

Research papers

Riverine concentrations and export of dissolved silicon, and potential controls on nutrient stoichiometry, across the land–ocean continuum in Great Britain

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ABSTRACT

Silicon (Si) is an essential nutrient element in freshwater and marine ecosystems, and its abundance relative to macro-nutrients (N, P) can impact phytoplankton communities in eutrophic rivers and estuaries. This study is the first national assessment examining (i) the primary sources (geological, biological, landcover) and controls (geomorphological, precipitation) on the transport of terrestrial dissolved silicon across Great Britain to the ocean, and (ii) the current extent and nature of its interactions with macro-nutrients in these catchments in relation to its potential impacts on phytoplankton community structure. It uses results from a year-long survey of 41 rivers along with historical data. Highest concentrations of dissolved Si (4–5.5 mg L⁻¹) were found in rivers of the chalk- and sedimentary sandstone-based catchments of southern Great Britain and the hard sandstone catchments of Scotland. Catchment yield rates for dissolved Si varied between 0.2 and 2.6 t km⁻² yr⁻¹, with highest yields found in catchments with higher precipitation and runoff. Analysis of river N:P and dissolved Si:N ratios suggested that the sampled rivers were typically N enriched, and P limited with respect to dissolved Si. Molar dissolved Si:N ratios < 1, an indicator of river eutrophication, were associated with total nitrogen concentrations exceeding 1.8 mg L⁻¹ or greater. The Indicator of Coastal Eutrophication index was used to assess the potential role of dissolved Si in the eutrophication of coastal waters. Negative values indicating limited

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eutrophication potential to non-siliceous algae were generally found, although some rivers had annual Indicator of Coastal Eutrophication index values exceeding 0, with values as high as $35 \text{ kg C km}^{-2} \text{ day}^{-1}$. In many eutrophic rivers, high dissolved Si concentrations derived from catchment lithology, kept the Indicator of Coastal Eutrophication index values below zero. Results have demonstrated that high N and P export have likely shifted most Great Britain rivers and coastal waters beyond the stoichiometric range where diatoms dominate production and into one where non-siliceous algae may be increasingly present. Thus, future assessments of macro-nutrient management schemes, such as those involving wetlands should include dissolved Si routinely due to its stoichiometric importance.

1. Introduction

Silicon (Si) is an essential nutrient for diatoms, sustaining aquatic primary production and ecosystems, and playing an important role in climate regulation (B-Béres et al. 2023). The Si biogeochemical cycle, and silicate weathering is linked to the carbon cycle over geological time scales and has acted as an essential factor in the drawdown of CO_2 , and in determining the earth's atmospheric gas concentrations (Bernier et al. 1963). In terrestrial ecosystems, dissolved silicon (DSi) is initially produced via the chemical weathering of Ca or Mg silicate minerals driven by dissolved CO_2 and other acids. These reactions include the chemical weathering of feldspars (e.g. albite, K-feldspars) to clay minerals such as kaolinite and montmorillonite (Wollast and Mackenzie, 1983). Whilst all rocks weather to produce DSi, lithologies known to produce high DSi concentrations include sandstones, shales and granites (Chen et al. 2014). In soil ecosystems, plant root exudates and rhizosphere microbial communities drive the natural chemical weathering process through the release of organic acids (Drever, 1984; Kelly et al. 1998). DSi, largely in the form of H_4SiO_4 , is readily absorbed by plants which produce solid amorphous Si in the form of phytoliths (microscopic silica bodies produced by plants to aid physical support), which, when released from decaying vegetation, undergo chemical weathering to DSi, thus re-entering the Si cycle. These pools of plant-derived Si are stored and recycled over different time scales, with forests, grassland, and wetland plant species (e.g. reeds, sedges and horsetails) being major stores (Conley, 2002; Struyf et al. 2009). The annual recycling of Si from phytolith dissolution may be twice that released through silicate mineral weathering (Alexandre et al., 1997). In addition, the soil Si pool in the form of phytoliths can be 500 to 1000 times larger than that of the living biomass of a deciduous or coniferous forest, respectively (Alexandre et al., 1997). Thus, the soil pool is an essential contributor of DSi along the land–ocean continuum (Street-Perrott & Baker, 2008).

Various estimates have been made regarding the size of the global Si biogeochemical cycle (e.g. Struyf et al. 2009; Conley and Carey, 2015). Struyf et al. (2009) estimated that globally $19\text{--}46 \text{ Tmol yr}^{-1}$ Si is released through weathering, whilst terrestrial ecosystems cycle $60\text{--}200 \text{ Tmol yr}^{-1}$ of Si in the form of phytoliths, (Conley, 2002). This figure was updated to an average $84 \pm 29 \text{ Tmol Si yr}^{-1}$ by Carey & Fulweiler (2021). Suggested losses from the terrestrial pool of silicon include 0.5 Tmol yr^{-1} through aeolian transport and 6 Tmol yr^{-1} as net riverine transport to the ocean. The recycling of Si predominantly by diatoms in the ocean accounts for $\sim 240 \text{ Tmol yr}^{-1}$, with 6.5 Tmol yr^{-1} buried on the ocean floor (Struyf et al. 2009).

