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Changes in chlorophyll-a in English rivers over the last 49 years

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ABSTRACT

Ongoing anthropogenically-driven environmental change in rivers (e.g. increasing air temperature, changing river flow extremes, increases in some key nutrients and decreasing concentrations of other key nutrients) is expected to impact ecological status and the magnitude and frequency of river algal blooms. In this study we considered 49 years of data from up to 161 river sites across England using water-column chlorophyll-a as a measure of suspended algal biomass and used a Bayesian hierarchical model to explore the potential drivers of changing river chlorophyll-a concentrations. Over a period of five decades the changes in chlorophyll-a concentrations in rivers across England showed a mixed pattern in relationships with key environmental variables and are almost evenly divided between significant increases and decreases in those chlorophyll-a concentrations. Most river sites showed no significant change in the probability of algal bloom events (chlorophyll-a > 15 μg/l; > 30 μg/l or 45 μg/l) over the last 49 years. These results indicate that there has been no clear directional response in algal bloom events across England's rivers to the changing pressures, including climate change and large-scale reductions in P concentrations achieved over the last 49 years from improved wastewater treatment. By identifying these differing patterns in chlorophyll-a trends and responses across England, this large-scale spatio-temporal analysis provides a basis for exploring the multiple pressures driving chlorophyll-a responses at local to regional scales.

1. Introduction

Eutrophication is often associated with decreased dissolved oxygen levels, the presence of toxic cyanobacteria, and the development of unpleasant tastes and odours in drinking water reservoirs (Perkins et al., 2019). A range of important drivers and controls for eutrophication in rivers have been identified and in most cases a combination of factors have been proposed as causing algal blooms. These causes include: increased nutrient supply; decreased flow; increased stream temperature; and increasing light intensity (Reynolds and Descy 1996; Balbi 2000; Waylett et al. 2013). With ongoing human-driven environmental change, algal bloom events are of increasing concern, and chlorophyll-a measurements are often used as a proxy for suspended (phytoplankton) algal biomass (Pinder et al, 1997; Neal et al, 2006). This study explores the trends in chlorophyll-a concentrations and exceedances across England in relation to physico-chemical drivers. England has a long-established national water quality monitoring network that has covered a diversity of catchments during a 50-year period of agricultural intensification, population growth and improved urban wastewater management, and is therefore an exemplar for the impact of changing pressures on river systems across the world.

River flow and in-stream residence time strongly influence chlorophyll-a concentrations (Neal et al., 2006; Søballe and Kimmel, 1987). Algal blooms often occur in rivers with residence times exceeding 4 days (Kinniburgh et al., 1997; Bowes et al., 2019), highlighting the importance of factors like catchment area and dead zones (Reynolds, 2000). However, climate change may alter this, as increased water cycle intensity could reduce low-flow, high-residence time periods (Huntington, 2006).

Light intensity influences algal growth (Figueroa-Nieves et al., 2006; Hardenbicker et al., 2014) and has been altered globally by anthropogenic emissions. Global dimming, a reduction in surface light intensity,

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occurred from the 1950s to 1980s (Stanhill and Cohen, 2001; Wild et al., 2005), coinciding with increased anthropogenic aerosols impacting clouds and water vapor (Romanou et al., 2006). This dimming involved changes in cloud properties and aerosol concentrations (Liepert and Tegen, 2002). Since the 1980s, brightening has occurred in industrial regions of the Northern Hemisphere due to reduced aerosol emissions (Wild et al., 2007). Over the past 50 years, chlorophyll-a may have responded to these dimming and brightening trends. Additionally, local factors like riparian tree shading can influence algal responses (Zhang et al., 2024).

A range of authors have shown chlorophyll-a to be correlated with water temperature (Neal et al., 2006; Desortova and Puncochar, 2011; van Vliet and Zwolsman, 2008; Larroude et al., 2013), and stream temperature would be commonly considered to increase with ongoing climate change. Global river water temperature increased by 0.16 K per decade between 1960 and 2011 (Wanders et al., 2019). However, UK stream temperature has risen slower than air temperature (0.1 vs 0.3 K per decade) due to deindustrialisation and groundwater buffering (Worrall et al., 2022). Annual average stream temperature may not be the best indicator for algal blooms, as higher temperatures can both promote and limit certain algal communities.

High nutrient concentrations in rivers are frequently cited as the primary cause of eutrophication and subsequent algal blooms (Vollenweider 1968; Herath 1997; Chetelat et al., 2006). Riverine nitrogen inputs can trigger near-shore algal blooms (Whelan et al., 2009). Moreover, increased nitrogen levels have been linked to shifts in the structure and diversity of lake plant and algae communities (Bunting et al., 2007; Olsen et al., 2015). Nitrogen, often a scarce resource in marine environments (Howarth and Marino, 2006), can significantly influence coastal ecosystems.

Nutrient concentrations in developed countries' rivers are mainly influenced by wastewater emissions and agricultural runoff, with minor atmospheric contributions (Whelan et al. 2022). Algal growth, often limited by phosphorus (P) (Turner et al., 2003), typically becomes restricted below P concentrations of 50–100 μgP/l (Mainstone and Parr, 2002; Jarvie et al, 2018), with lower thresholds in England's low alkalinity rivers (UK TAG, 2013). Though nitrate levels remain high (Howden et al, 2010), P concentrations have significantly decreased since the 1980 s due to P management strategies (Civan et al, 2018; Powers et al, 2016).

Silicon (Si) is crucial for diatoms (Tréguer et al. 2021), key to aquatic primary production. Weathering of rocks and soil, driven by CO_2 (Wollast and Mackenzie, 1983), is the main Si source in freshwater. While increased river transport of Si might be expected with climate change, a global study found no consistent trend, only a median increase of 0.08 mg Si/l/yr (Jankowski et al. 2023). Diatom growth in rivers may become limited by Si, when N and P are in excess of Si (as defined by Redfield molar ratio – Redfield, 1963), and non-siliceous algae, including toxic and harmful cyanobacteria, may come to dominate the phytoplankton community (Carey et al. 2019).

While multi-decadal investments in improved wastewater treatment and agri-environment schemes have led to long-term reduction of P loadings to rivers, other anthropogenic pressures on riverine eutrophication have increased. Therefore, this study seeks to explore the net impacts of these multiple anthropogenically-driven changes on (a) the trends chlorophyll-a concentrations in England's rivers, and (b) the changing probability of algal bloom events (chlorophyll-a concentrations above defined thresholds), over the last 50 years.

2. Approach & methodology

The approach of this study was to use four Bayesian hierarchical modelling approaches to understand the nature and long-term trend in suspended algae in rivers, as measured by chlorophyll-a (Chl-a) and the models considered:

- Concentration of Chl-a; and,
- Occurrence of Chl-a events, i.e. occurrence of Chl-a above a defined threshold.

These are referred to as the Concentration and Exceedance models respectively. Each of these two approaches were applied to two sets of descriptors:

- Relative to spatial and temporal factors, specifically, modelling including the inter- and intra-annual trends between monitoring sites;
- Relative to physio-chemical properties of the river water at the time of sampling, although these second models also included spatial and temporal factors.

The Bayesian approach, which values all data, can increase the precision of analyses on large datasets. This benefit means that the uncertainty surrounding estimated trends at individual sites will be reduced, making the analysis more sensitive to detecting significant trends. Additionally, this approach is robust against irregular sampling, a common issue in national monitoring programmes. Factorial information, such as the month of sampling, can be incorporated into the analysis to account for these irregularities. To highlight the benefits of the Bayesian hierarchical approach, a simple linear regression approach was also conducted on the dataset for comparison.

2.1. River monitoring data

This study uses data from the Harmonised Monitoring Scheme sites (HMS – Bellamy and Wilkinson, 2001). There are 161 sites in England where Chl-a has been monitored (Fig. 1 – Table 1). The original HMS monitoring programme included river sites if they were at the tidal limit of rivers with an average annual discharge > 2 m^3s^{-1}, or any tributaries that had a mean annual discharge > 2 m^3s^{-1} (Bellamy and Wilkinson, 2001). The catchments that could be included in the study vary area between 40 and 9885 km^2 (Table 1). Although the UK-wide HMS monitoring programme ceased at the end of 2014, since then the same monitoring sites in England have been maintained by the Environment Agency. Therefore, Chl-a and the other water quality data could be considered from 161 sites between 1974 and 2022 (49 years). The other chemical determinands included were: nitrate, phosphate, silica and stream temperature. The measurement of Chl-a in this monitoring programme was of Chl-a in the water column, and so would only represent algae that are in suspension. The samples are grab samples rather than depth-width integrated. Sampling protocols and analytical methods for the HMS sites were prescribed in DoE (1972) and outlined in Simpson (1980). Current procedures are outlined and controlled by the UK Government's Standing Committee of Analysts (http://standingcommitteeofanalysts.co.uk/).

Similarly, the HMS monitoring sites were associated with their nearest river flow gauging station and the discharge on the day of sampling was included in the analysis. In order to ensure comparability between monitoring sites with respect to river discharge, the river discharge was converted to the percentile flow at the time of sampling with respect to the whole flow record available for that gauging station. Samples were collected independent of river discharge and percentile flow varied between 0.01 and 99.99 %. The other physico-chemical properties including in the modelling were not normalised as to aid stoichiometric interpretation.

