance the activity of aquatic flora and fauna and thus increase the production of autochthonous DOC (Stanley *et al.*, 2012). In 2017 1.6 billion m^3 of sewage were treated in the 351 STWs in the Thames Water region (greater than the Thames basin), coming from 15 million customers (Thames Water, 2017). In addition, the increase in urban area is linked to increased combined sewer overflows (CSOs). In the tidal Thames River CSOs account for 39 million m^3 of sewage discharged per year (Tideway, 2017). This is a recognised problem which the construction of the Thames Tideway Tunnel is looking to address (Tideway, 2017). CSOs are flow dependent, therefore the effect of their increase on DOC variability is consistent with the estimated effect of high flows on increased DOC variability (section 4.2). For the Thames basin the impact of sewage effluent on DOC would be higher prior to the implementation of the Urban Waste Water Treatment Directive (UWWTD) in 1992 (EEC, 1991), which, by introducing additional treatment, would have reduced the level of organic matter discharged into the river. Indeed, after the implementation of the UWWTD DOC variability decreased by 46% in this study (Figure 8), which confirms sewage as a driver for the rise in DOC variability.

Previous studies have shown an increase in nitrogen and phosphorous, as well as DOC, in the river Thames since WWII (Howden *et al.*, 2011; Powers *et al.*, 2016). The increase in riverine nitrate has been ascribed as a consequence of extensive mechanical ploughing of grassland during WWII (due to the disturbance of stable organic matter, which would speed organic matter decomposition and therefore leaching of Carbon and Nitrogen). Nitrate levels in the UK kept increasing due to mineral-N fertilisers applications, which rose steadily since the 1940s (Mattikalli and Richards, 1996; DEFRA, 2016). This increase could also have contributed to short-term acceleration of soil organic matter turnover (the so-called priming effect) (Kuzyakov *et al.*, 2000), therefore increasing DOC export to the river. The acceleration of SOM mineralisation could be due to a lower C-to-N ratio and greater availability of substrate and energy source, which in turn accelerate microbial activity (Kuzyakov *et al.*, 2000). The size of the priming effect increases with the amount of mineral fertilisers applied, which agrees with the rise in riverine DOC concentration post-WWII until the late 1990s. This nutrient enrichment increases autochthonous production, therefore greater inputs of relatively labile DOC (Hilton *et al.*, 2006). However, nutrient enrichment could also increase microbial respiration and organic matter degradation (Benstead *et al.*, 2009; Stanley *et al.*, 2012), which decreases DOC, and therefore resulting in the observed more erratic behaviour of DOC. The interaction between different sources of Carbon could have contributed to the observed increased DOC variability, with different mechanisms more important at different times, hence the large variability in DOC concentrations. Nonetheless, further studies with isotopic analyses could confirm the proposed mechanism by labelling different pools of C and N, therefore elucidating the sources of C in the river.

To summarise, the variability of DOC seems to be strongly related to the increase in its average value over the period, as shown using GAMs. The long-term increase in the average value of fluvial DOC is due to higher loads being flushed out into the river either from sewage effluents, CSOs, or from diffuse sources due to land-use and land-management changes. These loads then gradually decrease downstream due to respiration of aquatic microorganisms and organic matter degradation, which are enhanced by nutrient enrichment (Benstead *et al.*, 2009; Stanley *et al.*, 2012). This mechanism would explain the less stable

DOC regime, which has an impact on aquatic life, even though the Thames River is cleaner today than it used to be. These findings have implications for future work, given that urban population increase is a constant trend globally (United Nations, 2008) and large scale land-use changes are increasingly happening in developing countries (Davis *et al.*, 2015).

5.3 Relevance of the study of DOC variability in an international context

This is the first study to consider both the predictable part of DOC variance (explained DOC standard deviation) and the unpredictable part of the variance (unexplained DOC standard deviation, i.e. the variability of DOC not predictable with the current variables available). The latter is very informative, in fact it tells us which hydroclimatic conditions (here high streamflow and low temperature) lead to high DOC variability, therefore indicating in which conditions DOC should be further investigated (e.g. with isotopic analysis) to understand DOC sources and when action should be taken to reduce potentially high levels. Our results can be easily extrapolated to form the basis of future explorations in other regions. In fact, this study, by incorporating 130 years of data, includes a wide range of hydroclimatic conditions and the Thames basin has undergone extensive land use and land management changes over the period of study. Moreover, the Thames basin is a large catchment, and therefore more spatially representative of how the drivers influence regional DOC dynamics, compared to small catchments which are more sensitive to specific basin characteristics. In the Thames basin we find that the magnitude of DOC variability (maximum annual SD over the period of 3.3 mg l^{-1}) is larger than its long-term trend (2.6 mg l^{-1} over the period, 0.02 mg l^{-1} per year). This highlights the importance of considering the variability of fluvial DOC concentration in order to identify emerging trends of worsening water quality due to human derived impacts and not to confuse them with the intrinsic variability of the system. Other studies, which investigated fluvial DOC trend, have short-term DOC variability which exceeds the magnitude of DOC trend. For example, a study in a small peat dominated catchment in the north-east of the UK found that weekly measurements of DOC concentration in the stream increased by 53.4% over 8 years, with an annual rate of increase of 0.6 mg l^{-1} (Worrall *et al.*, 2004a). Nonetheless the intra-annual variability was two orders of magnitude larger than the trend between 1993 and 2000. Worrall *et al.*, (2004a) found that only 6% of the DOC flux increase over the period was due to climate change, while the increased DOC production was due to the enzymic latch mechanism after severe droughts. In two forested catchments in the western Czech Republic temporal trends in DOC concentration were analysed over the period 1993-2007. While both catchments experienced positive DOC trends of 0.42 and 0.43 mg l^{-1} per year, resulting in a cumulative increase of 64 and 65%, their intra-annual variability was more marked, and two orders of magnitude larger than trend. It was also found that the lowest concentrations were at low flows (5^{th} flow percentile DOC was 4.1 and 4.2 mg l^{-1}), while very high concentrations were found at high flows (95^{th} flow percentile DOC was 26.1 and 28.0 mg l^{-1}). The long-term trends were associated to changes in the ionic strength of soil-water and streamwater, while the hydroclimate was not found to change during the study period (Hruška *et al.*, 2009). Another study of three catchments in Southwestern Nova Scotia, Canada, analysed the trends in total organic carbon concentrations over 25 years with weekly measurements (Clair *et al.*, 2008). Two of the three basins showed decreasing trends (-0.25 and -0.58 mg l^{-1} per year) between 1980 and 1995, contemporary to when most of the reduction in acid depositions occurred. While between 1995 and 2005 no trend was found in the three basins suggesting that the system had recovered from the earlier disturbance. However, the three basins had high seasonal organic carbon variability, which exceeded trends by two orders of magnitude, with peaks in organic carbon export in autumn due to high rainfalls and in spring due to snowmelt. In a study of three acid-sensitive, forested and undisturbed catchments in Norway with daily to weekly measurements significant increase in total organic carbon (with 90-95% DOC) was found between 1985 and 2003 and linked to declining acid deposition (de Wit *et al.*, 2007). Organic carbon increased between 0.06 to 0.13 mg l^{-1} per year, which resulted in a cumulative increase of between 14 and 36% over the period. These trends are lower than those for the previously mentioned studies (Worrall *et al.*, 2004a; Clair *et al.*, 2008; Hruška *et al.*, 2009), but comparable to Finnish lakes (0.03-0.22 mg l^{-1}) (Vuorenmaa *et al.*, 2006) and the present study. Nonetheless, de Wit *et al.*, (2007) recognised that the seasonal variability of fluvial organic carbon was considerably larger than the magnitude of the long-term trends (of 2-3 orders of magnitude) and climatically driven, with peak concentrations in late summer and early autumn, while the lowest values were in spring during snowmelt periods. Moreover, the seasonal pattern changed over the period of study, with organic carbon concentrations increasing significantly between August and October, while changes in the average annual discharge were not significant and less than 1%. These results highlight the importance of studying short-term variability in DOC concentrations. Moreover, the results also stress the importance of long-term sub-annual (e.g. at least daily or weekly) measurements campaigns of fluvial DOC concentrations, and warns against discontinuing long-term measurement campaigns, or making them less frequent (Burt *et al.*, 2014). In fact, this type of study allows to assess the full range of DOC variability, which would instead be masked by annual measurements.

6. Conclusions

This work represents a methodological advancement in the study of fluvial DOC variability, which, contrary to the trend in mean DOC, has never been systematically studied. In this study SSA was used to detect dominant oscillations at intra-annual to interannual time scales in hydroclimatic variables as well as in fluvial DOC for the Thames river basin, and to estimate the fraction of the total variance they explain. Interannual oscillations in precipitation are amplified in streamflow and DOC. Contrary to the results of other studies, teleconnections NAO and ENSO only seem to weakly influence the variability of streamflow, temperature or precipitation in the Thames basin. GAM analysis showed that hydroclimatic variables influence the short-term seasonal variability of DOC. Nonetheless they do not explain the increase in the variability of DOC over the 130 years studied. Our analysis suggests that the strongest driver of DOC variability increase is the rise in mean value of DOC over the last century, which is driven by increased sewage effluents and land-use and land-management changes. This study helps to identify the main drivers of fluvial DOC variability and the portion of DOC variability due to natural drivers, rather than anthropogenic ones. In turn, this analysis allows to detect signs of deteriorating water quality, which the natural variability of the system could obscure. Moreover, these findings highlight the complexity of fluvial DOC dynamics and how multiple processes combine to drive its variability. Knowledge from this study of the main drivers and conditions leading to high fluvial DOC variability is a useful basis for future attempts to distinguish trends from DOC variability.