The biogeochemical cycling of Si is susceptible to anthropogenic perturbation. Firstly, the historical intensification of agricultural practice has reduced soil Si through its offtake in plants and the introduction of the agricultural Si loop in the terrestrial Si cycle (Vandevenne et al. 2012), and secondly via the eutrophication of rivers, lakes and marine waters (Conley et al. 1993; Howarth et al. 2011). The enrichment of N and P from both point and diffuse sources (e.g. Poikane et al. 2019; Richards et al. 2022; Smith et al. 2017) to surface waters may impair water quality by stimulating excessive growth of (sometimes toxic) algae and bacteria. This can lead to hypoxia when the algae die and are decomposed by oxygen consuming microbes, impacting aquatic aerobic life and food webs, fisheries and potentially increasing N_2O production

(e.g. Blaszcak et al. 2022; Breitbart et al. 2018; Davidson et al. 2014; Karlson et al., 2021). Si interacts with excess N and P through in diatom production (Tréguer et al. 2021; Turner et al. 2008). When DSi is not present in sufficient quantities, non-siliceous algae, including toxic and harmful cyanobacteria, may increase in dominance in the phytoplankton community (Billen & Garnier, 2007; Carey et al. 2019; Davidson et al. 2014). Thus assessments in fresh and marine waters are based around the Redfield molar ratio of C:N:P:Si of 106:16:1:20 (Redfield, 1963). In rivers eutrophication work has focused on the Si:N ratio. When it drops below 1 it can indicate that microbial communities may be changing due to eutrophication (Turner et al. 2003). In marine systems this imbalance in nutrient cycles, based on Redfield ratios, is often reported through the concept of 'Indicators for Coastal Eutrophication (ICEP)' (Garnier et al., 2010), an index that assesses the potential for production of non-siliceous algae (especially harmful cyanobacteria) sustained by the delivery of riverine N and P fluxes relative to Si fluxes.

Due to the importance of Si as a nutrient and its role in the stoichiometric safe operating ranges of aquatic systems in which biological processes can effectively self-regulate, and beyond which detrimental impacts, such as algal blooms may occur there is an increasing need to have a fuller understanding of DSi along the land–ocean continuum. This paper provides the first national assessment of DSi along the land–ocean continuum for Great Britain (GB) with its aims being; (i) to explore the geological, geomorphological, biological and land-use controls on the concentration and yield of DSi leaving terrestrial environments and entering the estuarine and marine ecosystems of GB; (ii) to assess current concentrations of DSi in relation to the national long term monitoring data which was collected between 1978 and 2013 in light of reported decreases riverine DSi; (iii) to explore the potential imbalances that currently exist in macro-nutrient concentrations of Si, P and N in rivers across GB and; (iv) to use the ICEP concept to examine impacts of nutrient imbalances as rivers enter the marine environment. The study also provides a national assessment of baseline DSi concentrations prior to the increasing likelihood of 'Enhanced Rock Weathering' technologies being used in GB agricultural systems. This will involve ground rock (e.g. Basalt) being applied to agricultural land to mitigate climate change by drawing down CO_2 in the weathering reaction and releasing DSi (Harrington et al. 2023; Buckingham et al. 2022). DSi and macro-nutrient data were collected as part of a recent year-long survey of GB rivers and estuaries to examine the transfer of C along the land–ocean continuum (Williamson et al. 2021; Tye et al. 2022).

2. Materials and methods

2.1. Survey outline

This national-scale survey sampled 41 rivers, draining $\sim 36 \%$ of Great Britain (GB) (both the mainland and islands; $233,327 \text{ km}^2$) from a set of catchments (Fig. 1) that are representative of the land cover of GB (see Williamson et al. 2021; Tye et al. 2022). The major landcover types defined using the UKCEH Land Cover Map (LCM) 2015 were: Improved grassland (28 % for GB and 29 % for the catchments sampled), arable land (24 % of both GB and the sampled catchments) and acid grassland (9 % of GB and 11 % in the catchments sampled). Sampling sites were located close to, but above the tidal limits, the defined boundary for

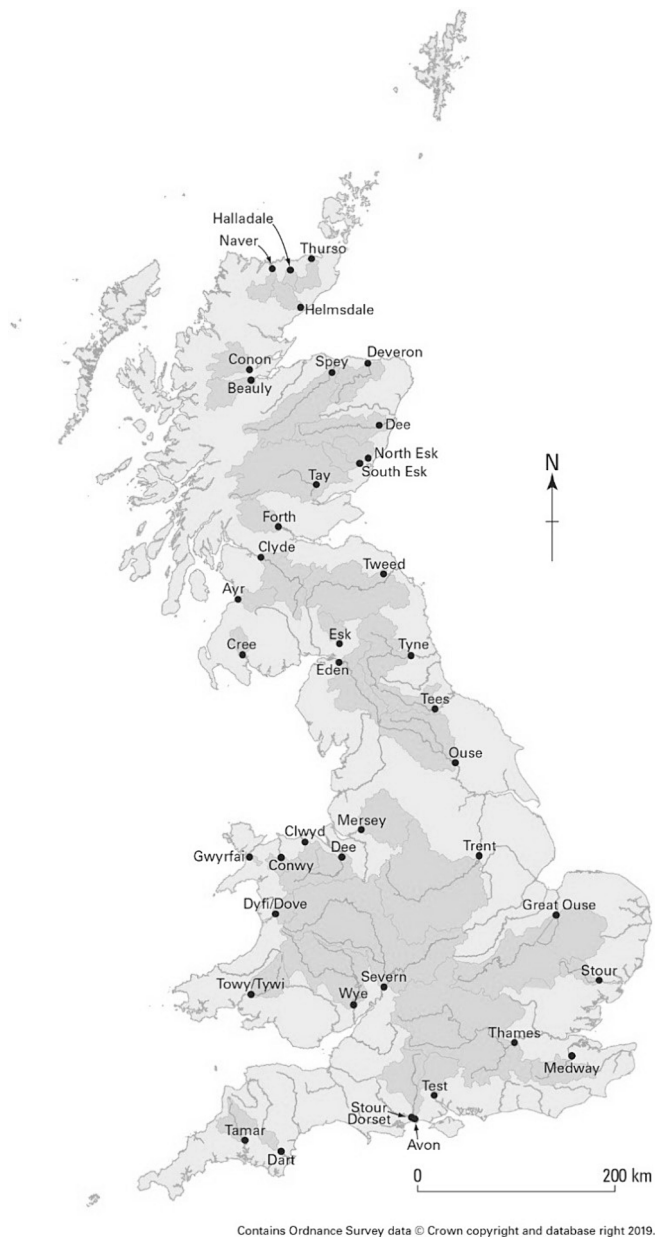


Fig. 1. Location of catchments and sampling points for the 2017 survey.

terrestrial to marine C export in this work (Williamson et al. 2021). The sampling positions were also close (within ~ 50 m) to monitoring sites used by either the National River Flow Archive (NRFA, 2024) or the UK Harmonised Monitoring Scheme (HMS, 2022) which provide GB with long-term water export and quality monitoring data.