2.2. Bayesian hierarchical modelling – the concentration model

The concentration model considered the concentration of Chl-a relative to both spatial and temporal factors, and to physio-chemical parameters. With respect to concentration model with spatial and temporal factors the model is:

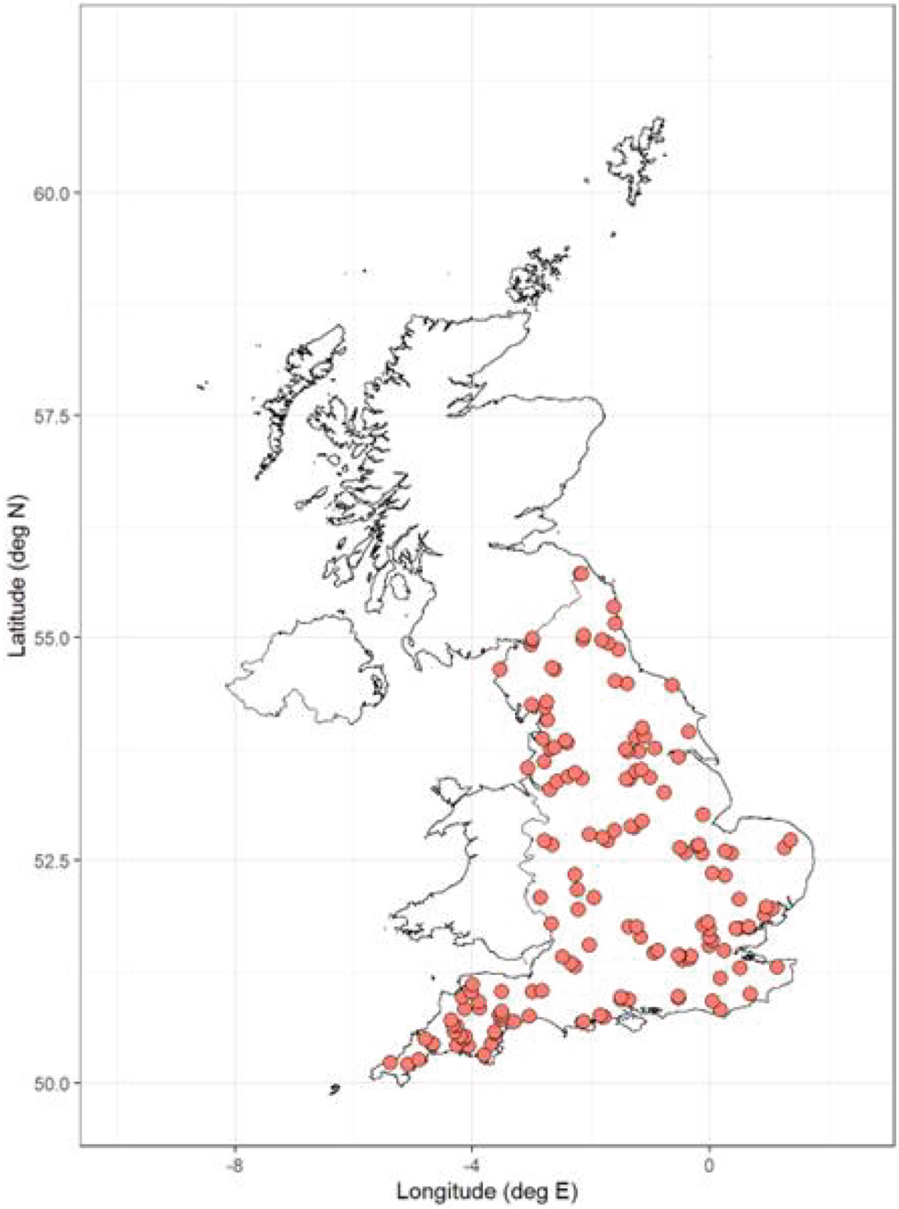

Fig. 1. The location of the monitoring sites used in this study.

Table 1
Range of properties of the catchments considered in this study.

Catchment property	Median	Range	Catchment property	Median	Range (%)
Area (km^2)	446	40–9885	Mineral soil cover	49	0–100
Actual evaporation (mm)	524	426–588	Organo-mineral soil cover	24	0–100
Annual rainfall (mm)	926	561–2606	Organic soil cover	0.7	0–100
Baseflow index	0.52	0.3–0.9	Arable land cover	15	0–70
			Urban land cover	34	0–78
			Grass land cover	5	0–36

$$Chla_{xt} = N\left(\mu_{xt}, \frac{1}{\sigma^2}\right) \quad \text{(i)}$$

$$\mu_{xt} = \alpha_{xt}(Site, Month) + \beta_{xt}(Site, Month)[Year]_{xt} \quad \text{(ii)}$$

where: $Chla_{xt}$, is the value of the Chl-a for Site x at time t (ug/l); Site, a factor representing the different monitoring sites for which data were available and so had a levels for each river monitoring site within the dataset. Month a factor representing the calendar month of sampling and hence there are 12 levels in this factor. The Chl-a concentration at time t was classified by its Month and Year and where there was more than one sample in any month all these data were included and no averaging was used. Year is the year of the sampling, but taken as a covariate and not as a factor. Furthermore, the value of year was re-scaled so that 1974 is year 0 – this was done so that if values of β were insignificant then model-fitting would return values of α that were the expected value for that monitoring site. N() is the normal distrbuton and σ^2 is the variance and $\frac{1}{\sigma^2}$ is the precision which is used to be consistent with the manner of Lunn et al. (2013) and in which the code operates (supplementary material provides R and JAGS code). In this way, β_{xt} were calculated for each monitoring site, for each month, across the record and represents the trend in the chlorophyll concentration across the period for a particular site and month. The model in Equations (i) – (ii) is henceforward referred to as the concentration model as it included both Site and Month factors.

The second approach for the concentration model was to use the physio-chemical descriptors:

$$\mu_{xt} = \alpha_{xt}(Site, Month) + \beta_P(Site, Month)[P]_{xt} + \beta_T(Site, Month)[T]_{xt} + \beta_{\%Q}(Site, Month)[\%Q]_{xt} + \beta_{Si}(Site, Month)[Si]_{xt} + \beta_{NO3}(Site, Month)[NO3]_{xt} + \beta_{year}(Site, Month)[Year]_{xt} \quad \text{(iii)}$$

where: $[P]_{xt}$ = orthophosphate concentration at Site x at time t (mg P/l); $[T]_{xt}$=stream temperature at Site x at time t (^{o}C); $[\%Q]_{xt}$ = the river discharge at Site x at time t expressed as percentile flow of the entire available record; $[Si]_{xt}$ = Silica concentration at Site X at time t (mg Si/l); $[NO3]_{xt}$ = nitrate concentration at Site at time t (mg N/l); and other terms as defined above. Note that Site and Month factors, as described above, were included for each of the variables, i.e. the influence of T, Si, N, P, %Q and Year were allowed to vary for each monitoring site and monitored month. The physico-chemical properties were those in the same grab sample in which the Chl-a was measured. In this analysis no auto-regressive terms could be used, i.e. it was not possible to consider whether the current measured Chl-a concentration reflected previous conditions.

2.3. Exceedance model

The exceedance model considered modelling the occurrence of Chl-a concentration above a set threshold (e.g. Bowes et al., 2016). Three thresholds were considered (Chl-a > 15 μg/l; > 30 μg/l; and > 50 μg/l – Bowes et al., 2016); and considered these events both relative to spatial and temporal factors and to physico-chemical parameters. Any sample with a Chl-a concentration above this threshold was considered to be an eutrophication event. With respect to spatial and temporal factors:

$$s(Chl)^{l}_{xt} = bin\left(\theta^{l}_{xt}, n_{xt}\right) \quad \text{(iv)}$$

$$log\left(\frac{\theta^{l}_{xt}}{1-\theta^{l}_{xt}}\right) = \alpha_{xt}(Site, Month) + \beta_{xt}(Site, Month)[Year]_{xt} \quad \text{(v)}$$

where: θ^{l}_{xt} = is the probability of Chl-a concentration > λ (with λ = 15 μg/l; = 30 μg/l; and = 50 μg/l) at site x at time t; $s(Chl)^{l}_{xt}$ = number of times within sample sizen that Chl-a will exceed limit λ at site x and time t; n_{xt} = number of samples taken at site x at time t. All other terms are as defined above with Site and Month as factors with same levels as described above and Year is a covariate and an integer.

Similar to Equation (iii) the binomial regression can also be expressed in terms of the physico-chemical parameters:

$$log\left(\frac{\theta^{l}_{xt}}{1-\theta^{l}_{xt}}\right) = \alpha_{xt}(Site, Month) + \beta_T(Site, Month)[T]_{xt} + \beta_{\%Q}(Site, Month)[\%Q]_{xt} + \beta_{Si}(Site, Month)[Si]_{xt} + \beta_{NO3}(Site, Month)[NO3]_{xt} + \beta_P(Site, Month)[P]_{xt} + \beta_{year}(Site, Month)[Year]_{xt} \quad \text{(vi)}$$

where all terms are as previously defined.