7. References

Adrian R, Reilly CMO, Zagarese H, Baines SB, Hessen DO, Keller W, Livingstone DM, Sommaruga R, Straile D, Van Donk E. 2009. Lakes as sentinels of climate change. *Limnology and Oceanography* **54** (6_part_2): 2283–2297 DOI: 10.4319/lo.2009.54.6_part_2.2283

Ågren A, Jansson M, Ivarsson H, Bishop K, Seibert J. 2008. Seasonal and runoff-related changes in total organic carbon concentrations in the River Öre, Northern Sweden. *Aquatic Sciences* **70** (1): 21–29 DOI: 10.1007/s00027-007-0943-9

Albert M, Schmidt M. 2010. Climate-sensitive modelling of site-productivity relationships for Norway spruce (Picea abies (L.) Karst.) and common beech (Fagus sylvatica L.). *Forest Ecology and Management* **259** (4): 739–749 DOI: 10.1016/j.foreco.2009.04.039

Alvarez-Cobelas M, Angeler DG, Sánchez-Carrillo S, Almendros G. 2012. A worldwide view of organic carbon export from catchments. *Biogeochemistry* **107** (1–3): 275–293 DOI: 10.1007/s10533-010-9553-z

Battin TJ, Kaplan L a., Findlay S, Hopkinson CS, Marti E, Packman AI, Newbold JD, Sabater F. 2009. Biophysical controls on organic carbon fluxes in fluvial networks. *Nature Geoscience* **2**: 595 DOI: 10.1038/ngeo602

Bauer JE, Cai W-J, Raymond PA, Bianchi TS, Hopkinson CS, Regnier PAG. 2013. The changing carbon cycle of the coastal ocean. *Nature* **504** (7478): 61–70 DOI: 10.1038/nature12857

Benstead JP, Rosemond AD, Cross WF, Wallace JB, Eggert SL, Suberkropp K, Gulis V, Greenwood JL, Tant CJ. 2009. Nutrient enrichment alters storage and fluxes of detritus in a headwater stream ecosystem. *Ecology* **90** (9): 2556–2566 DOI: 10.1890/08-0862.1

Bonan G. 2016. *Ecological Climatology*. Cambridge University Press: Cambridge. DOI: 10.1017/CBO9781107339200

Botta A. 2002. Long-term variations of climate and carbon fluxes over the Amazon basin. *Geophysical Research Letters* **29** (9): 10–13 DOI: 10.1029/2001GL013607

Bowes MJ, Loewenthal M, Read DS, Hutchins MG, Prudhomme C, Armstrong LK, Harman SA, Wickham HD, Gozzard E, Carvalho L. 2016. Identifying multiple stressor controls on phytoplankton dynamics in the River Thames (UK) using high-frequency water quality data. *Science of The Total Environment* DOI: 10.1016/j.scitotenv.2016.06.239

Burgess WT. 1902. Note on a simple apparatus for approximately estimating the colours of waters. *The Analyst* **27** (October): 294–298 DOI: 10.1039/AN9022700294

Burt TP, Howden NJK. 2013. North Atlantic Oscillation amplifies orographic precipitation and river flow in upland Britain. *Water Resources Research* **49** (6): 3504–3515 DOI: 10.1002/wrcr.20297

Burt TP, Howden NJK, Worrall F. 2014. On the importance of very long-term water quality records. *Wiley Interdisciplinary Reviews: Water* **1** (1): 41–48 DOI: 10.1002/wat2.1001

Burt TP, Howden NJK, Worrall F, Whelan MJ. 2008. Importance of long-term monitoring for detecting environmental change: lessons from a lowland river in south east England. *Biogeosciences* **5** (6): 1529–1535 DOI: 10.5194/bg-5-1529-2008

Butman DE, Wilson HF, Barnes RT, Xenopoulos MA, Raymond PA. 2014. Increased mobilization of aged carbon to rivers by human disturbance. *Nature Geoscience* **8** (2): 112–116 DOI: 10.1038/ngeo2322

Chebana F, Charron C, Ouarda TBMJ, Martel B. 2014. Regional Frequency Analysis at Ungauged Sites with the Generalized Additive Model. *Journal of Hydrometeorology* **15** (6): 2418–2428 DOI: 10.1175/JHM-D-14-0060.1

Christ MJ, David MB. 1996. Temperature and moisture effects on the production of dissolved organic carbon in a Spodosol. *Soil Biology and Biochemistry* **28** (9): 1191–1199 DOI: 10.1016/0038-0717(96)00120-4

Clair TA, Dennis IF, Vet R, Laudon H. 2008. Long-term trends in catchment organic carbon and nitrogen exports from three acidified catchments in Nova Scotia, Canada. *Biogeochemistry* **87** (1): 83–97 DOI: 10.1007/s10533-007-9170-7

Clark JM, Ashley D, Wagner M, Chapman PJ, Lane SN, Evans CD, Heathwaite AL. 2009. Increased temperature sensitivity of net DOC production from ombrotrophic peat due to water table draw-down. *Global Change Biology* **15** (4): 794–807 DOI: 10.1111/j.1365-2486.2008.01683.x

Clark JM, Bottrell SH, Evans CD, Monteith DT, Bartlett R, Rose R, Newton RJ, Chapman PJ. 2010. The importance of the relationship between scale and process in understanding long-term DOC dynamics. *Science of The Total Environment* **408** (13): 2768–2775 DOI: 10.1016/j.scitotenv.2010.02.046

Clark JM, Chapman PJ, Adamson JK, Lane SN. 2005. Influence of drought-induced acidification on the mobility of dissolved organic carbon in peat soils. *Global Change Biology* **11** (5): 791–809 DOI: 10.1111/j.1365-2486.2005.00937.x

Cole JJ, Prairie YT, Caraco NF, McDowell WH, Tranvik LJ, Striegl RG, Duarte CM, Kortelainen P, Downing J a., Middelburg JJ, et al. 2007. Plumbing the global carbon cycle: Integrating inland waters into the terrestrial carbon budget. *Ecosystems* **10** (1): 171–184 DOI: 10.1007/s10021-006-9013-8

Davey MK, Brookshaw A, Ineson S. 2014. The probability of the impact of ENSO on precipitation and near-surface temperature. *Climate Risk Management* **1**: 5–24 DOI: 10.1016/j.crm.2013.12.002

Davis KF, Yu K, Rulli MC, Pichdara L, D'Odorico P. 2015. Accelerated deforestation driven by large-scale land acquisitions in Cambodia. *Nature Geoscience* **8** (10): 772–775 DOI: 10.1038/ngeo2540

DEFRA. 2016. The British Survey of Fertiliser Practice - Dataset Available at:

http://www.defra.gov.uk/statistics/foodfarm/enviro/fertiliserpractice/

EEC. 1991. Urban Waste Water directive. Council Directive (91/271/EEC). *Official J. Eur. Commun. L* **34** (May 1991): 1–16 DOI: http://eur-lex.europa.eu/legal-content/en/ALL/?uri=CELEX:31991L0271

Eikebrokk B, Vogt RD, Liltved H. 2004. NOM increase in Northern European source waters: discussion of possible causes and impacts on coagulation/contact filtration processes. *Water Science and Technology: Water Supply* **4** (4): 47–54 DOI: 10.2166/ws.2004.0060

Eimers MC, Buttle J, Watmough SA. 2008. Influence of seasonal changes in runoff and extreme events on dissolved organic carbon trends in wetland- and upland-draining streams. *Canadian Journal of Fisheries and Aquatic Sciences* **65** (5): 796–808 DOI: 10.1139/f07-194

Environment Agency. 2009. River Basin Management Plan Thames River Basin District. *Water for Life and Livelihoods*: 1–90

Erlandsson M, Buffam I, Fölster J, Laudon H, Temnerud J, Weyhenmeyer GA, Bishop K. 2008. Thirty-five years of synchrony in the organic matter concentrations of Swedish rivers explained by variation in flow and sulphate. *Global Change Biology* **14** (5): 1191–1198 DOI: 10.1111/j.1365-2486.2008.01551.x

European Union. 2000. Common implementation strategy for the water framework directive (2000/60/EC) Guidance document no. 5. Transitional and coastal waters: typology, reference conditions and classification systems

Farley KA, Jobbagy EG, Jackson RB. 2005. Effects of afforestation on water yield: a global synthesis with implications for policy. *Global Change Biology* **11** (10): 1565–1576 DOI: 10.1111/j.1365-2486.2005.01011.x

Filella M, Rodríguez-Murillo J. 2014. Long-term Trends of Organic Carbon Concentrations in Freshwaters: Strengths and Weaknesses of Existing Evidence. *Water* **6** (5): 1360–

1418 DOI: 10.3390/w6051360

Finstad AG, Andersen T, Larsen S, Tominaga K, Blumentrath S, de Wit HA, Tømmervik H, Hessen DO. 2016. From greening to browning: Catchment vegetation development and reduced S-deposition promote organic carbon load on decadal time scales in Nordic lakes. *Scientific Reports* **6**: 31944 DOI: 10.1038/srep31944

Friedlaender A, Halpin P, Qian S, Lawson G, Wiebe P, Thiele D, Read A. 2006. Whale distribution in relation to prey abundance and oceanographic processes in shelf waters of the Western Antarctic Peninsula. *Marine Ecology Progress Series* **317**: 297–310 DOI: 10.3354/meps317297

Futter M, Dewit H. 2008. Testing seasonal and long-term controls of streamwater DOC using empirical and process-based models? *Science of The Total Environment* **407** (1): 698–707 DOI: 10.1016/j.scitotenv.2008.10.002

Ghil M, Vautard R. 1991. Interdecadal oscillations and the warming trend in global temperature time series. *Nature* **350** (6316): 324–327 DOI: 10.1038/350324a0

Gillooly JF. 2001. Effects of Size and Temperature on Metabolic Rate. *Science* **293** (5538): 2248–2251 DOI: 10.1126/science.1061967

Golyandina N, Zhigljavsky A. 2013. *Singular Spectrum Analysis for Time Series*. Springer. Available at: https://books.google.co.uk/books?id=CUpEAAAAQBAJ