2.2. Sampling and collection methods

Since several institutes and laboratories were involved in this project, a major aim was a consistency of approach in laboratory, field, and analytical work. Specific determinants were analysed by only one laboratory, ensuring consistency in analytical procedures. Rivers were sampled monthly from January 2017 to December 2017, with samples collected during the third week of each month, to minimise within-month temporal variation between catchments. Water samples were collected from near the centre of the river, or from fast-flowing water away from the riverbank. Water temperature and conductivity were measured and recorded immediately after sample collection. Samples

collected (also see Williamson et al. 2021 and Tye et al. 2022) and specific to this study, included DSi (filtered using 0.45 μm cellulose acetate syringe filters, stored in HDPE bottles and acidified to 1 % with conc. HNO_3), Total N (TN) and Total P (TP) (collected as unfiltered samples into 250 ml HDPE bottles). After collection, samples were sent under cool (ice packs) and dark conditions using overnight couriers to the laboratories responsible for each of the specific analyses.

2.3. Laboratory analysis

Dissolved silicon (DSi) concentrations were analysed using ICP-MS under UKAS accredited procedures at the British Geological Survey (Tye et al. 2024). DSi concentrations from this study were compared to data collected from 1978 to 2013 as part of the UK Water Quality Sampling Harmonised Monitoring Programme (Simpson, 1980; HMS 2022). HMS data were not available for some rivers including the Avon, Great Ouse, Halladale, Helmsdale, Naver and Ouse. The HMS data were analysed as molybdate reactive Si (dissolved reactive silica), which typically includes dissolved simple silicates, monomeric silica and silicic acid, and an undetermined fraction of polymeric silica (Neal et al. 2005). Measurement by ICP-MS may include submicron (<0.45 μm) colloidal forms of Si and may therefore be slightly higher than the HMS measurement. However, a comparison to the historic HMS data is useful to make after recent work describing how land use change has decreased terrestrial Si mobilisation (Struyf et al. 2010). For the comparison, concentrations of molybdate reactive silicate in $\text{mg-SiO}_2 \text{ L}^{-1}$ were converted to mg-Si L^{-1} . A Shimadzu TOC-L analyser with a TNM-L module was used to measure TN, and TP was analysed using an acid $\text{K}_2\text{S}_2\text{O}_8$ digestion and subsequent molybdenum blue colorimetric analysis on a Seal AQ2 discrete analyser. The dataset for TP and TN along with metadata is available (Tye et al. 2024).

2.4. Ancillary data

Ancillary data for the statistical and modelling analysis were the same as used in Williamson et al. (2021) and Tye et al. (2022). The percentages of carbonate and sedimentary sandstone in the catchments (SI:1) were determined by combining UK catchment and sub-catchment maps with the British Geological Survey's 50 k soil parent material model and using the European Soil Bureau bedrock classification (Lawley et al. 2014). Catchment areas, of other rock types known for producing high weathering rates and DSi concentrations (basalt and shale) in groundwater were also determined, although contributions from these lithologies in the catchments studied were minimal and were not included in the dataset. Mean catchment altitude and Standard period Average Annual Rainfall (SAAR) were included in the modelling data set (SI:2 and SI:3). Both these variables explained significant variability in Dissolved Inorganic Carbon (DIC) export across Great Britain (Tye et al. 2022). Catchment area and land cover characteristics (15 broad habitats) were obtained from the 2015 UKCEH Land Cover Map (LCM, 2015) (Rowland et al. 2017) and are shown in SI:4. Grassland types (e.g. acid or calcareous grassland) were considered separately as they were expected to show some dependency on the geological and hydrological variables considered above. Estimates of catchment human population were made by summing the proportion of population for each local authority area (ONS, 2020) that intersected the catchment. Catchment mean elevation (m) and area along with hydrogeology including Base Flow Index (BFI) were obtained from the NRFA (2024). A complete list of the modelling variables used is shown in SI: 5.

Mean daily water fluxes for the rivers were obtained via the UK National River Flow Archive (NRFA 2024). At most sites, water sampling and flow gauging were located within a few hundred metres of each other. Flows at the gauging station were assumed to be indicative of those at the water sampling site. However, for three rivers (i.e. Eden, Mersey and Welsh Dee) co-located flow data were not available during 2017. For these, gauging data from sites upstream were used to estimate

flows. Past annual discharge data were calculated for each of these upstream gauging stations to ensure that total annual discharge was estimated to within 10 % of observations, with a correction made to the annual discharge calculation for 2017 if differences between upstream and downstream gauging stations were greater than 10 %. The relationship between upstream and downstream daily flows during 2015, the most recent year with comparable data, was calculated using regression analysis and daily flows for the sampling site for 2017 were estimated from the regression equation (Williamson et al. 2021). In addition, daily flows for the River Conon were used to represent those in the nearby River Beauly, assuming the same mean areal runoff for both catchments, that are similar in area and topography. Daily flow data for 2017 were unavailable for the Dyfi, whilst only half a year's data were collected for the Dorset Stour, so these two rivers were excluded from calculations of Si and yield.