2.4. Fitting Bayesian models

For all model types, Bayesian estimation was performed using Markov Chain Monte Carlo (MCMC) simulation implemented in JAGS, called from R via the R2Jags library (supplementary material provides R and JAGS code). A 10000-iteration MCMC chain was run for each model, discarding the first 2000 iterations as burn-in and saving every 10th iteration from three independent chains.

Prior distributions were specified as follows: for all Bayesian models, regardless of distribution (normal or binomial) or factor combination, the prior for the regression coefficients (β) was a normal distribution centered at zero, allowing for both positive and negative trends. The prior for the intercepts (α) was also taken as normally distributed, but centered on the overall dataset mean with a standard deviation chosen to minimize the probability of negative values. This choice is justified as, when β values are small, α represents the predicted expected value for a specific monitoring site, which should approximate the overall dataset mean. For concentration models, the standard deviation priors were half-t distributions to ensure positive values. For exceedance models, gamma distributions were used for standard deviation priors. Given the dataset size, the influence of these prior assumptions diminishes rapidly.

A number of approaches were used to test the fit of the Bayesian models:

i) Convergence statistic ($\widehat{R}$)– the adequacy of the MCMC process was assessed using $\widehat{R}$, the convergence statistic, with $1 <- \widehat{R} < 1.1$ considered as acceptable. If $\widehat{R} > 1.1$ then the burn in process and number of iterations could be increased although this never proved necessary.
ii) Credible interval of factors – for each factor included in any model, the factor was considered significant if the 95 % credible interval did not include zero. Henceforward the credible interval was discussed as the 95 % probability of being significantly different from zero.
iii) Model deviance – for a factor or covariate to be included in a model it would be that it caused the total model deviance to decrease – deviance is a goodness of fit measure and is a generalization of the idea of using the sum of squares of residuals in ordinary least squares fitting.
iv) Deviance Information criteria (DIC) – when additional factors or covariates are included in any model we would expect there to be a resulting decrease in the deviance information criterion (DIC). Because inclusion of additional factors, or covariates, will increase the degrees of freedom of any fitted model, it would be expected that any such inclusion would lead to a decrease in the total deviance of any particular model, and hence the need for another measure rather than just the total deviance. The DIC accounts for the trade-off between the inclusion of more parameters against the additional fit of the model and penalises for additional parameters relative to the fit of a particular model – DIC is the general case of Aikake Information Criterion. As for the third criterion, this fourth criterion was assessed by fitting models with the separate factors (e.g. Site or Month) in comparison to the model including both the Site and Month factors.
v) Effective number of parameters (pD) – it would be expected that as a factor or covariate was added to a model, then the number of effective parameters (pD) would likewise increase. If pD did not increase with inclusion of a factor or covariate, then that parameter is having no effect on a model and can be removed. Furthermore, pD should be close to the ideal case if all parameters are contributing, and so the calculated pD can be expressed as a percentage of that maximum possible – this value can never be greater than 100 %.
vi) Posterior prediction – for each models the posterior predictions were compared to the observed values. For concentration models (i.e. Equations (i) – (iii)) the output of the preferred concentration model was plotted against the observed values – for a good fit model the best-fit line between observed and posterior predicted values would have a gradient = 1 and a high r^2 value. For the exceedance models (Equations (iv)-(vi)), the output is probability

and so the classification rate was checked using a receiver operator curve (ROC) and the area under the curve (AUC) was used as a measure of fit, i.e. AUC = 1 would be perfect fit; AUC = 0.5 no classification.

The assumptions of the concentration models (Equations (i)-(iii)) were tested. Specifically, it is assumed that the model residuals would be independent over time. Consequently, the residuals from the preferred concentration model were tested for normality, homoscedasticity, and autocorrelation. Normality was evaluated using the Anderson-Darling test (Anderson and Darling, 1952), while homoscedasticity (or its absence, heteroscedasticity) was assessed through residual plots against fitted values and the Breusch-Pagan test (Breusch and Pagan, 1979). Finally, autocorrelation within the residuals was examined using the Durbin-Watson statistic (Durbin and Watson, 1950).

To quantify the benefit of using a Bayesian hierarchical approach, the non-Bayesian equivalent of each of Equations (i) – (vi) was fitted to the data. The Bayesian hierarchical model was fitted to the entire dataset in one model (all sites across all dates) whereas the non-Bayesian approach was fitted in several different ways. The first non-Bayesian comparison fit two linear regressions to each site, using all the dates sampled at that site. One regression included spatial and temporal factors only and the other regression included physio-chemical properties along with spatial and temporal factors. These models are the non-Bayesian equivalents to the Bayesian concentration models. The linear regressions took the following form:

$$Chl = \alpha + \beta_{year}(Year) + \beta_{month}(Month) \tag{vii}$$

$$Chla = \alpha + \beta_T(T) + \beta_{\%Q}(\%Q) + \beta_{Si}(Si) + \beta_P(P) + \beta_N(N) + \beta_s sinM + \beta_c cosM + \beta_{year} Year \tag{viii}$$

Terms were defined as above, where; Year = calendar year; and Month = month in the calendar year. The Year was included as an integer so that β was the annual trend for that measure. In Equation (vii), Month was included as a factor with 12 levels from January to December. Using Month as a factor makes Equation (vii) more flexible than just considering the year or month as variables.

As another point of comparison to the Bayesian concentration models, linear regression was used again to fit the concentration model containing physio-chemical parameters (Equation vii) using all the data (all sites and all dates – Equation (viii)). In Equation (viii) the Month was transformed to the continuous variables sinM = $\frac{\pi sin(m)}{6}$ and cosM = $\frac{\pi cos(m)}{6}$where m is the month number with January = 1 and December = 12. Unless otherwise stated, significance of the annual trend was assessed at the 95 % probability of being different from zero.

As for the concentration models, and for comparison to the Bayesian hierarchical exceedance model, non-Bayesian exceedance model was fitted to each site across all the dates sampled. Unlike for the concentration data, a non-Bayesian approach was not taken to all the exceedance data together. The non-Bayesian hierarchical model fitted to each site was:

$$s(Chl)^l_{xt} = bin(\theta^l_{xt}, n_{xt}) \tag{ix}$$

$$log\left(\frac{\theta^l_{xt}}{1-\theta^l_{xt}}\right) = \alpha + \beta(Year) + \gamma(Month) \tag{x}$$

$$log\left(\frac{\theta^l_{xt}}{1-\theta^l_{xt}}\right) = \alpha + \beta_T(T) + \beta_{\%Q}(\%Q) + \beta_{Si}(Si) + \beta_P(P) + \beta_N(N) + \beta_s sinM + \beta_c cosM + \beta_{year} Year \tag{xi}$$

where all terms are as defined above.

2.5. Principal component analysis

To understand the pattern of behaviour between sites included in the study a principal component analysis was performed. The slopes from Equations (iii) and (vi) were analysed by principal component analysis where the values of β for P, T, %Q, Si, NO_3 and Year were considered from both the Equation (iii) and (vi). The values of β were z-transformed prior to the analysis and components were considered with eigenvalue > 1.

2.6. Catchment characteristics

This research investigated the reasons behind observed trends by comparing the estimated slopes (β) of these trends with various catchment properties listed in Table 1. First, the land use was classified as arable, grassland, or urban across England for 1 km^2 grid squares using data from the June 2004 Agricultural Census (Defra, 2005). It was assumed that proportions of these land uses did not vary significantly across the study period. Secondly, the dominant soil type (mineral, organo-mineral, or organic) for each 1 km^2 grid square for England was determined based on the Hodgson (1997) classification system. Third, the catchment area to each monitoring point was calculated using the CEH Wallingford digital terrain model, which boasts a 50-meter grid interval and 0.1-meter altitude resolution (Morris and Flavin, 1994). Land use and soil characteristics within each 1 km^2 square were then summed to represent the entire catchment area feeding the monitoring points with available water quality data.

For each catchment in the dataset, several hydrological characteristics were considered: base flow index, average actual evaporation, average annual total river discharge, and average annual rainfall. This hydrological data came from the National River Flow Archive (https://www.ceh.ac.uk/data/nrfa/).

The trends were compared to the collated catchment properties in two ways. First, multiple linear regression was performed on both untransformed and log-transformed data for the explanatory and response variables. Normality of both transformed and untransformed variables was assessed using the Anderson-Darling test (Anderson and Darling, 1952). Only statistically significant variables ($p < 0.05$) were retained in the final model. Second, logistic regression was used to analyze trends categorized as either “significant decrease” or “not significant” in relation to catchment characteristics. Logistic regression can only be used to distinguish two categories whereas the significant tests could give three categories (significancat increase, significant decrease, and not significant), and hence to assess reasons behind trends two categories were chosen.

3. Results

Between 1974 and 2022, there were 78,414 grab sample measurements of Chl-a from 161 sites and 45,391 samples where all determinands and the flow data were available (Fig. 1 – Tables 1 & 2). The arithmetic median Chl-a concentration was 4.5 μg/l (an arithmetic mean = 12.6 μg/l) with a 95th percentile range of 0.6 to 89 μg/l. When judged relative to chlorophyll (algal bloom) event values then 16 % of all values > 15 μg/l; 8 % > 30 μg/l; and 5 % > 50 μg/l. The year with the

Table 2
Number and range of river water data used in this study. There were a total of 161 sites.