Gremillion P, Gonyeau A, Wanielista M. 2000. Application of alternative hydrograph separation models to detect changes in flow paths in a watershed undergoing urban development. *Hydrological Processes* **14** (8): 1485–1501 DOI: 10.1002/1099-1085(20000615)14:8<1485::AID-HYP988>3.0.CO;2-1

Grieve IC. 1984. Concentrations and annual loading of dissolved organic matter in a small moorland stream. *Freshwater Biology* **14** (5): 533–537 DOI: 10.1111/j.1365-2427.1984.tb00173.x

Hallett TB, Coulson T, Pilkington JG, Clutton-Brock TH, Pemberton JM, Grenfell BT. 2004. Why large-scale climate indices seem to predict ecological processes better than local weather. *Nature* **430** (6995): 71–75 DOI: 10.1038/nature02708

Hannaford J, Marsh TJ. 2008. High- flow and flood trends in a network of undisturbed catchments in the UK. *International Journal of Climatology* **28** (10): 1325–1338 DOI: 10.1002/joc.1643

Hannaford J, Buys G, Stahl K, Tallaksen LM. 2013. The influence of decadal-scale variability on trends in long European streamflow records. *Hydrology and Earth System Sciences Discussions* **10** (2): 1859–1896 DOI: 10.5194/hessd-10-1859-2013

Hanson RT, Dettinger MD, Newhouse MW. 2006. Relations between climatic variability and hydrologic time series from four alluvial basins across the southwestern United States. *Hydrogeology Journal* **14** (7): 1122–1146 DOI: 10.1007/s10040-006-0067-7

Harding LW, Gallegos CL, Perry ES, Miller WD, Adolf JE, Mallonee ME, Paerl HW. 2016. Long-Term Trends of Nutrients and Phytoplankton in Chesapeake Bay. *Estuaries and Coasts* **39** (3): 664–681 DOI: 10.1007/s12237-015-0023-7

Hilton J, O'Hare M, Bowes MJ, Jones JI. 2006. How green is my river? A new paradigm of eutrophication in rivers. *Science of The Total Environment* **365** (1–3): 66–83 DOI: 10.1016/j.scitotenv.2006.02.055

Hope D, Billett MF, Cresser MS. 1994. A review of the export of carbon in river water: fluxes and processes. *Environmental pollution (Barking, Essex : 1987)* **84** (3): 301–24 Available at: http://www.ncbi.nlm.nih.gov/pubmed/15091702 [Accessed 19 February 2016]

Howden NJK, Burt TP, Worrall F, Mathias S, Whelan MJ. 2011. Nitrate pollution in intensively farmed regions: What are the prospects for sustaining high-quality groundwater? *Water Resources Research* **47**: W00L02 DOI: 10.1029/2011WR010843

Howden NJK, Burt TP, Worrall F, Mathias SA, Whelan MJ. 2013. Farming for Water Quality: Balancing Food Security and Nitrate Pollution in UK River Basins. *Annals of the Association of American Geographers* **103**: 397–407 DOI: 10.1080/00045608.2013.754672

Howden NJK, Burt TP, Worrall F, Whelan MJ, Bieroza M. 2010. Nitrate concentrations and fluxes in the River Thames over 140 years (1868-2008): are increases irreversible? *Hydrological Processes* **24**: 2657–2662 DOI: 10.1002/hyp.7835

Hruška J, Krám P, McDowell WH, Oulehle F. 2009. Increased Dissolved Organic Carbon (DOC) in Central European Streams is Driven by Reductions in Ionic Strength Rather than Climate Change or Decreasing Acidity. *Environmental Science & Technology* **43** (12): 4320–4326 DOI: 10.1021/es803645w

Hsu C-HH, Jeng W-LL, Chang R-MM, Chien L-CC, Han B-CC. 2001. Estimation of Potential Lifetime Cancer Risks for Trihalomethanes from Consuming Chlorinated Drinking Water in Taiwan. *Environmental Research* **85** (2): 77–82 DOI: 10.1006/enrs.2000.4102

Hwang S-A, Hwang S-J, Park S-R, Lee S-W. 2016. Examining the Relationships between Watershed Urban Land Use and Stream Water Quality Using Linear and Generalized Additive Models. *Water* **8** (4): 155 DOI: 10.3390/w8040155

Hytteborn JK, Temnerud J, Alexander RB, Boyer EW, Futter MN, Fröberg M, Dahné J, Bishop KH. 2015. Patterns and predictability in the intra-annual organic carbon variability across the boreal and hemiboreal landscape. *Science of The Total Environment* **520**: 260–269 DOI: 10.1016/j.scitotenv.2015.03.041

Karlsson J, Byström P, Ask J, Ask P, Persson L, Jansson M. 2009. Light limitation of nutrient-poor lake ecosystems. *Nature* **460** (7254): 506–509 DOI: 10.1038/nature08179

Kindler R, Siemens J, Kaiser K, Walmsley DC, Bernhofer C, Buchmann N, Cellier P, Eugster W, Gleixner G, Grũnwald T, et al. 2011. Dissolved carbon leaching from soil is a crucial component of the net ecosystem carbon balance. *Global Change Biology* **17** (2): 1167–1185 DOI: 10.1111/j.1365-2486.2010.02282.x

Kingston DG, Hannah DM, Lawler DM, McGregor GR. 2009. Climate-river flow relationships across montane and lowland environments in northern Europe. *Hydrological Processes* **23** (7): 985–996 DOI: 10.1002/hyp.7202

Kingston DG, Lawler DM, McGregor GR. 2006. Linkages between atmospheric circulation, climate and streamflow in the northern North Atlantic: research prospects. *Progress in Physical Geography* **30** (2): 143–174 DOI: 10.1191/0309133306pp471ra

Kinniburgh JH, Barnett M. 2009. Orthophosphate concentrations in the River Thames: reductions in the past decade. *Water and Environment Journal* **24** (2): 107–115 DOI: 10.1111/j.1747-6593.2008.00161.x

Köhler SJ, Buffam I, Laudon H, Bishop KH. 2008. Climate's control of intra-annual and interannual variability of total organic carbon concentration and flux in two contrasting boreal landscape elements. *Journal of Geophysical Research* **113** (G3): G03012 DOI: 10.1029/2007JG000629

Konrad C, Booth D. 2005. Hydrologic changes in urban streams and their ecological significance. *American Fisheries Society Symposium*: 157–177 Available at: http://water.usgs.gov/nawqa/urban/pdf/157-178_Konrad.pdf

Kosanic A, Harrison S, Anderson K, Kavcic I. 2014. Present and historical climate variability in South West England. *Climatic Change* **124** (1–2): 221–237 DOI: 10.1007/s10584-014-1101-8

Kullberg A (Lund U (Sweden). LI., Bishop KH, Hargeby A, Jansson M, Petersen RCJ. The ecological significance of dissolved organic carbon in acidified waters. *Ambio (Sweden)* **v. 22**

Kumar M, Duffy CJ. 2009. Detecting hydroclimatic change using spatio-temporal analysis of time series in Colorado River Basin. *Journal of Hydrology* **374** (1–2): 1–15 DOI: 10.1016/j.jhydrol.2009.03.039

Kuzyakov Y, Friedel JK, Stahr K. 2000. Review of mechanisms and quantification of priming effects. *Soil Biology & Biochemistry* **32**

Larsen K. 2015. GAM: The Predictive Modeling Silver Bullet Available at: http://multithreaded.stitchfix.com/blog/2015/07/30/gam/

Laudon H, Buttle J, Carey SK, McDonnell J, McGuire K, Seibert J, Shanley J, Soulsby C, Tetzlaff D. 2012. Cross-regional prediction of long-term trajectory of stream water DOC response to climate change. *Geophysical Research Letters* **39** (18): n/a-n/a DOI: 10.1029/2012GL053033

Lavers D, Prudhomme C, Hannah DM. 2010. Large-scale climate, precipitation and British river flows: Identifying hydroclimatological connections and dynamics. *Journal of Hydrology* **395** (3–4): 242–255 DOI: 10.1016/j.jhydrol.2010.10.036

Leach JA, Larsson A, Wallin MB, Nilsson MB, Laudon H. 2016. Twelve year interannual and seasonal variability of stream carbon export from a boreal peatland catchment. *Journal of Geophysical Research: Biogeosciences* DOI: 10.1002/2016JG003357

Ledesma JLJ, Köhler SJ, Futter MN. 2012. Long-term dynamics of dissolved organic carbon: Implications for drinking water supply. *Science of The Total Environment* **432**: 1–11 DOI: 10.1016/j.scitotenv.2012.05.071

Lerner DN. 2002. Identifying and quantifying urban recharge: a review. *Hydrogeology Journal* **10** (1): 143–152 DOI: 10.1007/s10040-001-0177-1

Lisi F, Nicolis O, Sandri M. 1995. Combining Singular-Spectrum Analysis and neural networks for time series forecasting. *Neural Processing Letters* **2** (4): 6–10 DOI: 10.1007/BF02279931

Mariotti A, Zeng N, Lau K-M. 2002. Euro-Mediterranean rainfall and ENSO—a seasonally varying relationship. *Geophysical Research Letters* **29** (12): 54–59 DOI: 10.1029/2001GL014248

Marques CAF, Ferreira J a., Rocha a., Castanheira JM, Melo-Gonçalves P, Vaz N, Dias JM. 2006. Singular spectrum analysis and forecasting of hydrological time series. *Physics and Chemistry of the Earth, Parts A/B/C* **31** (18): 1172–1179 DOI: 10.1016/j.pce.2006.02.061

Marsh TJ, Hannaford J. 2008. UK Hydrometric Register. *Hydrological data UK series.*: 210pp

Martin EH, Kelleher C, Wagener T. 2012. Has urbanization changed ecological streamflow characteristics in Maine (USA)? *Hydrological Sciences Journal* **57** (December 2014): 1337–1354 DOI: 10.1080/02626667.2012.707318