2.5. Data treatment

Flow weighted mean (FWM) concentrations of DSi and macronutrients were calculated for each river over a year according to eqn. (1)

$$C_w = \frac{\sum_{i=1}^n c_i q_i}{\sum_{i=1}^n q_i} \quad (1)$$

Where C_w is the Mean Flow Weighted concentration of the determinand (FWM), n is the number of measuring periods, c_i is the average concentration of determinand during i_{th} measurement period and q_i is the average flow rate during i_{th} measurement period (EA, 2024). All statistical analyses were undertaken using the R statistical package v3.5.1 (R Core Team, 2018). Stepwise regression models were produced to explore relationships between catchment variables (SI: 5) on Mean Flow Weighted Concentration (mg L^{-1}), yield ($\text{t km}^{-2} \text{ yr}^{-1}$) and the Indicator of Coastal Eutrophication Potential (ICEP) (see section 2.8). Stepwise regression analysis was undertaken using the 'MASS' and 'leaps' R packages, with the model selected having the lowest Bayesian Information Criteria (BIC) value. Tests for skewness were undertaken on the dependent variables and were Log_{10} transformed if skewness was < -1 or > 1 . DSi, TP and TN yields were calculated using "method 5" of Littlewood et al. (1998), detailed in Eqn. (2), whereby k specifies a conversion factor for the length of sampling, C_i refers to the concentration at sampling time i , Q_i refers to flow at sampling time i , Q_T refers to the mean flow over the whole sampling period, and n is the number of samples taken.

$$DSi_{\text{yield}} = k \frac{\sum_{i=1}^n [C_i Q_i]}{\sum_{i=1}^n Q_i} Q_T \quad (2)$$

It is acknowledged that using such integrating methods may produce some underestimation as compared to using high resolution data (Worrall et al. 2013).

2.6. Riverine nutrient ratios and Indicator of Coastal eutrophication potential

Nutrient imbalances, particularly excess N and P with respect to Si, can lead to river and coastal eutrophication, and conditions where the potential for diatom growth linked to the availability of DSi is limited, causing increases in non-siliceous algae. Typically, macro-nutrient ratios are compared with the approximate Redfield ratios of C:N:P:Si found in marine seston (106:16:1:20). The molar ratios calculated in this work are based on TN, TP and DSi as described by Billen & Garnier (2007). TN was used as it has been shown that both organic and inorganic forms of N can be used in diatom nutrition (Antia et al. 1991), whilst TP was used rather than phosphate, as P has been shown to desorb from suspended particles with increasing salinity, therefore becoming bioavailable (e.g. Tye et al., 2018). The relationship between TN and $\text{NO}_3\text{-N}$ concentrations (mg L^{-1}) in samples from the whole dataset was $\text{TN} = 1.0115 * \text{NO}_3\text{-N}$

$\text{N} - 0.2785$ ($R^2 = 0.98$) demonstrating that TN is dominated by nitrate (NO_3). The dissolved fraction of Si (i.e. DSi) was used because particulate Si has a very slow rate of dissolution in sea water and is therefore discounted as biologically important (Billen and Garnier, 2007).

In addition to exploring the nutrient ratios of the rivers, 'Indicators of Coastal Eutrophication Potential (ICEP)' indices were calculated (e.g. Billen and Garnier, 2007). The ICEP is defined as the carbon biomass potentially produced in the receiving coastal waters resulting from the yield of N or P (according to which one is limiting with respect to each other) and delivered more than DSi. The ICEP expresses the potential production of new non-siliceous algae through the riverine delivery of nutrients, and is expressed as kg C day^{-1} , the unit typically used to describe marine primary productivity. To allow comparisons between rivers, the ICEP is expressed based on catchment area (i.e. $\text{kg C km}^{-2} \text{ day}^{-1}$). Calculations are based on the Redfield molar ratios and are as follows:

$$ICEP = [N_{\text{yield}}/(14*16) - Si_{\text{yield}}/(28*20)]*106*12 \quad \text{if N/P} < 16(N_{\text{limiting}}) \quad (3)$$

$$ICEP = [P_{\text{yield}}/31 - Si_{\text{yield}}/(28*20)]*106*12 \quad \text{if N/P} > 16(P_{\text{limiting}}) \quad (4)$$

where P_{yield} , N_{yield} and Si_{yield} are the mean yields of TN, TP and DSi (in $\text{kg km}^{-2} \text{ day}^{-1}$) delivered at the sampling point. A negative value of the ICEP indicates that Si is in excess over either N or P (the limiting nutrients), and therefore, within this context suggests reduced eutrophication potential from non-siliceous algae. When the ICEP for N or P is positive, the supply exceeds DSi and there is potential for non-siliceous algal production.

Two ICEP indices were calculated. The first was determined using the annual MFW concentrations of the river nutrients DSi, TN and TP, and provides an annual analysis based on the river nutrients being exported from catchments to the ocean. The second ICEP value was calculated on the nutrients being exported by each river on the day of sampling. This second ICEP index provides a snapshot of conditions and is likely to identify the influence of antecedent conditions (e.g. precipitation, season) on the nutrient stoichiometry.

3. Results

3.1. Dsi concentrations in rivers across GB

Maximum and minimum DSi concentrations across all rivers during the survey were 6.87 mg L^{-1} (November) and 0.03 mg L^{-1} (April) respectively. The monthly range of DSi concentrations show a general consistency, but with noticeably lower concentrations of each of the box and whisker percentile concentrations in April (Fig. 2). Whilst Fig. 2 shows a depletion in DSi percentile concentrations during April, for March and May the upper quartile concentration remained at similar concentrations to those in the spring and summer period of March – September. A comparison to the long-term HMS silica results was made to examine whether substantial changes had occurred in the intervening years due to land-use change (Section 2.6). Results demonstrated very similar mean concentrations between the 2017 data and the long-term data (Fig. 3a). The variation in the yearly concentrations of river DSi is plotted for the HMS dataset along with the 2017 survey result (Fig. 3b). Whilst the 2017 concentrations percentiles are low in comparison to some survey years they fit within the overall time series, which shows no obvious downward trend with time. Further comparison of DSi concentrations from the two surveys are presented in SI:6.