Determinand	N	Median	95th percentile range
Chlorophyll-a (μg/l)	78,414	4.5	0.6–89
Nitrate (mg N/l)	45,391	5.2	0.6–13.8
Phosphate (mg P/l)	45,391	0.25	0.02–2.46
Silica (mg SiO_2/l)	45,391	7.1	0.8–14.4
Temperature (°C)	45,391	11.6	3–20
Percentile flow (%)	45,391	49	3–98

most chlorophyll events was 1990 for > 15 μg/l and > 50 μg/l, and 1986 for the > 30 μg/l threshold categories. The least sampled year was 2020 when 341 samples were analysed for Chl-a and the most sampled year was 2011 when 3043 samples were analysed. The least sampled site was River Wye at Redbrook (−2.67 °E, 51.8 °N) with 12 samples and the most sampled site was the River Ribble at Mitton (−2.41°E, 53.8 °N) with 1075 samples – further details provided in Table S1.

3.1. Concentration models

The comparison between the fitted models for the concentration model with spatial and temporal factors is given in Table 3. There was very little difference in efficiency between the three models fitted, but the DIC and deviance both showed that the best model was the Site + Month model. The Anderson-Darling test showed that the residuals of the Site + Month model were not significantly different from normally distributed ($P < 0.00$). The Breusch-Pagan test suggested that residuals of the Site + Month model were homoscedastic at $P < 0.00$, likewise, the Durbin-Watson statistic suggested no significant autocorrelation in the residuals. Therefore, the Site + Month model was sufficient to meet the assumptions of the likelihood function and the Bayesian hierarchical model has removed sufficient temporal structure in the dataset. The posterior prediction plots (Fig. 2) shows that the Site + Month model underpredicts Chl-a for values of Chl-a > 11 μg/l and this suggests that the concentration model with Site and Month factors will be poor at predicting algal bloom events where Chl-a > 15 μg/l.

The trend of Chl-a was significant at 157 out of 161 sites (Table 4), with 85 sites showing significant negative trends and 76 showing significant positive trends. The significant negative trends ranged from −0.00034 to −0.01584 μg/l/yr. The significant positive trends ranged from 0.001 to 0.127 μg/l/yr. The smallest significant slope found was 0.001 μg/l/yr. The median change was −0.007 μg/l/yr, i.e. a median decrease of 0.36 μg/l over the 49 years of the study, or a percentage change of 7 %, and the median root mean square error was 6.5 %. The spatial distribution of trends does not show a discernible distribution across England (Fig. 3).

The slope from the fit of the concentration model to the spatial temporal variables was classified as significantly negative or not, i.e. significant positive slopes, and this classification was compared to the available catchment characteristics using logistic regression, the best-fit equation was:

$$log\left(\frac{\theta_{xt}^{l}}{1-\theta_{xt}^{l}}\right) = -2.47 - 0.0005(Area) + 3.9(BFI) + 4.12(Northing) \tag{xii}$$

where θ = the probability of the site being a site with significant decline in Chl-a concentration; Area = the catchment area for each study site (km^2); BFI = base flow index; and Northing = northing gird reference in British national grid. Equation (xii) implies that those sites which show declines in Chl-a concentration are more likely to be in smaller catchment with permeable geology (high BFI) and further north in England. However, Equation (xii) explained only 9 % of the variance in the original dataset.

When trend was assessed in a non-Bayesian concentration model (Equation viii) then 68 out of 161 sites show a significant trend. The trends vary from −6.1 to 74.1 μg/l/yr with a median of −0.16 μg/l with 58 sites showing a significant negative trend and only 10 showing a positive trend. The smallest significant trend that could be detected was −0.02 μg/l/yr. So, the Bayesian method was able to detect smaller trends than the non-Bayesian model and of those trends that were found to be significant the relative 95 % confidence interval was 50 % of the result for the Bayesian method and 58 % for the linear model, i.e. the Bayesian approach gave more precise results.

For comparison with the Bayesian concentration models for Chl-a concentration compared to physio-chemical properties, then the non-Bayesian approach using all the data, the best-fit line was:

$$Chl-a = -0.0005Year + 5.4sin\left(\frac{M\pi}{6}\right) - 0.9cos\left(\frac{M\pi}{6}\right) + 5.25Q\% + 0.56N + 5.2P - 1.3Si + 1.18T$$

$$r^2 = 0.29, n = 45391 \tag{xiii}$$

(0.0003) (0.2) (0.3) (0.4) (0.03) (0.2) (0.03) (0.04)

where all terms are as defined above. The fit of Equation (xiii) did not improve if the data were log-normalised. The values in brackets are the standard errors in each coefficient. Equation (xiii) implies that when other determinands were considered, then there has been a decrease in Chl-a over the time period. However, the change over the 49 years of the study predicted by Equation (xiii) was small, only 0.5 % of the median over the 49-year study period. Equally, Equation (xiii) also implies that Chl-a is positively correlated with percentile flow (Q%), nitrate (N), phosphate (P) and stream temperature (T), but negatively correlated with silica (Si).

When fitted with the physical–chemical properties using the Bayesian hierarchical approach, the deviance = 386121, DIC = 394932, and pD = 8812 (33 % of the expected). The posterior plot shows no visible difference from the posterior plot for the concentration model with Site + Month model (Fig. 2) with underprediction for Chl-a > 11 μg/l and the best-fit line that is significantly different from the 1:1 line. Models for the different combinations of physio-chemical properties were not run, but the results by each property when all parameters were included shows that for each of the properties there were sites where that property had no significant impact on Chl-a concentration (Table 5). Only for stream temperature (T) is the response dominated by positive slopes, i.e. increasing stream temperature increases Chl-a at 43 out of 73 sites where a significant relationship was found. However, median slope for stream temperature was zero and 89 sites showed either no significant slope or a negative relationship with stream temperature. The relationship between Chl-a concentration and all other variables is dominantly negative, though for phosphate the median slope was zero.

The number of sites with significantly positive, significantly negative and with no significant slope at all does not lend itself to binary classification; therefore, to better understand the patterns of controls for the Chl-a concentration the principal component analysis (PCA) was used. The PCA showed that three components had eigenvalues > 1 and that these explained 69 % of the variance in the original dataset (Table 6). The first component (PC1) is strongly, negatively correlated with β_{Si} and $\beta_{\%Q}$, i.e. high scores in PC1 are correlated with sites where Chl-a concentration increase is correlated with decreasing flow and decreasing Si concentrations. The second component (PC2) is strongly positively correlated β_N and negatively correlated with β_{year}, i.e. sites plotting at high values of PC2 will be those where Chl-a concentrations are correlated with increasing nitrate concentration but Chl-a concentrations decreasing over time. Finally, the third component (PC3) is strongly negatively correlated with β_P, i.e. sites with a high value of PC3 are those where increases in Chl-a concentration are correlated with decreasing phosphate. Plotting sites relative to their scores on PC1, PC2 and PC3

Table 3
Fitting properties of the concentration model combinations. The pD is expressed as both its absolute value and the % of that which could be expected if all new parameters included in the model were effective.

Factors	pD (% expected)	DIC	Deviance
Year	88 (90)	751,583	751,451
Site	157 (49)	741,822	741,635
Month	14 (58)	744,568	744,399
Site + Month	1903 (49)	721,449	719,580

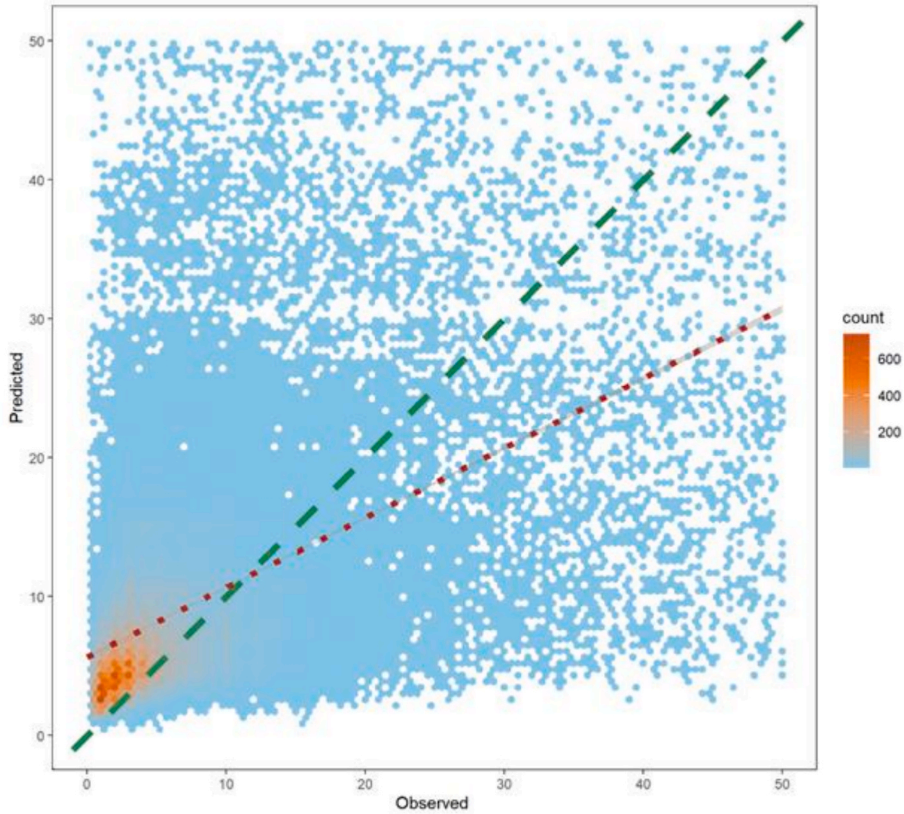

Fig. 2. The observed vs. predicted Chl-a concentrations as predicted from the normal model with spatio-temporal factors (Site + Month). with each hexagonal bin representing 100 datapoints. (−−−) the 1:1 line; and (…) the best-fit line.