Mattikalli NM, Richards KS. 1996. Estimation of Surface Water Quality Changes in Response to Land Use Change: Application of The Export Coefficient Model Using Remote Sensing and Geographical Information System. *Journal of Environmental Management* **48** (3): 263–282 DOI: 10.1006/jema.1996.0077

Merrett S. 2007. The Thames catchment: a river basin at the tipping point. *Water Policy* **9** (4): 393 DOI: 10.2166/wp.2007.016

Meynard CN, Quinn JF. 2007. Predicting species distributions: a critical comparison of the most common statistical models using artificial species. *Journal of Biogeography* **34** (8): 1455–1469 DOI: 10.1111/j.1365-2699.2007.01720.x

Monteith DT, Stoddard JL, Evans CD, de Wit HA, Forsius M, Høgåsen T, Wilander A, Skjelkvåle BL, Jeffries DS, Vuorenmaa J, et al. 2007. Dissolved organic carbon trends resulting from changes in atmospheric deposition chemistry. *Nature* **450** (7169): 537–540 DOI: 10.1038/nature06316

Moody CS, Worrall F, Evans CD, Jones TG. 2013. The rate of loss of dissolved organic carbon (DOC) through a catchment. *Journal of Hydrology* **492**: 139–150 DOI: 10.1016/j.jhydrol.2013.03.016

Morton R, Henderson BL. 2008. Estimation of nonlinear trends in water quality: An improved approach using generalized additive models. *Water Resources Research* **44** (7): n/a-n/a DOI: 10.1029/2007WR006191

Murase H, Nagashima H, Yonezaki S, Matsukura R, Kitakado T. 2009. Application of a generalized additive model (GAM) to reveal relationships between environmental factors and distributions of pelagic fish and krill: a case study in Sendai Bay, Japan. *ICES Journal of Marine Science* **66** (6): 1417–1424 DOI: 10.1093/icesjms/fsp105

Neff JC, Hooper DU. 2002. Vegetation and climate controls on potential CO2, DOC and DON production in northern latitude soils. *Global Change Biology* **8** (9): 872–884 DOI: 10.1046/j.1365-2486.2002.00517.x

NOAA. 2017. Teleconnections. *National Centers for Environmental Information* Available at: https://www.ncdc.noaa.gov/teleconnections/ [Accessed 12 July 2017]

Noacco V, Wagener T, Worrall F, Burt TP, Howden NJK. 2017a. Human impact on long-term organic carbon export to rivers. *Journal of Geophysical Research: Biogeosciences* DOI: 10.1002/2016JG003614

Noacco V, Wagener T, Worrall F, Burt TP, Howden NJK. 2017b. Monthly Dissolved Organic Carbon (DOC) concentration time series (1883 to 2014) measured at the outlet of the Thames basin (UK) DOI: 10.5285/57943561-4587-4eb6-b14c-7adb90dc1dc8

Oh N-H, Raymond PA. 2006. Contribution of agricultural liming to riverine bicarbonate export and CO 2 sequestration in the Ohio River basin. *Global Biogeochemical Cycles* **20** (3): n/a-n/a DOI: 10.1029/2005GB002565

Oosthoek S. 2016. Global browning: Why the world's fresh water is getting murkier. *New*

Scientist Available at: https://www.newscientist.com/article/mg22930550-600-global-browning-why-the-worlds-fresh-water-is-getting-murkier/ [Accessed 18 January 2016]

Piao S, Friedlingstein P, Ciais P, de Noblet-Ducoudre N, Labat D, Zaehle S. 2007. Changes in climate and land use have a larger direct impact than rising CO2 on global river runoff trends. *Proceedings of the National Academy of Sciences* **104** (39): 15242–15247 DOI: 10.1073/pnas.0707213104

Pitt R, Chen S-E, Clark S. 2002. Compacted Urban Soils Effects on Infiltration and Bioretention Stormwater Control Designs. In *Global Solutions for Urban Drainage*American Society of Civil Engineers: Reston, VA; 1–21. DOI: 10.1061/40644(2002)14

Powers SM, Bruulsema TW, Burt TP, Chan NI, Elser JJ, Haygarth PM, Howden NJK, Jarvie HP, Lyu Y, Peterson HM, et al. 2016. Long-term accumulation and transport of anthropogenic phosphorus in three river basins. *Nature Geoscience* **9** (5): 353–356 DOI: 10.1038/ngeo2693

Pozo-Vázquez D, Gámiz-Fortis SR, Tovar-Pescador J, Esteban-Parra MJ, Castro-Díez Y. 2005. El Niño–southern oscillation events and associated European winter precipitation anomalies. *International Journal of Climatology* **25** (1): 17–31 DOI: 10.1002/joc.1097

Priestley MB (Maurice B, Priestley B. 1981. *Spectral Analysis and Time Series*. Academic Press: London ; New York. Available at: https://books.google.co.uk/books?id=bHxGAAAAYAAJ

Putro B, Kjeldsen TRR, Hutchins MGG, Miller J. 2016. An empirical investigation of climate and land-use effects on water quantity and quality in two urbanising catchments in the southern United Kingdom. *Science of The Total Environment* **548**–**549**: 164–172 DOI: 10.1016/j.scitotenv.2015.12.132

Raymond PA. 2003. Increase in the Export of Alkalinity from North America's Largest

River. *Science* **301** (5629): 88–91 DOI: 10.1126/science.1083788

Regnier P, Friedlingstein P, Ciais P, Mackenzie FT, Gruber N, Janssens IA, Laruelle GG, Lauerwald R, Luyssaert S, Andersson AJ, et al. 2013. Anthropogenic perturbation of the carbon fluxes from land to ocean. *Nature Geoscience* **6** (8): 597–607 DOI: 10.1038/ngeo1830

Roulet N, Moore TR. 2006. Environmental chemistry: Browning the waters. *Nature* **444** (7117): 283–284 DOI: 10.1038/444283a

Ryder E, de Eyto E, Dillane M, Poole R, Jennings E. 2014. Identifying the role of environmental drivers in organic carbon export from a forested peat catchment. *Science of The Total Environment* **490**: 28–36 DOI: 10.1016/j.scitotenv.2014.04.091

Salmaso N, Buzzi F, Garibaldi L, Morabito G, Simona M. 2012. Effects of nutrient availability and temperature on phytoplankton development: a case study from large lakes south of the Alps. *Aquatic Sciences* **74** (3): 555–570 DOI: 10.1007/s00027-012-0248-5

Schlesinger WH, Lichter J. 2001. No Title. *Nature* **411** (6836): 466–469 DOI: 10.1038/35078060

Sivapragasam C, Liong S-Y, Pasha MFK. 2001. Rainfall and runoff forecasting with SSA–SVM approach. *Journal of Hydroinformatics* **3** (3): 141–152 Available at: http://jh.iwaponline.com/content/3/3/141.abstract

Smith CA, Sardeshmukh PD. 2000. The effect of ENSO on the intraseasonal variance of surface temperatures in winter. *International Journal of Climatology* **20** (13): 1543–1557 DOI: 10.1002/1097-0088(20001115)20:13<1543::AID-JOC579>3.0.CO;2-A

Stanley EH, Powers SM, Lottig NR, Buffam I, Crawford JT. 2012. Contemporary changes in dissolved organic carbon (DOC) in human-dominated rivers: is there a role for DOC management? *Freshwater Biology* **57** (SUPPL. 1): 26–42 DOI: 10.1111/j.1365-

2427.2011.02613.x

Thames Water. 2017. Facts and figures Available at: https://corporate.thameswater.co.uk/Media/Facts-and-figures [Accessed 14 December 2018]

Tian H, Ren W, Yang J, Tao B, Cai W-J, Lohrenz SE, Hopkinson CS, Liu M, Yang Q, Lu C, et al. 2015a. Climate extremes dominating seasonal and interannual variations in carbon export from the Mississippi River Basin. *Global Biogeochemical Cycles* **29** (9): 1333–1347 DOI: 10.1002/2014GB005068

Tian H, Yang Q, Najjar RG, Ren W, Friedrichs MAM, Hopkinson CS, Pan S. 2015b. Anthropogenic and climatic influences on carbon fluxes from eastern North America to the Atlantic Ocean: A process-based modeling study. *Journal of Geophysical Research: Biogeosciences* **120** (4): 757–772 DOI: 10.1002/2014JG002760

Tideway. 2017. The Tunnel: Our Solution

Tsai C-Y, Forest CE, Wagener T. 2015. Estimating the regional climate responses over river basins to changes in tropical sea surface temperature patterns. *Climate Dynamics* **45** (7–8): 1965–1982 DOI: 10.1007/s00382-014-2449-1

United Nations. 2008. United Nations expert group meeting on Population Distribution, Urbanization, Internal Migration and Development. Available at: https://sustainabledevelopment.un.org/content/documents/2529P01_UNPopDiv.pdf [Accessed 21 February 2016]

Vautard R, Yiou P, Ghil M. 1992. Singular-spectrum analysis: A toolkit for short, noisy chaotic signals. *Physica D: Nonlinear Phenomena* **58** (1–4): 95–126 DOI: 10.1016/0167-2789(92)90103-T

Vuorenmaa J, Forsius M, Mannio J. 2006. Increasing trends of total organic carbon concentrations in small forest lakes in Finland from 1987 to 2003. *Science of The Total*

Environment **365** (1–3): 47–65 DOI: 10.1016/j.scitotenv.2006.02.038

Wallenstein MD, Weintraub MN. 2008. Emerging tools for measuring and modeling the in situ activity of soil extracellular enzymes. *Soil Biology and Biochemistry* **40** (9): 2098–2106 DOI: 10.1016/j.soilbio.2008.01.024

Wang H, Sankarasubramanian A, Ranjithan RS. 2015. Understanding the low-frequency variability in hydroclimatic attributes over the southeastern US. *Journal of Hydrology* **521**: 170–181 DOI: 10.1016/j.jhydrol.2014.09.081