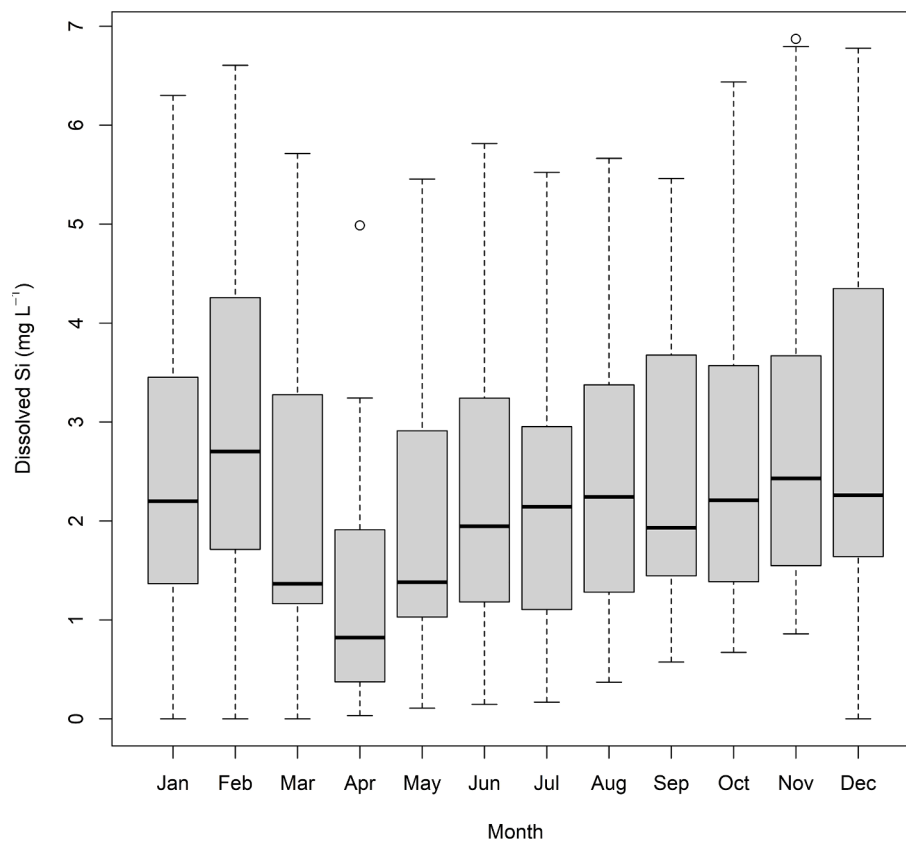


Fig. 2. Box and whisker plots showing the range of DSi concentrations in the 41 rivers sampled during the 2017 survey. The whiskers represent the 5th and 95th percentiles, and the box represents the 25th, 50th and 75th percentiles.

3.2. Concentration and yield of DSi and macro-nutrients in rivers across GB

Fig. 4a shows the annual MFW concentration of DSi across the river catchments surveyed during 2017 whilst the monthly measured DSi concentrations for each river are shown in SI:7. The highest MFW concentrations of DSi (between 4 and 5.5 mg L⁻¹) occurred in the southern catchments, particularly the chalk-based catchments of the Great Ouse, the Thames, Avon, and Test. Other catchments with high DSi included the Trent, Severn, Mersey and Medway and Ouse had MFW concentrations between 2.9 and 4.1 mg L⁻¹. These catchments typically had both limestone and sandstone as dominant geologies (SI: 1). The sandstone-based catchments in eastern Scotland also had relatively high DSi concentrations, as did the granite dominated catchments such as the Tamar and Dart. However, many of the high-altitude, hard rock (schist, quartzite based) catchments in northern GB had relatively low DSi MFW concentrations. These catchments have large areas of peat that potentially reduce contact of precipitation with the bedrock and vegetation types known to act as a DSi sink. A regression model was parametrised for MFW DSi using the variables in SI:5. The best fitting (lowest BIC) model, explained 88 % of the variance in MFW DSi ($P < 0.001$) (Table 1). The area of urban land and degree to which the catchment was influenced by groundwater (i.e. Base Flow Index) were positively associated with MFW DSi, while SAAR, and the areas of 'Bog' and 'Fresh Water' within the catchment were negatively associated. The Observed v Predicted graph is shown in SI:8.

Dissolved silicon yield ($\text{t km}^{-2} \text{yr}^{-1}$) was calculated using equation (2), with rates varying between 0.2 and 2.62 $\text{t km}^{-2} \text{yr}^{-1}$ (Fig. 4b). Catchments with the highest yields included the chalk-based Stour catchment, the granite-based Dart and Tamar catchments in the southwest of England, the Conwy and Tywi in Wales and the Cree, Ayr, Clyde, North Esk, South Esk and Deveron in Scotland. In this case, the

best fitting (lowest BIC) stepwise regression model explained 44 % of the variance in DSi yield ($P < 0.001$). Significant landcover variables of fen and bog along with broadleaf woodland, were identified and had negative coefficients (Table 2; SI:9).

The variation in monthly concentrations of TN and TP for the sampled rivers is shown in SI:10 and SI:11. Highest concentrations of TN ($> 5 \text{ mg L}^{-1}$) and TP were generally found in those catchments with high populations and intensive agriculture. Annual nutrient yields ($\text{t km}^{-2} \text{yr}^{-1}$) of Si, TN and TP for each river were calculated and used to calculate molar Si:N, N:P, and Si:P nutrient ratios (Table 3). Nutrient yields to estuaries from the 41 rivers sampled during 2017 ranged from 0.26 to 5.20 $\text{t km}^{-2} \text{yr}^{-1}$ for TN and 0.01 to 0.42 $\text{t km}^{-2} \text{yr}^{-1}$ for TP.