Table 4
Summary of trend results for concentration and exceedance models. Where No. positive is the number of sites with slope significantly greater than zero; and No. negative is the number of sites with a slope significantly less than zero. Values are for the Bayesian hierarchical model and those in the brackets are for the non-Bayesian model.

Model	Approach	No. significant	No. positive	No. negative
Concentration	Spatio-temporal	157 (68)	76 (10)	85 (58)
	Physico-chemical	123	25	98
Exceedance	Spatio-temporal	161 (58)	28 (7)	133 (51)
	Physico-chemical	119	22	97

(Fig. 4) means that sites could be classified according to their scores on these components.

3.2. Exceedance models

When a non-Bayesian model was fitted to all the data, the trend in the prediction of events was, for > 15 μg/l = -0.023 ± 0.003 /y; for > 30 μg/l = -0.023 ± 0.003 /yr; and for > 50 μg/l = -0.021 ± 0.003 /yr, i.e. for each chosen threshold there was a significant decrease in the probability of exceeding the given value.

The binomial regression applied at each site (Equation (vii)) for Chl-a > 15 μg/l, 58 of the 161 sites showed a significant trend over time of which 51 were significant negative trends and 7 were significant positive trends. The significant trends ranged from −1.74 to 0.22 /yr with a median of −0.05 /yr. For events defined by Chl-a > 30 μg/l, there were 47 of the 161 sites with a significant trend, with 7 sites showing positive trends and 40 sites showing negative trends, with significant trends ranging from −0.28 to 0.24 /yr. For events defined by Chl-a > 50 μg/l, there were 32 out of 161 sites with significant trends, with 7 sites showing positive trends and 40 sites showing negative trends, with significant trends ranged from −0.28 to 0.24 /yr. Therefore, for all the non-Bayesian approaches the result, or results, were that the probability of an event has been in long-term decline.

The fit of Bayesian binomial regression model for the spatial temporal factors showed that the deviance was the lowest for the model including Site + Month, but the DIC is lowest for the model which included no other factors other than the trend at each site (Table 7): the pattern of fitting was the same for the different definition of a Chl-a event (> 15; > 30; > 50 μg/l). The AUC of the binomial regression with Site + Month factors was 0.7. Of the 161 sites where analysis could be done all showed a significant trend, with 28 sites showing a positive trend with variation from 0.05 to 0.0002 /yr, and there were 133 sites showing a significant negative trend with trends −0.0008 to −0.08/yr. There is a clear long-term decline in probability of events at all thresholds (Fig. 5), but it is difficult to see a particular pattern to the spatial distribution of the slopes of the binomial regression (Fig. 6). There are noticeably fewer significant trends in the concentration model than for the exceedance model and then can be ascribed to the small changes detected in the concentration of Chl-a, over 49 years the median change of −0.36 μg/l: a percentage change of 7 %. (Fig. 7).

The fit of the exceedance model to the physico-chemical data showed that the fitting parameters were deviance = 24046; DIC = 160339; and pD = 136293. In comparison with results for the Site + Month model (Table 7), then the exceedance model with physico-chemical parameters has a lower deviance but higher DIC implying the additional parameters do not make the model more efficient. The AUC of the binomial regression with physico-chemical data was 0.88. The pattern of significant trends across the parameters shows that Year and Silica have a significant role for most sites (91 and 89 % of sites respectively) whereas

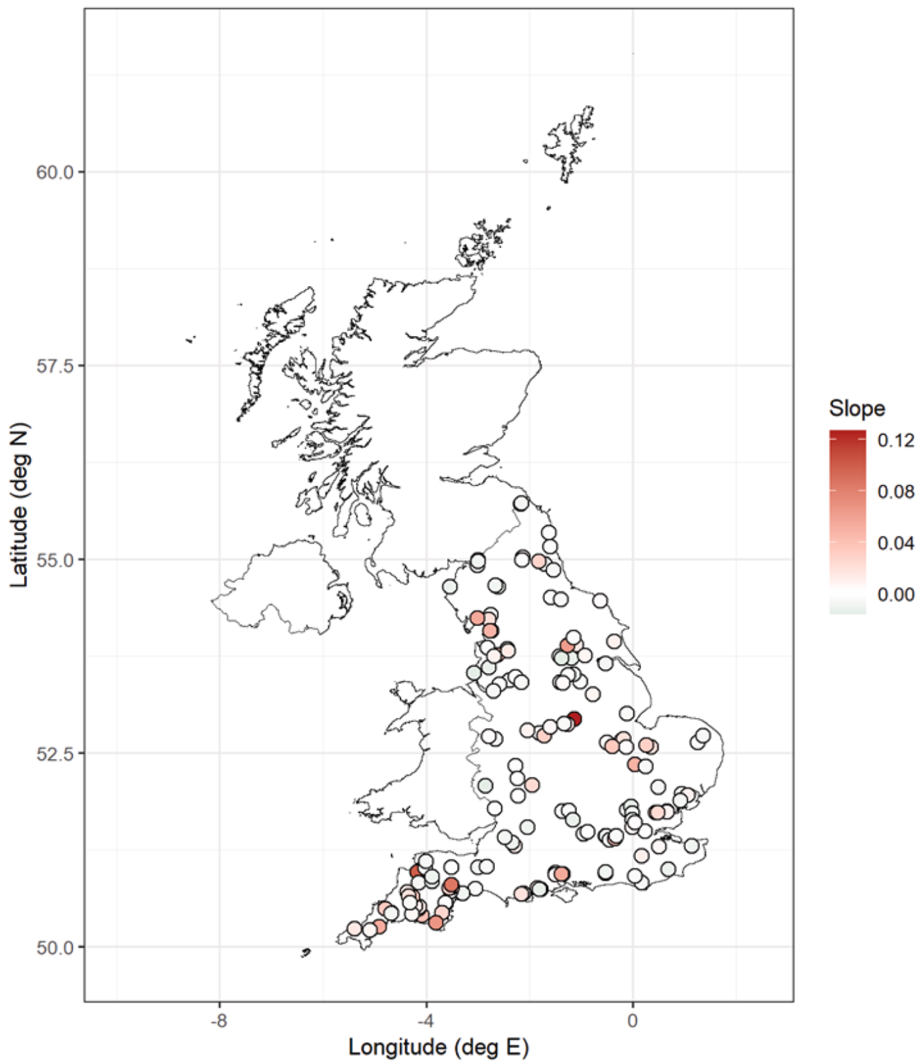

Fig. 3. Spatial distribution of the 49- year trend of the Chl-a concentration.

Table 5
The number of the sites which show a significant relationship with which physico-chemical parameters for the concentration model. Where No. + ve is the number of sites with slope significantly greater than zero; and No.-ve is the number of sites with a slope significantly less than zero, The Median is the median of all slopes while Median + ve is the median slope of all those sites with significant + ve slopes; and Median −ve is the median slope of all those sites with significant −ve slopes. NB. There were 161 sites in total.

	Year	Percentile flow (%Q)	Nitrate (N)	Phosphate (P)	Silica (Si)	Stream temperature (T)
No. significant	123	68	101	74	123	73
No. + ve	25	0	21	21	0	43
No. −ve	98	68	80	53	123	30
Range	−0.181 to 0.018	−1.94 to −0.19	−3.95 to 1.36	−0.99 to 2.18	−7.34 to −0.18	−1.14 to 2.60
Median	−0.003	−0.195	−0.302	0	−0.677	0
Median + ve	0.003	na	0.44	0.48	na	0.49
Median −ve	−0.004	−0.33	−0.41	−0.28	−0.73	−0.26

for phosphate (P) less than 50 % of the sites showed a significant relationship with event probability (Table 8). The majority of study sites showed negative slopes for Year, %Q, nitrate (N), phosphate (P) and silica (Si), but not for stream temperature (T) where the majority of sites that do have a significant relationship with the event probability show a positive relationship.