Wilby RL, O'Hare G, Barnsley N. 1997. The North Atlantic Oscillation and British Isles climate variability, 1865-1996. *Weather* **52** (9): 266–276 DOI: 10.1002/j.1477-8696.1997.tb06323.x

Winterdahl M, Erlandsson M, Futter MN, Weyhenmeyer GA, Bishop K. 2014. Intra-annual variability of organic carbon concentrations in running waters: Drivers along a climatic gradient. *Global Biogeochemical Cycles* **28** (4): 451–464 DOI: 10.1002/2013GB004770

Winterdahl M, Laudon H, Lyon SW, Pers C, Bishop K. 2016. Sensitivity of stream dissolved organic carbon to temperature and discharge: Implications of future climates. *Journal of Geophysical Research: Biogeosciences* **121** (1): 126–144 DOI: 10.1002/2015JG002922

Winterdahl M, Temnerud J, Futter MN, Löfgren S, Moldan F, Bishop K. 2011. Riparian Zone Influence on Stream Water Dissolved Organic Carbon Concentrations at the Swedish Integrated Monitoring Sites. *AMBIO* **40** (8): 920–930 DOI: 10.1007/s13280-011-0199-4

de Wit HA, Mulder J, Hindar A, Hole L. 2007. Long-Term Increase in Dissolved Organic Carbon in Streamwaters in Norway Is Response to Reduced Acid Deposition. *Environmental Science & Technology* **41** (22): 7706–7713 DOI: 10.1021/es070557f

Wood SN. 2004. Stable and Efficient Multiple Smoothing Parameter Estimation for Generalized Additive Models. *Journal of the American Statistical Association* **99** (467):

673–686 DOI: 10.1198/016214504000000980

Woollings T, Franzke C, Hodson DLR, Dong B, Barnes EA, Raible CC, Pinto JG. 2015. Contrasting interannual and multidecadal NAO variability. *Climate Dynamics* **45** (1–2): 539–556 DOI: 10.1007/s00382-014-2237-y

Worrall F, Burt T. 2004. Time series analysis of long-term river dissolved organic carbon records. *Hydrological Processes* **18** (5): 893–911 DOI: 10.1002/hyp.1321

Worrall F, Burt T. 2005. Predicting the future DOC flux from upland peat catchments. *Journal of Hydrology* **300** (1–4): 126–139 DOI: 10.1016/j.jhydrol.2004.06.007

Worrall F, Burt TP. 2007a. Trends in DOC concentration in Great Britain. *Journal of Hydrology* **346**: 81–92 DOI: 10.1016/j.jhydrol.2007.08.021

Worrall F, Burt TP. 2007b. Flux of dissolved organic carbon from U.K. rivers. *Global Biogeochemical Cycles* **21** (1) DOI: 10.1029/2006GB002709

Worrall F, Moody CS. 2014. Modeling the rate of turnover of DOC and particulate organic carbon in a UK, peat-hosted stream: Including diurnal cycling in short-residence time systems. *Journal of Geophysical Research: Biogeosciences* **119** (10): 1934–1946 DOI: 10.1002/2014JG002671

Worrall F, Burt T, Adamson J. 2004a. Can climate change explain increases in DOC flux from upland peat catchments? *Science of the Total Environment* **326**: 95–112 DOI: 10.1016/j.scitotenv.2003.11.022

Worrall F, Harriman R, Evans CD, Watts CD, Adamson J, Neal C, Tipping E, Burt T, Grieve I, Monteith D, et al. 2004b. Trends in Dissolved Organic Carbon in UK Rivers and Lakes. *Biogeochemistry* **70** (3): 369–402 DOI: 10.1007/s10533-004-8131-7

Worrall F, Howden NJK, Burt TP, Bartlett R. 2018. Declines in the dissolved organic carbon (DOC) concentration and flux from the UK. *Journal of Hydrology* **556**: 775–789 DOI: 10.1016/j.jhydrol.2017.12.001

Xu N, Saiers JE. 2010. Temperature and Hydrologic Controls on Dissolved Organic Matter Mobilization and Transport within a Forest Topsoil. *Environmental Science & Technology* **44** (14): 5423–5429 DOI: 10.1021/es1002296

Zanchettin D, Franks SW, Traverso P, Tomasino M. 2008. On ENSO impacts on European wintertime rainfalls and their modulation by the NAO and the Pacific multi-decadal variability described through the PDO index. *International Journal of Climatology* **28** (8): 995–1006 DOI: 10.1002/joc.1601

Zeng T, Arnold WA. 2014. Clustering Chlorine Reactivity of Haloacetic Acid Precursors in Inland Lakes. *Environmental Science & Technology* **48** (1): 139–148 DOI: 10.1021/es403766n

Zhang Q, Xu C-Y, Chen X. 2011. Reference evapotranspiration changes in China: natural processes or human influences? *Theoretical and Applied Climatology* **103** (3–4): 479–488 DOI: 10.1007/s00704-010-0315-6

Zhu Z, Piao S, Xu Y, Bastos A, Ciais P, Peng S. 2017. The effects of teleconnections on carbon fluxes of global terrestrial ecosystems. *Geophysical Research Letters* **44** (7): 3209–3218 DOI: 10.1002/2016GL071743

8. Tables

Table 1 Dominant time periods present in DOC (mg l^{-1}), temperature (°C), rainfall (mm), streamflow (m^3 s^{-1}), ENSO and NAO; and corresponding fraction of variance explained of the original time series determined with singular spectrum analysis.

	Dominant oscillations with time periods (years)	Variance explained (%)	Total variance explained (%)	Oscillatory pair
DOC	4.6	10.7	36.2	1~2
	1	10		3~4
	3.2	7.3		5~6
	0.5	4.2		9~10
	0.7	4		11~12
Temperature	1	91	92.2	1~2
	0.5	0.9		3~4
	0.7	0.3		9~10
Rainfall	1	5	10	1~2
	2.8	2.7		3~4
	2	2.3		5~6
Streamflow	1	40.4	50.5	1~2
	6.9-7.5	4.6		3~4
	2.8	4		5~6
	0.5	1.5		24~25
ENSO	4.6-5.2	17.3	62.7	1~2
	3.5-3.8	16.2		3~4
	2.6	12.3		5~6
	8.3	10.8		7~8
	1.8	3.4		14~15
	1.5	2.7		16~17
NAO	1	3.9	11.8	1~2
	0.5	3.2		3~4
	0.8	2.4		5~6
	0.3	2.3		7~8

Table 2. Periods with different sampling frequency and analytical technique for DOC concentration (mg l^{-1}) and water colour; and dummy variables used for GAM analysis.

Covariate	**Dummy variable for Equation 3**	**Period**	**Sampling frequency**
Freq_Sampl	1	1884-1952	Daily
	2	1952-1985	Weekly
	3	1985-2013	Monthly
			Analytical technique
An_Techn	1	1884-1974	Burgess units of colour
	2	1974-1990	Hazen units of colour
	3	1990-1998	DOC measured

Table 3. Standard deviations of the variables reconstructed with SSA (streamflow ($m^3\ s^{-1}$), temperature (°C), precipitation (mm), DOC (mg l^{-1}), ENSO and NAO) considered for the periods 1884 - 1989, 1884 – 1938, 1938 - 1898, and the whole year, summer period (June-August) and winter period (December-February).

	1884-1989	pre-1938	post-1938
SD Streamflow			
annual	0.22	0.22	0.22
summer	0.07	0.07	0.07
winter	0.1	0.1	0.1
SD Temperature			
annual	0.32	0.31	0.32
summer	0.02	0.02	0.02
winter	0.02	0.02	0.02
SD Precipitation			
annual	0.17	0.17	0.17
summer	0.12	0.12	0.13
winter	0.12	0.11	0.12
SD DOC			
annual	0.13	0.07	0.15
summer	0.11	0.05	0.14
winter	0.11	0.06	0.14
SD ENSO			
annual	0.17	0.15	0.18
summer	0.16	0.14	0.18
winter	0.17	0.16	0.19
SD NAO			
annual	0.18	0.18	0.19
summer	0.16	0.15	0.16
winter	0.17	0.15	0.18

9. Author contributions

V.N., N.J.K.H., T.W. and C.J.D. designed the study; V.N. conducted the analyses presented here and wrote most of the manuscript; C.J.D. developed some of the methods used and provided help in designing and interpreting the SSA analysis; M.F. provided help in designing and interpreting the GAM analysis; all authors contributed to the interpretation of the results and edited manuscript drafts.