3.3. River water nutrient stoichiometry

Molar nutrient ratios (Si:N, Si:P and N:P) were calculated for each sampling for individual rivers (SI:12–14). Si:N molar ratios were reasonably consistent across the year in many rivers. However, generally larger and more temporally variable Si:N ratios occurred in some rivers with less populated and less intensively farmed catchments (e.g. the Cree, Halladale, Helmsdale, and Spey). With lower concentrations of TN the Si:N ratio in these rivers may be more susceptible to changes in antecedent precipitation and river flow. Turner et al. (2003) identified the molar Si:N ratio as a proposed indicator of aquatic (freshwater and marine) health. Both Officer & Ryther (1980) and Smayda (1990) suggested that when the DSi:DIN ratio in marine waters $< 1:1$ alternative phytoplankton communities could be enabled. Plotting annual MFW TN concentration against the molar Si:N (Fig. 5) shows that ratios < 1 are associated with TN concentrations exceeding $\sim 1.7 \text{ mg L}^{-1}$. For the whole dataset using all monthly river samples this value was $\sim 1.8 \text{ mg L}^{-1}$. For the molar ratio of Si:P, the greatest variation and highest ratios (up to 300) were found in less populated and less intensively farmed

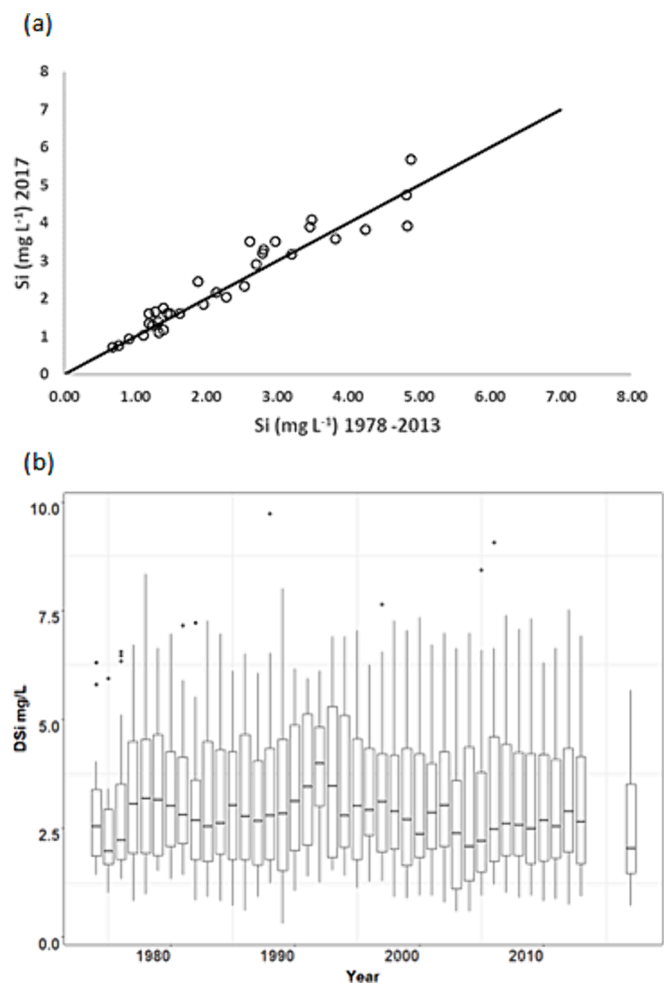


Fig. 3. Relationship between the annual MFW concentrations of DSi from the 2017 survey and annual mean data collected during the long term (1978–2013) Harmonised Monitoring Scheme program (Fig. 3a). The solid line is the 1:1 relationship and the regression relationship between the two surveys was $Si_{2017} = 0.983 \cdot Si_{1978-2013} + 0.158$ ($R^2 = 0.91$). In Fig. 3b the time series shows the distribution of mean DSi concentrations from the HMS survey and this study.

catchments such as the Dart, Dee (Scotland), Deveron, Halladale, Helmsdale, South Esk and Spey (SI:13). The relationship between the molar ratios of N:P v Si:N (Fig. 6) and Si:N v Si:P (Fig. 7) were plotted together with Redfield ratio values. Fig. 6 shows that, for all rivers except the river Ayr, the ratio of N:P was > 16. The inferred P limitation of the remaining sites occurred both in rivers with or without excess Si. Fig. 6 shows the Si:N v Si:P plot, which also demonstrates, with the exception of the river Ayr, a similar P limitation in relation to the Redfield Ratio used.

3.4. Assessment of coastal eutrophication potential – calculation of ICEP values

Assessments of how catchment DSi, N, and P yields could have

Table 1

Model coefficients selected through stepwise regression to predict the MFW DSi concentration in rivers sampled as part of the 2017 survey across Great Britain. Significance codes are *** $P < 0.001$, ** $P < 0.01$, * $P < 0.05$.

Coefficients	Estimate	Std. Error	Pr(> t)
Intercept	3.462e + 00	5.130e-01	1.09e-07 ***
Acid Grassland	-9.391e-06	2.301e-06	0.000267 ***
SAAR	-1.745e-03	2.205e-04	3.99e-09 ***
Fen & bog	-4.571e-05	6.867e-06	1.42e-07 ***
BFI	2.897e + 00	6.316e-01	6.21e-05 ***
Population	3.120e-07	9.849e-08	0.00329 **

Multiple R-squared: 0.8991
 p-value: 1.763e-15
 Residual standard error: 0.4557 on 33 degrees of freedom

Table 2

Model coefficients selected through stepwise regression for a model predicting the yield of DSi ($t\ km^{-2}\ yr^{-1}$) from catchments across Great Britain sampled as part of the 2017 survey. Significance codes are *** $P < 0.001$, ** $P < 0.01$, * $P < 0.05$.