As for the fit of the concentration model with the physico-chemical parameters so too with PCA of the parameters from the fit of the physico-chemical parameters in a exceedance model showed that three components had eigenvalues > 1 and that these explained 79 % of the variance in the original dataset (Table 9). The first component is strongly, negatively correlated with β_{Si} and $\beta_{\%Q}$, but positively correlated with β_{year}, i.e. high scores in PC1 are correlated with sites where Chl-a events are more likely with decreasing flow and decreasing Si concentrations, but more likely over time. The second component is strongly positively correlated with β_N and negatively correlated with β_T, i.e. sites plotting at high values of PC2 will be those where Chl-a events are more likely with increasing nitrate concentration and more likely with decreasing stream temperature. Finally, the third component is strongly negatively correlated with β_P, i.e. sites with a high value of PC3

Table 6
The loadings on the first three principal components of the principal component analysis of the beta slopes from fitting of Equation (viii).

Variable	PC1	PC2	PC3
Silica	−0.54	0.33	0.33
Nitrate	0.16	0.75	0.23
Year	0.26	−0.48	0.34
Phosphate	−0.26	0.06	−0.82
Percentile flow	−0.54	−0.11	0.12
Stream temperature	0.50	0.28	−0.18
Cumulative variance explained (%)	32	52	69

are those where increased probability of Chl-a events are correlated with decreasing phosphate.

4. Discussion

This study has hypothesized that there are competing trends in the drivers for riverine chlorophyll-a concentrations, an indicator of algal blooms. While P concentration is commonly observed to be decreasing across Western European catchments (e.g, Minaudo et al., 2015), other drivers of algal blooms, including stream temperature; low-flow events and other key nutrients, are known to be increasing. The study showed a mixed picture in trends of Chl-a concentrations in England's rivers since 1974: 53 % of the 161 sites demonstrated significant declining trends (an average decline of 2 μg/L), and 47 % of showed significant increasing trends (average increase of 0.4 μg/L) (Fig. 3). Overall, across all 161 sites there was a decline of 7 %. The majority of sites (71 %) showed no significant trend in the probability of algal bloom events exceeding a > 30 μg/L chlorophyll-a threshold, with 25 % showing a decrease and only 4 % showing an increase in algal bloom probability (Fig. 5). Decreases in Chl-a concentration have been observed for UK's largest lake (Lough Neagh – Elliott et al., 2016), where Chl-a concentration peaked in the mid-1990 s and has decreased since. Changes in rivers and lakes are then reflected in marine Chl-a, Huguet et al. (2024) have shown decreasing Chl-a in the English Channel which supports the earlier work of Romero et al. (2016) and Groetsch et al. (2016) who observed a decrease of the mean biomass and Chl-a in western European seas. The decline of the phytoplankton biomass (Romero et al., 2016) is generally attributed to lower phosphate concentrations in rivers, with a decrease close to 75 % between 1970 and 2013 for the Seine River whereas nitrogen is not a limiting factor. However, Jarvie et al. (2025) have shown that despite several decades of declining phosphate concentration I the River Thamesthe potential for algal blooms has remained close to constant. Further afield a mix of long term changes for Chl-a have been reported. Raike et al. (2003), studied the 25 year trends in Chl-a for Finnish lakes and rivers and found a mixture of significant increase and decreases in Chl-a concentration for both rivers and lakes. Similarly, Jackson et al. (2015) shows significant decreases and increases in coastal Chl-a concentrations across the coast of British Columbia over a 24 year period.

One reason for the observed mixture of the significant trends would be the more sensitive methodology. The Bayesian approach was more sensitive than the non-Bayesian approach at detecting trends in chlorophyll-a. This sensitivity was the case even for sites with low sample frequency as Bayesian analysis is using the whole dataset at once and so is essentially gap-filling. For example, given the use of Site and Month factors and Year as a covariate within the Bayesian hierarchical model it is not necessary that a particular site is sampled in a particular month or year merely that is sampled during the study period at that site and that other sites are sampled for the month or year of interest.

When potential drivers (stream temperature, Si, nitrate, phosphate, and river flow) were considered, then there was a still a decline in the

Table 7
Fitting properties of the exceedance model combinations applied. The pD is expressed as both its absolute value and the % of that which could expected if all new parameters included in the model were effective.

Factors	pD (% expected)	DIC	Deviance
Year	1.9 (85)	64,557	65,556
Site	74.3 (28.3)	65,145	64,422
Month	23.6 (98)	65,185	64,592
Site + Month	3012 (78)	65,906	62,895

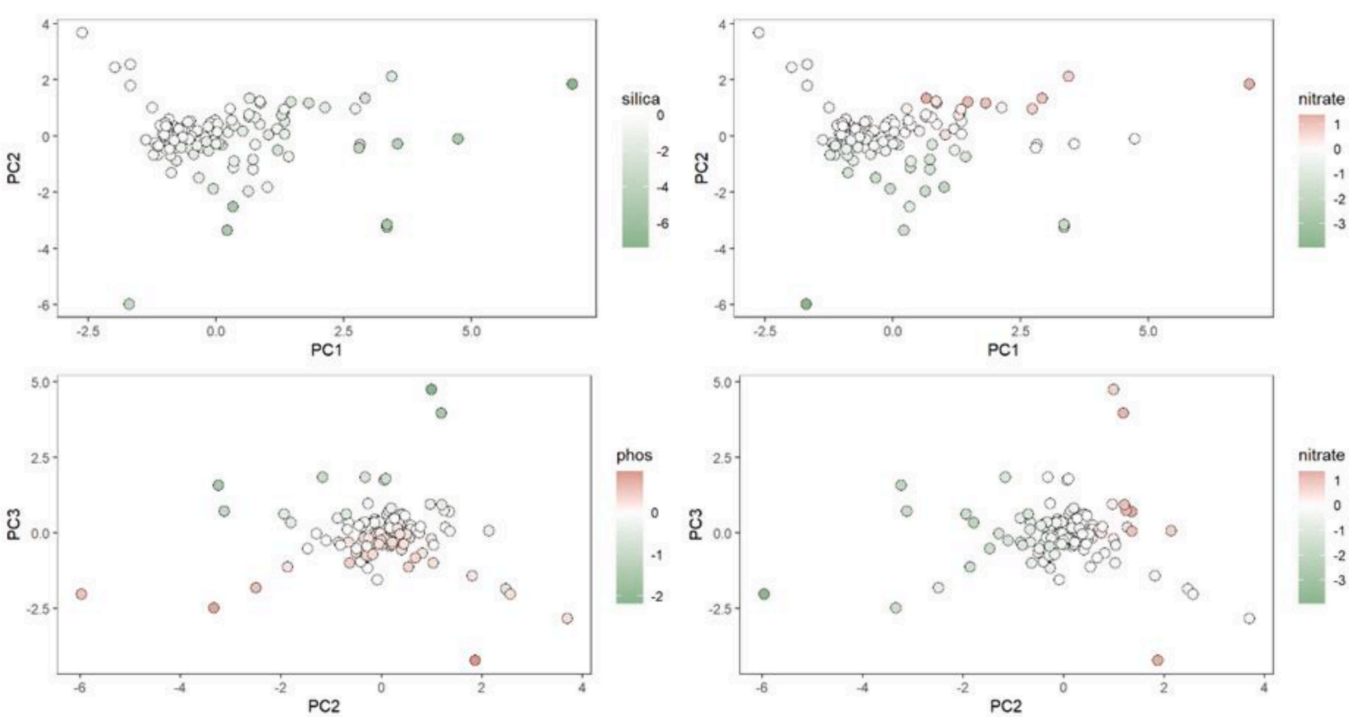

Fig. 4. Scores on PC1, PC2 and PC3 coloured by the values of Si, N and P. Note that this is not a matrix plot.