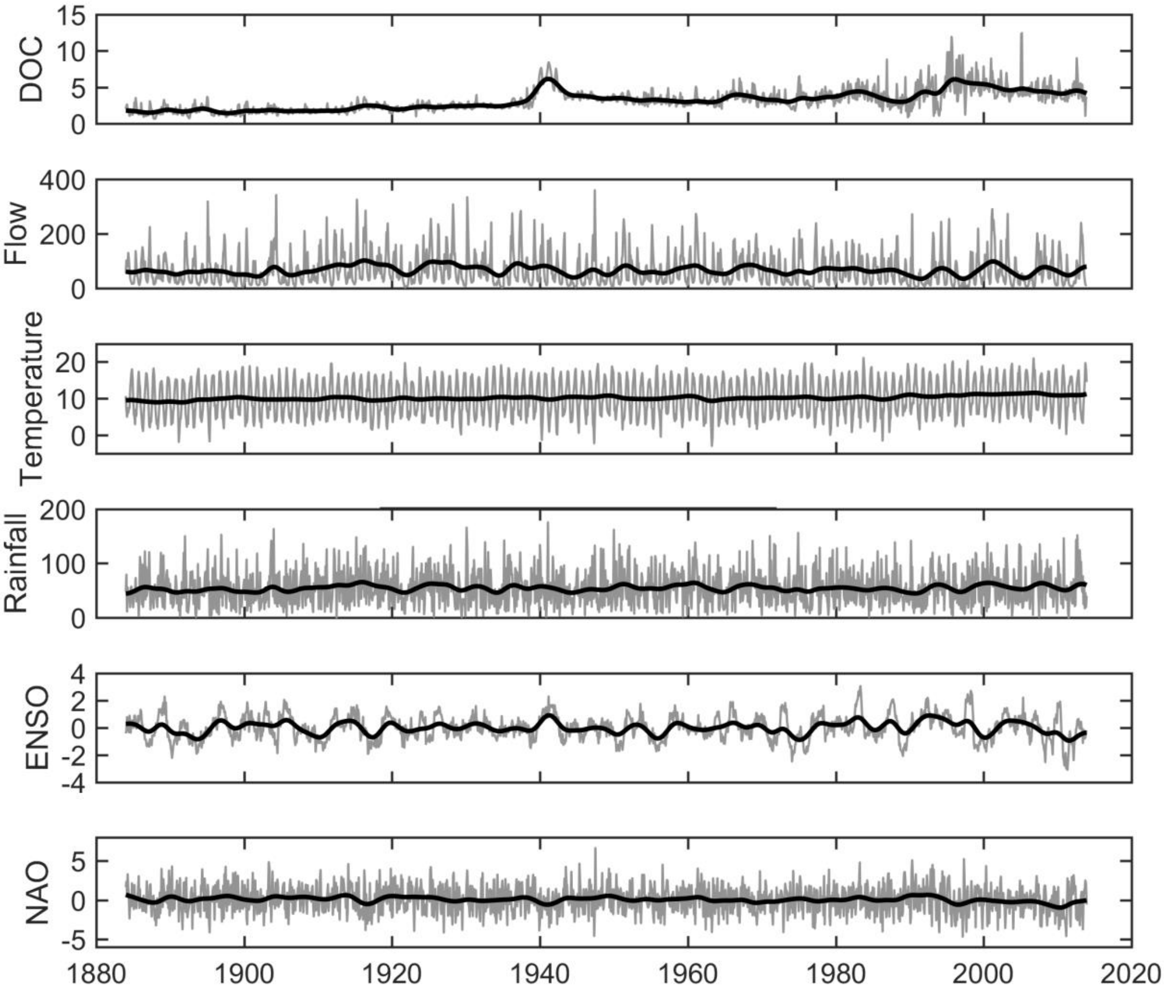

Figure 1 Original monthly time series (grey lines) and smoothed time series with approximately decadal Kernel moving average (black lines) for DOC (mg l^{-1}), flow (m^3 s^{-1}), temperature (°C), rainfall (mm), ENSO and NAO between 1884 and 2013.

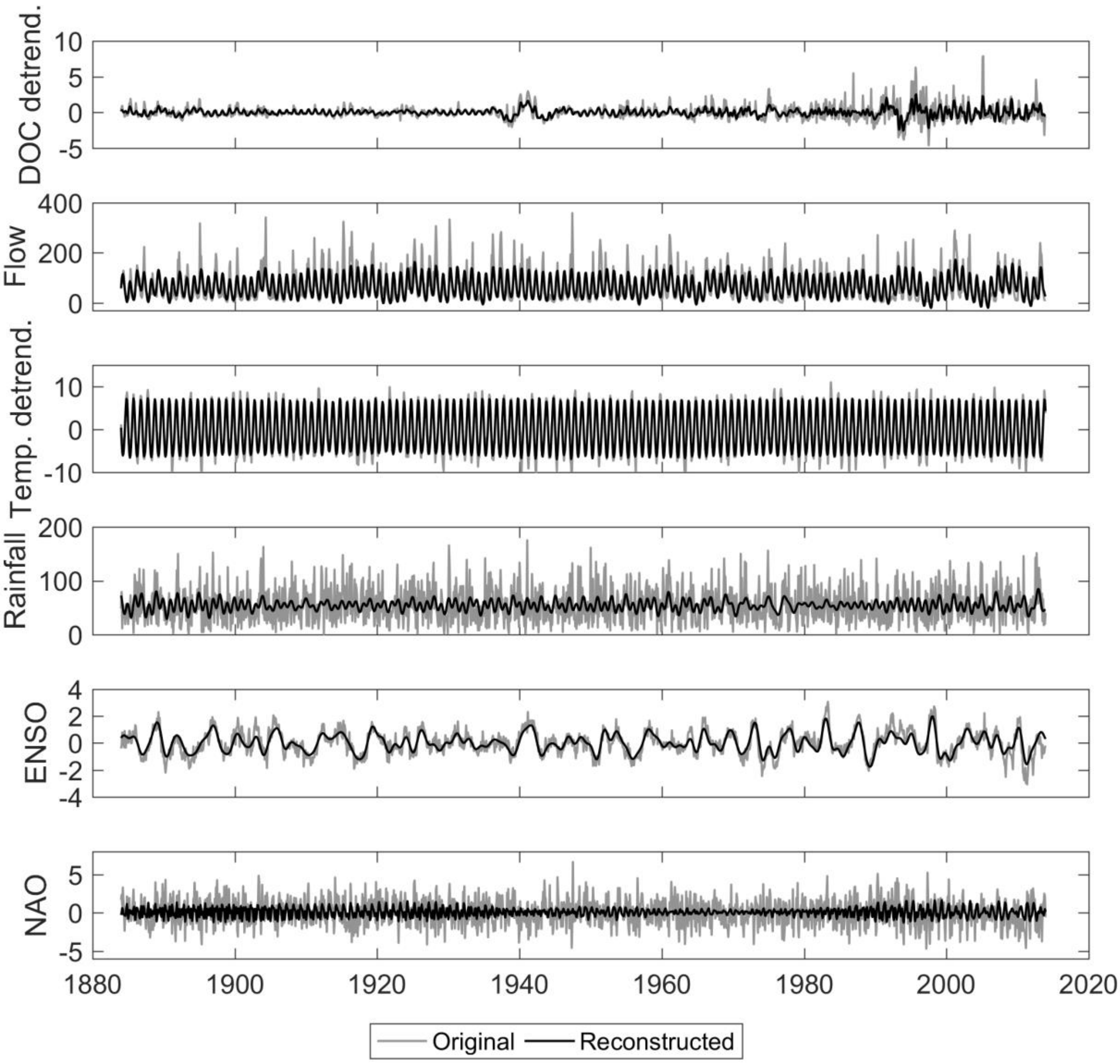

Figure 2 Original noisy time series for DOC (mg l^{-1}), flow (m^3 s^{-1}), temperature (°C), rainfall (mm), ENSO and NAO (with DOC and temperature detrended) and noise-removed reconstructed time series using dominant frequency modes.

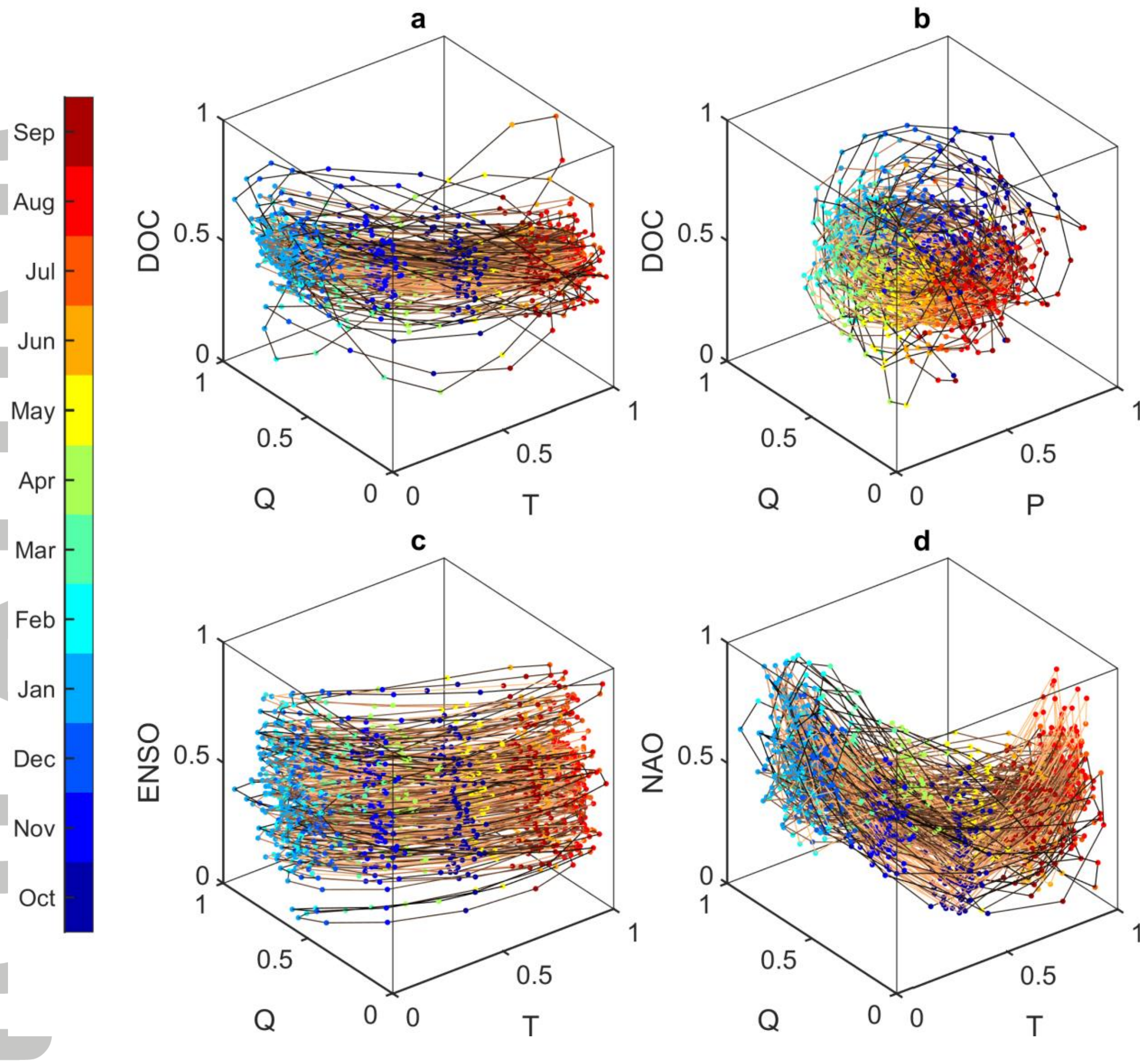

Figure 3 Phase plane trajectories for normalized DOC-Q-T, DOC-Q-P, ENSO-Q-T and NAO-Q-T for reconstructed time series between 1884 and 2013 (DOC in mg l^{-1}; Q in $m^3 s^{-1}$; T in °C and P in mm). Every loop constitutes a water year (month 1 = October), so that changes in early and late winter are considered together, and they are colour coded so that earlier years are lighter brown while later years are darker brown. Dots are coloured by month, with cold colours used for winter and warm colours for summer.