Coefficients	Estimate	Std. Error	Pr(> t)
Intercept	1.813e + 00	1.146e-01	< 2e-16 ***
Broadleaf woodland	-1.559e-05	3.693e-06	0.000157 ***
Fen & Bog	-2.814e-05	7.027e-06	0.000297 ***

Multiple R-squared: 0.4423
 p-value: 2.723e-05
 Residual standard error: 0.4855 on 36 degrees of freedom

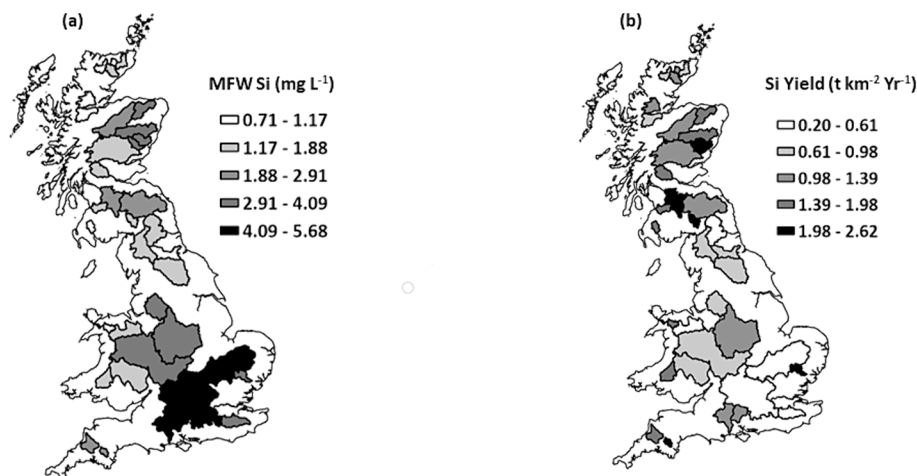


Fig. 4. Diagram showing (a) Flow Weighted Mean concentrations of DSi for the 41 catchments sampled as part of the 2017 river survey; (b) Calculated annual DSi yield ($t\ km^{-2}\ yr^{-1}$) for the 41 catchments sampled as part of the 2017 river survey. Contains Ordnance Survey data (C) Crown Copyright & database right 2019.

Table 3

Annual macro-nutrient yields, molar ratios and ICEP values calculated for each of the 39 rivers where flow data allowed calculations to be undertaken.

Sample	Yield (T Km ⁻² Yr ⁻¹)		Total P	Molar Ratio			ICEP kg C km ⁻² day ⁻¹
	DSi	Total N		N:P	Si:N	Si:P	
AVON	1.12	1.16	0.02	106.01	0.48	51.08	-4.16
AYR	1.82	1.52	0.42	8.28	0.60	4.93	35.84
BEAU	0.77	0.26	0.01	41.02	1.48	60.73	-3.18
CLWYD	2.61	2.93	0.13	51.46	0.44	22.85	-1.61
CLYDE	2.08	1.52	0.15	22.77	0.68	15.53	4.22
CONO	1.22	0.51	0.03	39.64	1.19	47.15	-4.27
CONW	1.92	1.09	0.05	54.25	0.88	47.54	-6.78
CREE	1.95	1.00	0.06	40.47	0.97	39.19	-5.76
DART	2.62	1.16	0.04	67.51	1.12	75.67	-11.87
DEES	1.77	0.60	0.02	61.88	1.48	91.51	-8.52
DEEW	0.38	0.97	0.05	43.75	0.19	8.52	3.33
DEVE	1.77	1.13	0.04	60.95	0.78	47.74	-6.28
EDEN	0.86	1.11	0.10	24.67	0.39	9.58	6.16
ESK	2.13	0.89	0.05	38.30	1.19	45.77	-7.30
FORTH	1.77	0.95	0.12	18.16	0.93	16.93	2.39
GREA	0.20	0.39	0.01	85.73	0.25	21.86	-0.07
GWYR	2.02	0.98	0.03	73.09	1.03	75.05	-9.11
HALLADALE	1.05	0.31	0.04	20.52	1.66	34.16	-2.60
HELM	1.12	0.24	0.01	40.94	2.30	94.20	-5.46
MEDWAY	0.56	0.90	0.05	44.28	0.31	13.84	1.71
MERSEY	0.87	1.28	0.16	18.07	0.34	6.11	12.84
NAVE	0.90	0.28	0.01	45.30	1.60	72.49	-4.00
NESK	2.19	1.60	0.06	60.70	0.68	41.34	-6.84
OUSE	0.74	0.94	0.06	38.85	0.39	15.24	1.62
SESK	2.20	1.10	0.02	126.65	0.99	125.48	-11.42
SEVE	0.90	1.48	0.07	49.55	0.30	15.01	2.08
SPEY	1.39	0.49	0.01	79.72	1.41	112.46	-7.07
STOU	2.06	5.20	0.15	80.81	0.20	15.92	3.75
TAMAR	1.62	1.90	0.16	26.41	0.42	11.18	8.47
TAY	1.24	0.55	0.03	42.91	1.14	48.75	-4.47
TEES	0.92	1.53	0.16	21.40	0.30	6.39	12.65
TEST	1.25	1.88	0.02	190.51	0.33	62.95	-5.22
THAMES	0.54	0.81	0.03	65.04	0.34	21.80	-0.19
THURSO	0.98	0.41	0.03	36.72	1.18	43.43	-3.21
TRENT	1.13	2.37	0.12	43.91	0.24	10.44	6.83
TWEE	1.16	0.78	0.02	80.82	0.74	60.01	-4.75
TYNE	0.61	0.47	0.02	47.26	0.65	30.67	-1.25
TYWI	1.98	1.41	0.09	35.62	0.70	25.03	-2.19
WYE	0.82	1.00	0.04	54.74	0.41	22.30	-0.39

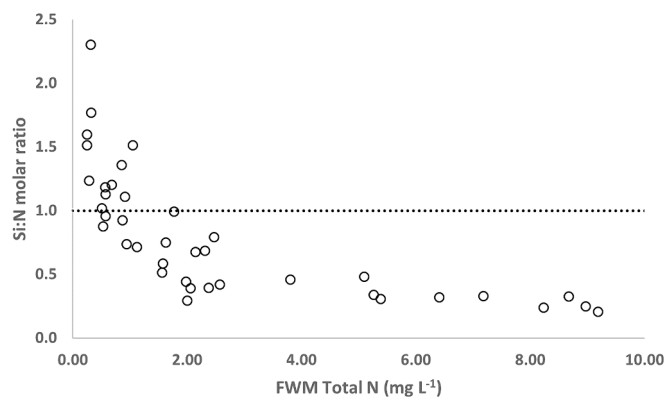


Fig. 5. Molar Si:N ratios vs annual flow weighted mean total N concentrations from the 2017 survey. The dashed line represents Si:N=1. Values < 1 are associated with TN concentrations exceeding ~ 1.8 mg L⁻¹.