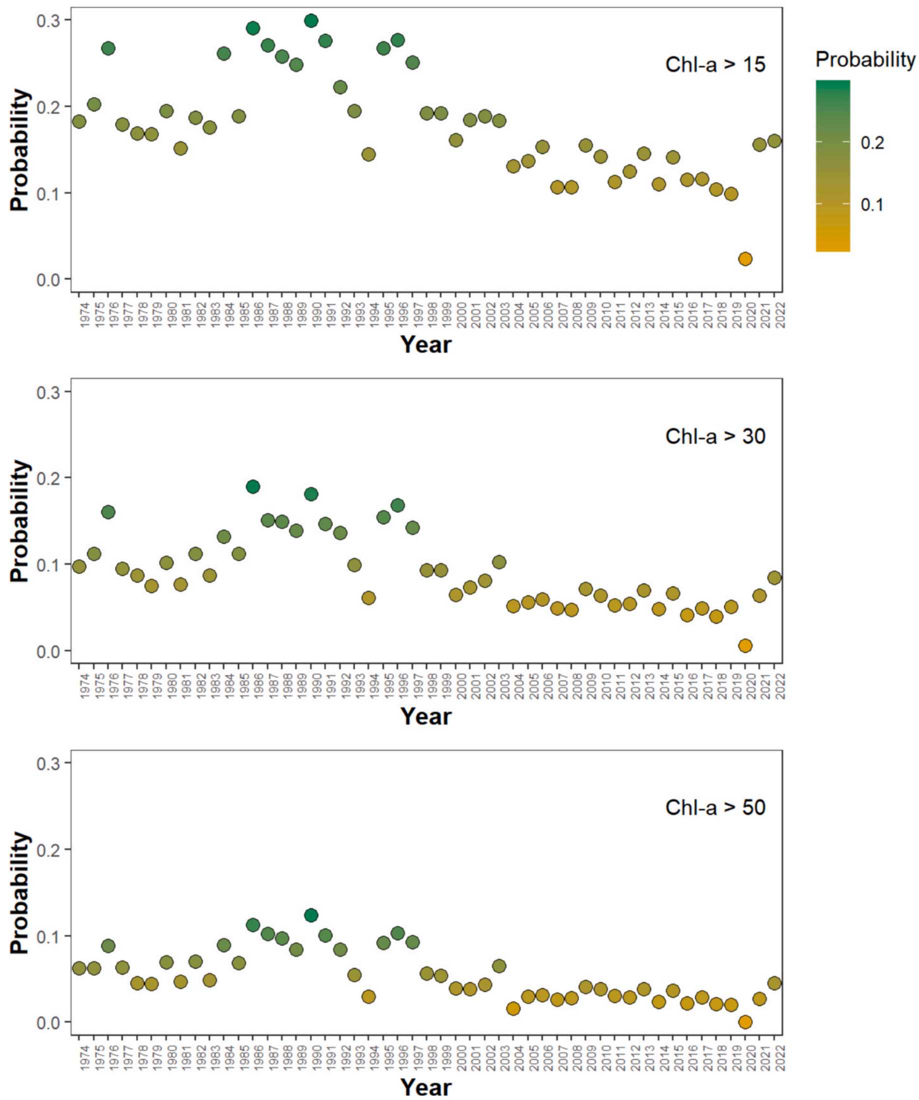

Fig. 5. The main effects plots of the change in the probability of Chl-a events, a) Chl-a > 15 μg/l; b) Chl-a > 30 μg/l; and c) Chl-a > 50 μg/l.

Chl-a concentration at most sites and in fact the proportion of sites showing a significant decline actually increases (74 % of 133 sites), i.e. the physico-chemical variables that could be included were driving increases in the some of the study sites, but, that there is a more general decline in Chl-a concentration. Likewise, the inclusion of physico-chemical variables mask, i.e. partially explain, a general decline in the probability of a Chl-a event.

Over the timescale of this study what were the changes in these physico-chemical drivers? There has been speculation that increasing air temperatures resulting from anthropogenic climate change could drive increasing water temperatures and an increase in magnitude and frequency of algal bloom events. However, whilst there has been a long-term increase in air temperature, even if there is evidence that streams have been buffered against this change (Worrall et al., 2022) and, when the physico-chemical parameters are considered, the majority of study sites showed no significant positive relationship with the stream temperature (67 % of 131 sites, for Chl-a concentration; and 64 % of 131 sites for Chl-a event probability). So, there were sites where there was a significant positive relationship with stream temperature, but also sites where there was a significant negative relationship with stream temperature. These results suggest a complex interplay between a wider suite of both physico-chemical and biological drivers of these variable trends, including water temperature, light levels, flow velocity, nutrients and potentially also top-down grazing by zooplankton, which is not considered in this study but can play an important role in phytoplankton bloom dynamics (Gosselain et al., 1998). Bowes et al. (2009) have identified peak Chl-a in English rivers with diatom blooms in late spring rather than cyano-bacteria blooms in summer and this has been associated with temperature being a limited factor. In contrast, harmful algal blooms (HAB) have been reported for English lakes during times of elevated temperature (Wagstaff et al., 2021).

When considered across all sites and years, then the non-Bayesian approach would predict that a decrease in percentile flow by 1 % would increase Chl-a concentration by a median of 0.2 μg/l (Equation xiii) – which is a smaller change than was detectable by even the Bayesian approach. Marsh and Dixon (2012) demonstrated a rise in river discharge from the UK between 1961 and 2011, with statistically significant increases particularly evident in Scotland, but not in England. Hannaford and Marsh (2006) examined two periods (1963–2002 and 1973–2002) and found increased runoff in western and northern Britain, especially Scotland, while southern and eastern England exhibited no discernible trend. Marsh and Dixon (2012) reported substantial annual runoff increases, reaching 22.2 % in Scotland, but only 1.7 % in England. However, these studies documenting changes in UK river dischargeThe average decline in Chl-a concentration observed in this study was 2 μg/l, significantly greater than what a minor shift in English flows would

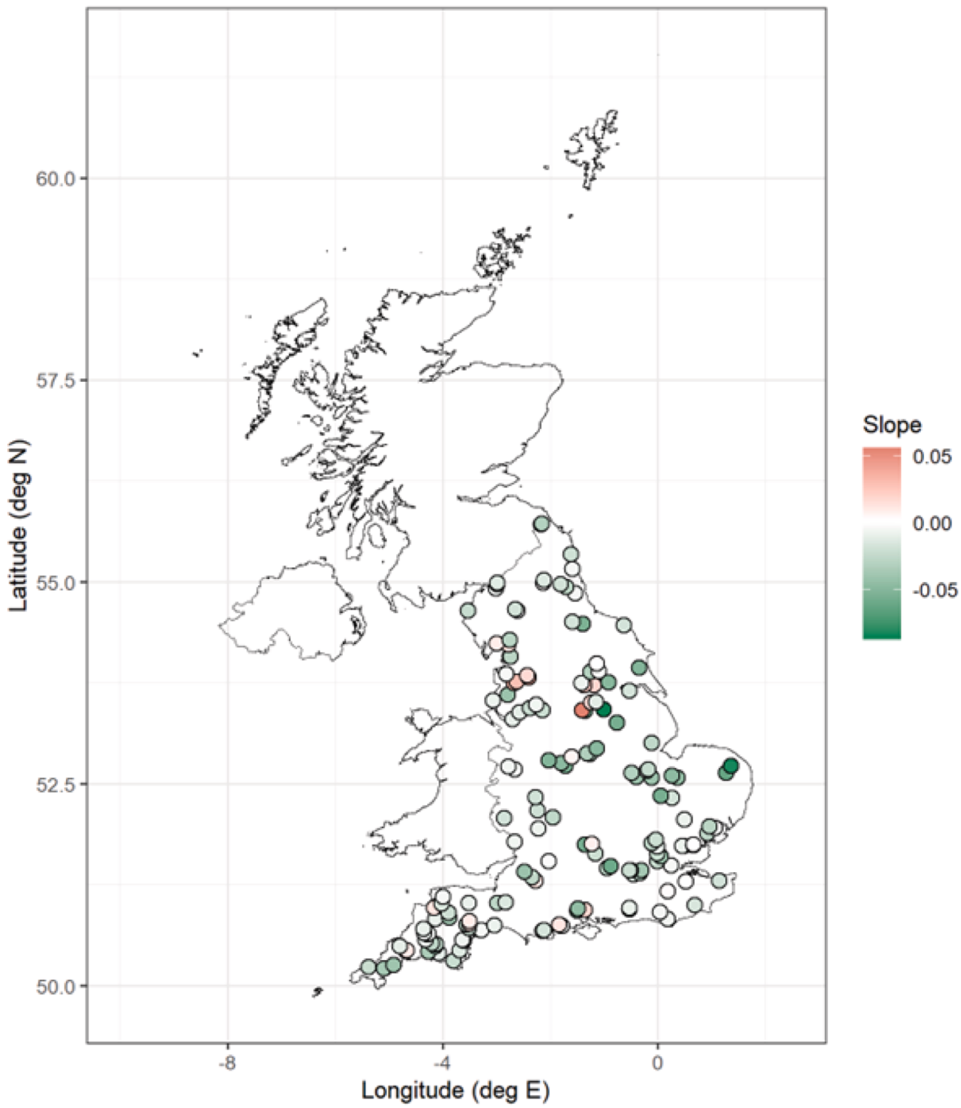

Fig. 6. Distribution of slopes of Bayesian binomial regression based upon spatial and temporal factors.

predict. Moreover, 42 % of sites showed no significant correlation between Chl-a concentration and percentile flow, and this figure rises to 50 % when considering event probability and percentile flow. However, in the physico-chemical models it is the flow at the time of sampling that is considered whereas Chl-a concentration and events may respond to periods of low flow and not just a single day of low flow.

For the concentration models using physico-chemical variables, then we would expect that a unit increase in Chl-a concentration would be accompanied by declines in the concentration of nutrients in proportion to the extended Redfield ratio (Redfield et al., 1963, Brzezinski, 1985) – C:N:P:Si of 106:16:1:16 for balanced diatom growth. From Table 5 and allowing for the atomic mass of Si, N and P for a unit N:P:Si is 14:0:16, i. e. for the Si and N the ratio is very close to that expected and could readily be explained by diatoms using alternative sources of N, e.g. ammonium, or dissolved organic N. The lack of relationship with phosphate (P) could be a matter of limit of detection. If, instead of the median value, the lowest detected change in P was used, then the observed ratio becomes 16:15:3, i.e. the value of P in the median Redfield ratio is 0 and 3. However, this median stoichiometry does not account for the variation in the coefficients and indeed that in 16 % of cases the rise in Chl-a concentration was accompanied by rises in nitrate and phosphate concentrations and not decreases. Spear et al. (2013) considered 94 lakes across the UK and Ireland and found the mass ratio Chl:TP ranged between 0.02 and 0.96 in 2008. The wide variation in Chl:TP shows that some UK lakes were insensitive to changes in P just as observed in this study.