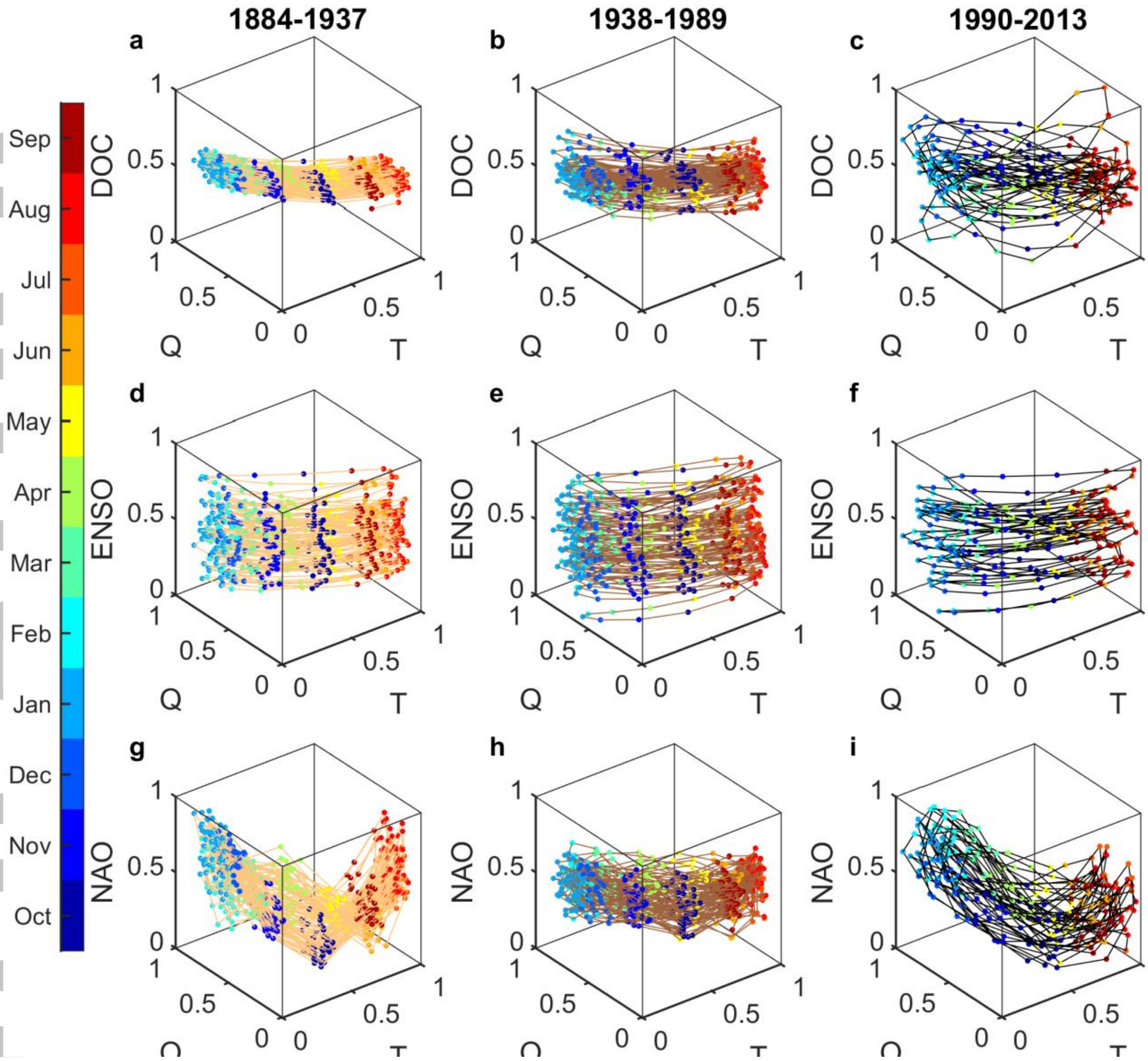

Figure 4 Phase plane trajectories for normalized reconstructed time series of DOC-Q-T, ENSO-Q-T and NAO-Q-T for three periods (1884-1937 (light brown), 1938-1989 (brown), 1990-2013 (black); DOC in mg l^{-1}; Q in $m^3 s^{-1}$ and T in °C).

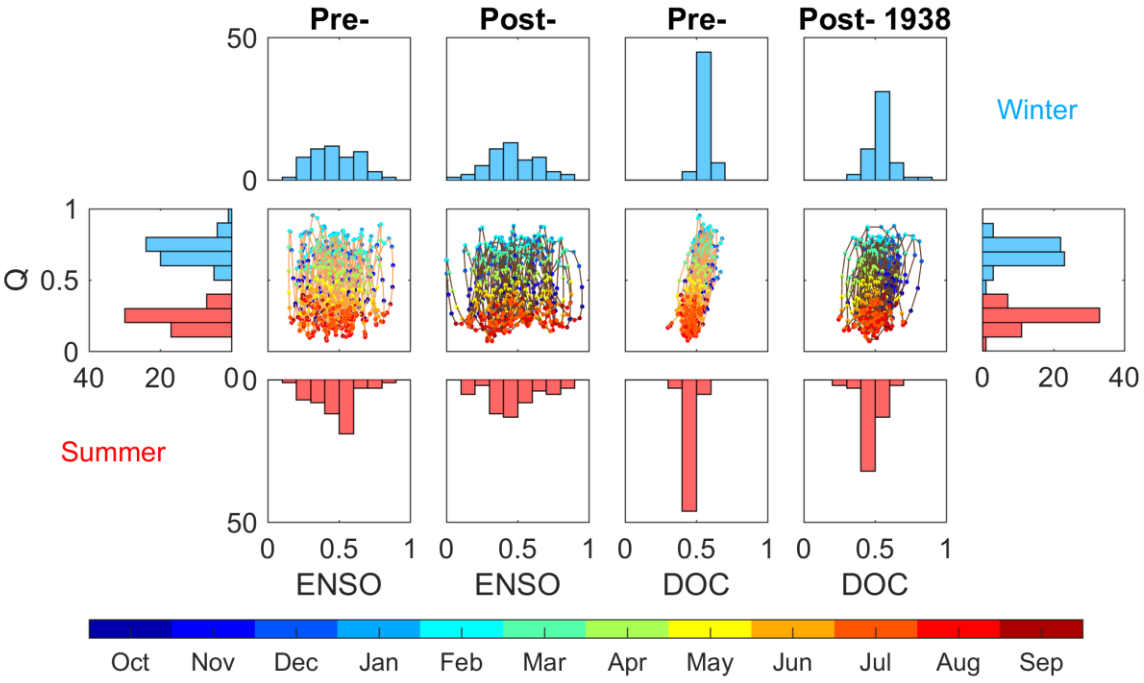

Figure 5 Planar projections of the phase plane trajectories for normalized reconstructed time series of Q-ENSO pre-1938 (1884-1938) and post-1938 (1938-1989), and histograms of ENSO and Q for summer (June-August) and winter (December-February) pre and post-1938; and for Q-DOC pre and post-1938, and histograms of DOC and Q for summer and winter pre and post-1938 (DOC in mg l^{-1} and Q in m^3 s^{-1}).

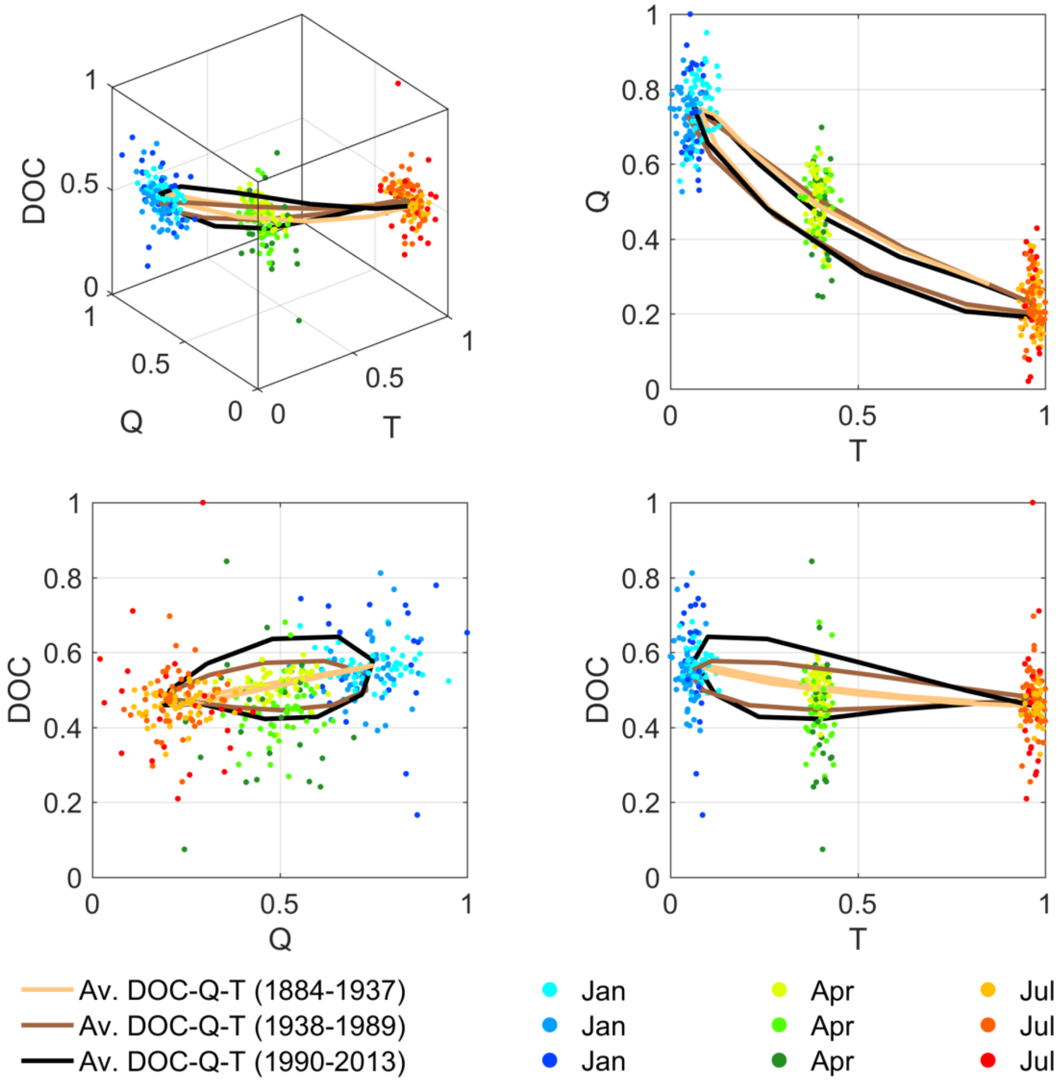

Figure 6 Time averaged normalized DOC-Q-T trajectory of reconstructed time series for three periods and planar projections, with unaveraged-value of DOC, Q and T data for the months of January, April and July, respectively (DOC in mg l^{-1}; Q in $m^3 s^{-1}$ and T in °C).

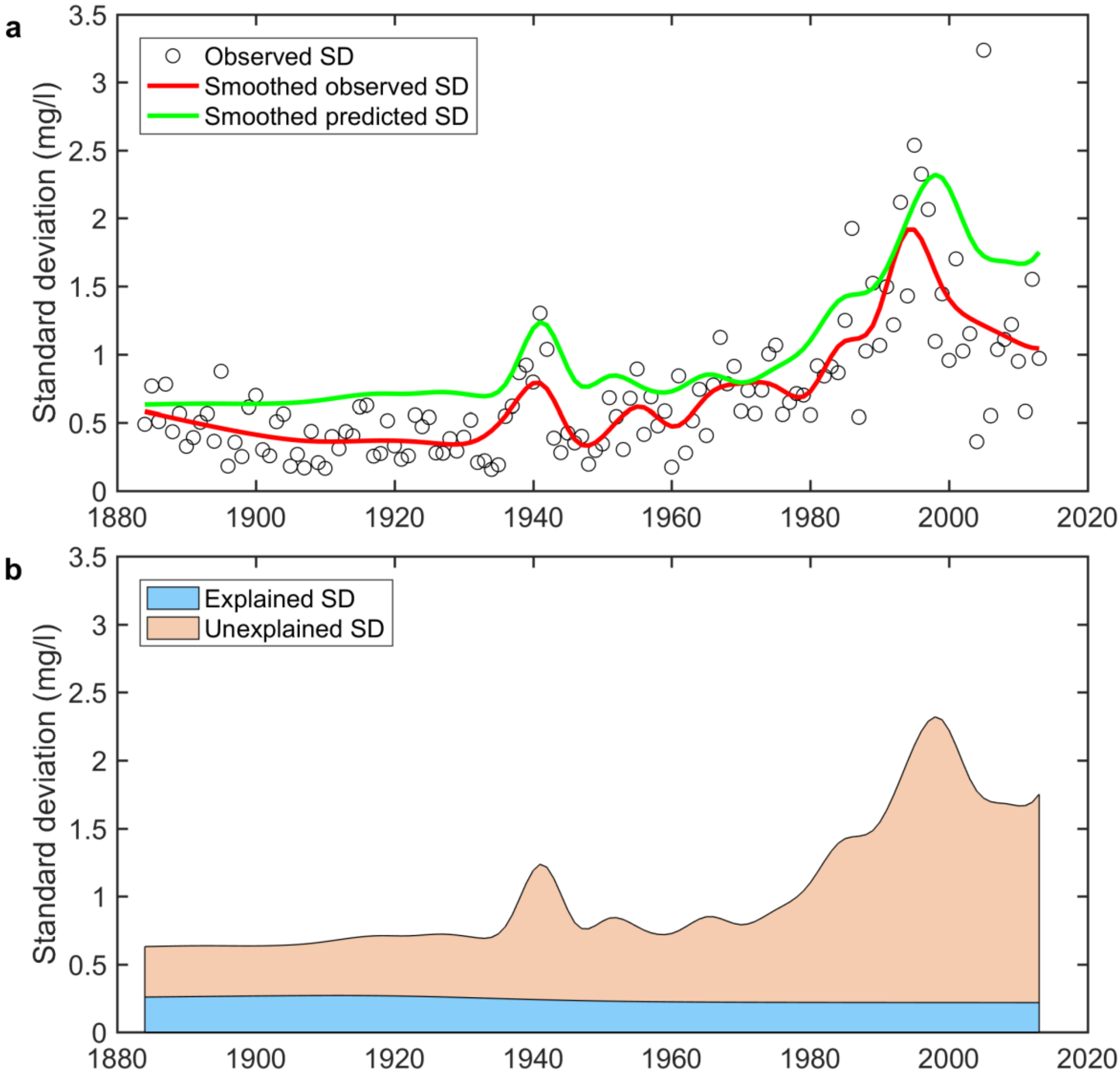

Figure 7 Annual standard deviation of DOC predicted with GAM model (Equation 4). (a) SD of observed DOC, smoothed SD of observed DOC, smoothed SD of DOC predicted with GAM with streamflow, precipitation, temperature and ENSO, average DOC, factors for change in analytical technique, and sampling frequency. (b) Smoothed decomposition of the SD: explained SD and unexplained SD (their sum gives the smoothed predicted SD).

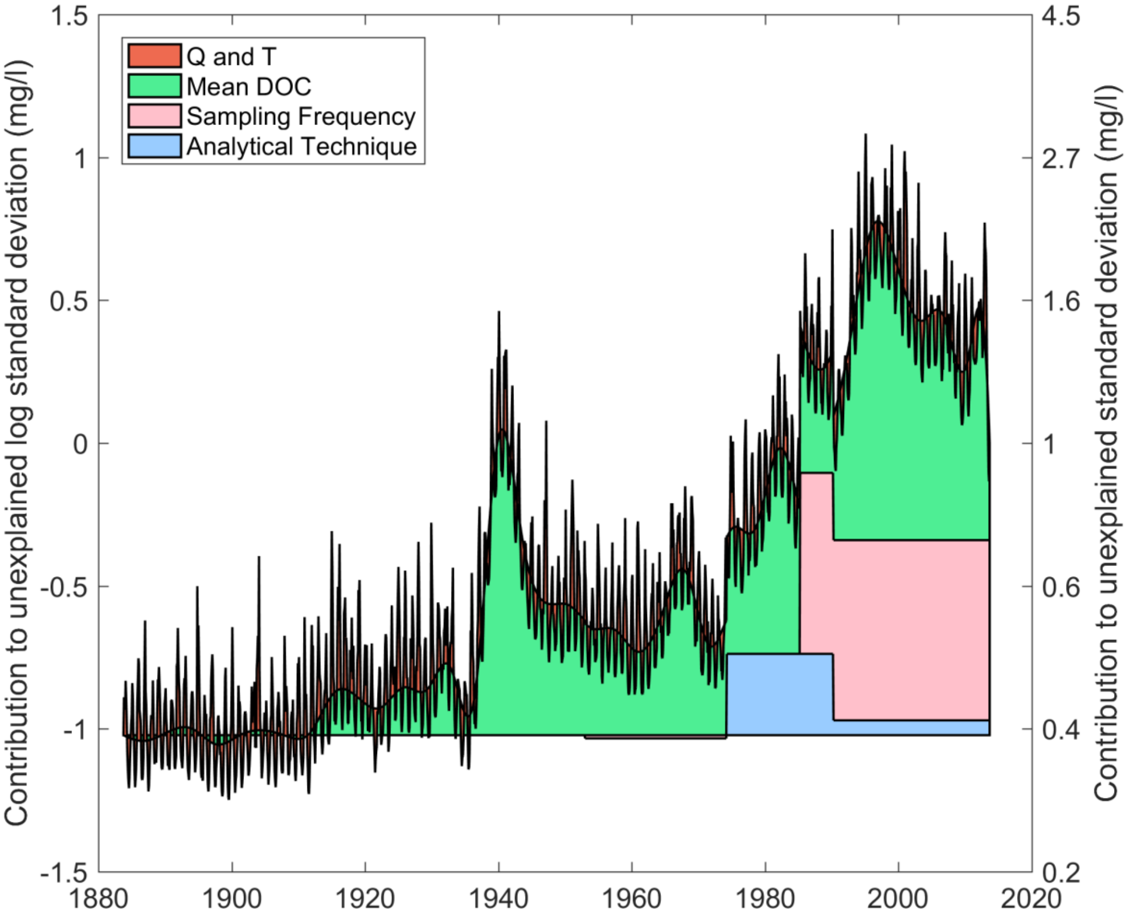

Figure 8 Decomposition of the contribution to the log unexplained SD of DOC of streamflow and temperature, the average value of DOC, the factor change in sampling frequency, and the factor change in analytical technique over the period 1884-2013.