The study has important implications for the ongoing debate about water quality in western European countries facing as they are increasing pressure on surface water resources. Within the UK there has much recent controversy about serious pollution incidents associated with discharges of untreated sewage into rivers (Lawton, 2023, Purnell et al., 2021). The rise in pollution incidents has been attributed to: decades of underinvestment in wastewater infrastructure; expansion in housing and commercial developments; and greater intensity of rainfall events resulting from climate change (Lawton, 2023; Allsop, 2023). The low-frequency water quality data used in this study are never going to be sufficient to examine responses to individual sewage discharge incidents. Increased discharge from sewage treatment works might be expected to have chronic effects, for example developing supplies of nutrients into the fluvial system, but this study shows no evidence for such a build-up. A number of recent studies have shown long-term recovery in macroinvertebrates (Pharoah et al., 2023) and nutrient concentrations (Whelan et al., 2022) in UK rivers. The improvement in UK rivers can be ascribed to improvement in discharges from sewage treatment plants as a result of the implementation of the EU's Urban Wastewater Treatment Directive (European Commission, 1991) which

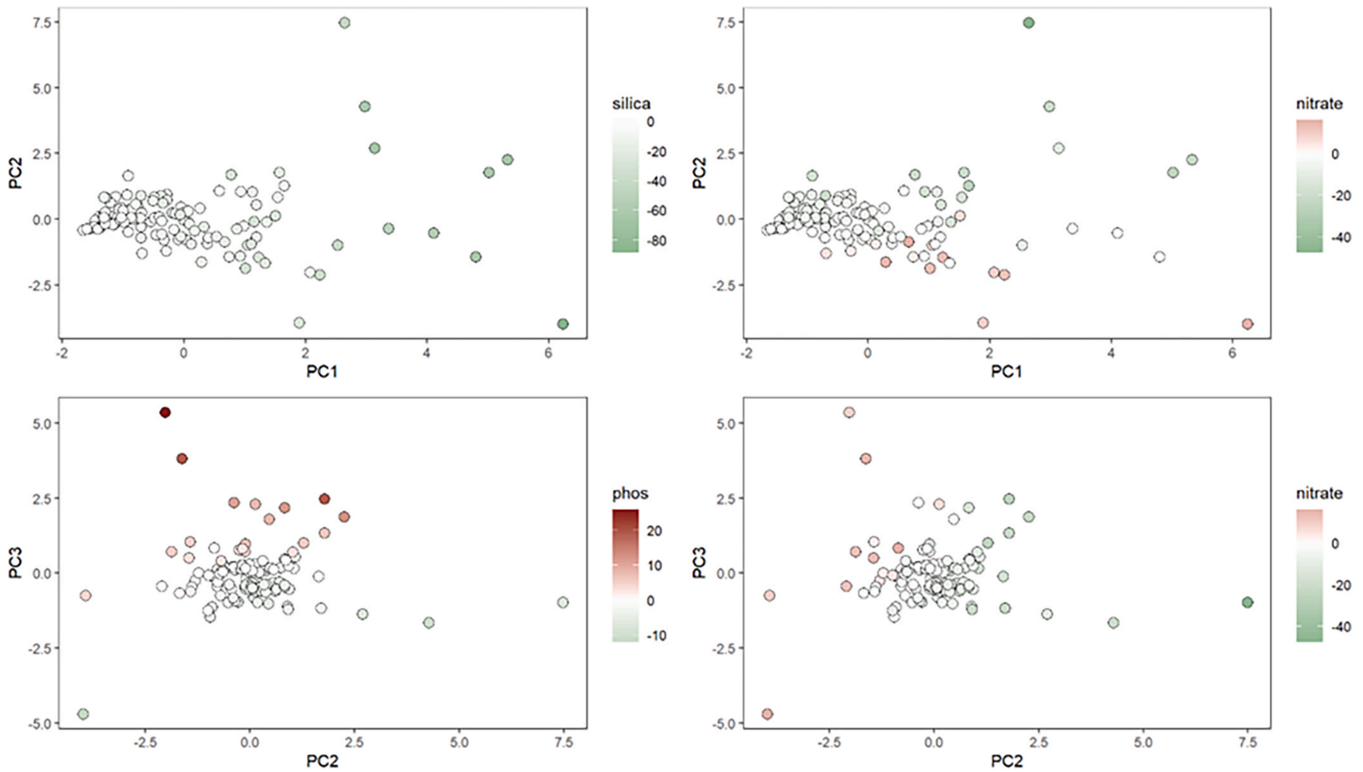

Fig. 7. Scores on PC1, PC2 and PC3 for slopes on the Bayesian binomial model coloured by the values of βSi, βN and βP. Note that this is not a matrix plot.

Table 8
The number of the sites which show a significant relationship with which physico-chemical parameters for the exceedance model. Where No. + ve is the number of sites with slope significantly greater than zero; and No.-ve is the number of sites with a slope significantly less than zero, The Median is the median of all slopes while Median + ve is the median slope of all those sites with significant + ve slopes; and Median −ve is the median slope of all those sites with significant −ve slopes. NB. There were 161 sites in total.

	Year	Percentile flow (Q)	Nitrate (N)	Phosphate (P)	Silica (Si)	Stream temperature (T)
No. significant	119	66	87	63	117	68
No + ve	22	1	18	21	1	46
No −ve	97	65	69	42	116	22
Range + ve	−0.09–0.22	−12.2–2.6	−47.3–16.3	−12.2–26.1	−88–1.25	−13.7–31
Median	0.03	0	3.04	0	7.97	0
Median + ve	0.04	2.6	6.4	5.8	1.25	5.2
Median −ve	−0.05	−4.1	−5.6	−3.3	−9.2	−3.5

Table 9
The loadings on the first three principal components of the principal component analysis of the beta slopes from fitting of Equation (xi).

Variable	PC1	PC2	PC3
Silica	−0.59	−0.07	0.25
Nitrate	0.10	0.69	0.09
Year	0.52	0.35	0.08
Phosphate	0.19	0.14	0.89
Percentile flow	−0.50	0.22	−0.07
Stream temperature	0.28	−0.56	−0.34
Cumulative variance explained (%)	38	61	79

has been demonstrated to lead to step improvements in discharge from sewage treatment works (Civan et al., 2018). Fig. 5 shows occurrence of chlorophyll concentrations above threshold events peaked in 1991–1992 and declined subsequently, which may indicate reduction in algal bloom events in response to improved wastewater treatment. However, caution must be applied in use of the monthly sampling of suspended (water-column) chlorophyll-a data used in this study to characterise algal bloom events. Firstly, algal blooms dynamics respond to changes in physio-chemical conditions on daily to sub-daily scales, so a large proportion of algal bloom events will be missed by monthly sampling. However, the Bayesian approach does show improved precision over more conventional approaches. Secondly, by sampling water-column chlorophyll-a, these measurements only capture suspended algae, thus excluding a large proportion of algal growth in rivers as periphyton (attached algae), especially in the shallower and smaller rivers where phytoplankton do not dominate primary production (Royer et al, 2008). Nevertheless, by identifying these differing patterns in chlorophyll-a trends and responses across England, the large-scale spatio-temporal analysis undertaken in this study provides an important basis for exploring the multiple pressures driving chlorophyll-a responses and algal bloom dynamics at regional to local scales and at higher temporal resolution, particularly in larger, deeper, slower-flowing rivers where phytoplankton dominate.

5. Conclusions

The study provides the first national-scale spatio-temporal analysis of changes in chlorophyll-a in England's rivers over the last five decades. The results reveal no clear and consistent pattern in relationships with key environmental variables across England's network rivers: trends in chlorophyll-a concentration were almost evenly divided between sites with decreasing trends (53 %) and increasing trends (47 %). The majority of river sites (73 %) showed no significant change in the probability of algal bloom events (>30 μg/L) over the last 50 years, with 25 % of river sites showing a decrease, and only 4 % showing an increase in algal bloom probability. The observed significant declines in both Chl-a concentration and probability of algal bloom events were independent of changes in stream temperature; river flow; nitrate; phosphate and silica concentration. These results indicate that there has been no consistent directional response in algal bloom events across England's rivers to the pressures from anthropogenic climate change and the large-scale reductions in P concentrations achieved over the last 50 years, largely from improved wastewater treatment. However, by capturing a unique national-scale picture of differing patterns in chlorophyll-a trends and responses over the last five decades, this spatio-temporal analysis now provides an important basis from which to explore the multiple pressures driving chlorophyll-a responses and dynamics at local to regional scales.

CRediT authorship contribution statement

Fred Worrall: Writing – original draft, Formal analysis, Conceptualization. **N.J.K. Howden:** Writing – review & editing, Conceptualization. **T.P. Burt:** Writing – review & editing, Conceptualization. **H.P. Jarvie:** Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jhydrol.2025.134394.

Data availability

All data used in this study are publicly available. Water quality data can be found at https://environment.data.gov.uk/water-quality/view/landing, and flow and catchment data at https://nrfa.ceh.ac.uk/.

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