affected coastal eutrophication were made using the ICEP methodology (outlined in Section 2.8), for the 39 rivers where flow data were available. The first analysis examined annual ICEP values based on MFW concentrations of macro-nutrients. As previously stated, Eqn. (4) was used where N:P ratios were > 16, and this was used for all rivers except the River Ayr, where the N:P ratios was < 16 and Eqn. (3) was therefore applied instead. Fig. 8 shows the distribution of calculated annual ICEP indices (kg C km⁻² day⁻¹) for the sampled catchments. Positive values

for ICEP (indicative of enrichment with N and/or P relative to Si) are largely found in the southern catchments with large urban areas and intensive agriculture, whilst smaller catchments, especially those in Scotland, show negative values of ICEP. Overall, the highest ICEP value of 35.8 kg C km⁻² day⁻¹ was found for the river Ayr in Scotland. Typically, the southern catchments with intensive agriculture and high populations had ICEP values of between 0 to 12 kg C km⁻² day⁻¹ meaning that the excess of N, P or both relative to DSi had the potential to increase non-siliceous algae production and change community structure. To explore the likely variables contributing towards the ICEP values a stepwise regression analysis was undertaken (Table 4 and SI:15). The model ($R^2 = 0.43$, $P < 0.001$) coefficients selected indicated a negative correlation with altitude and a positive correlation with % sandstone in the catchments.

ICEP values (kg C km⁻² day⁻¹) were calculated for the day of sampling for the 39 rivers where flow data were available (Fig. 9). As for the yearly calculation, when ICEP values were calculated for individual sampling days most rivers were found to be P limited and having N in excess. Firstly, results show that most rivers in each month had negative ICEP values. However, some rivers had relatively large positive ICEP values. Many of these positive ICEP values can be related to precipitation events occurring before sampling, suggesting that this may increase N and P inputs (relative to Si) from diffuse or point sources. These events occurred in March 2017 (rivers Ayr: ICEP=124; Clyde: ICEP=49; Eden: ICEP=49; Mersey: ICEP=30; Tamar: ICEP=41), April 2017 (river Mersey: ICEP=46); August 2017 (rivers Ayr: ICEP=62; Mersey: ICEP=25) and November 2017 (River Mersey: ICEP=109; Ayr: ICEP=170). The second key finding was that there was a strong seasonal effect in the

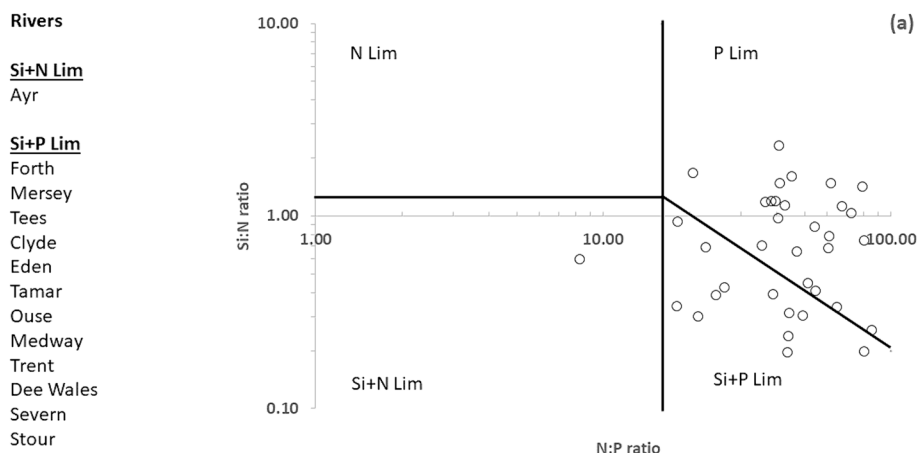


Fig. 6. Molar N:P v Si:N plot rivers sampled in the 2017 survey based on annual flux. The graph has 4 quadrants from upper left quadrant and moving clockwise these represent (i) an area where N is limited and Si is in excess; (b) an area where P is limited and Si is in excess; (c) an area where Si is limited along with P and (d) an area where Si is limited along with N.

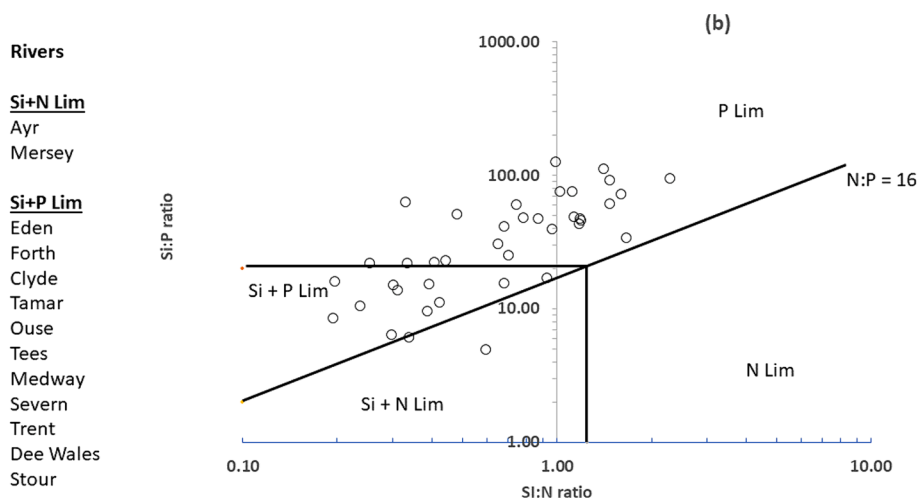


Fig. 7. Si:N v Si:P plot for the rivers sampled in the 2017 survey based on annual flux. The plot has 5 areas from the upper left quadrant and going clockwise these represent (a) an area where Si is in excess and P is limited; (b) an area where Si is in excess and N is limited; (c) an area where N is limited but Si is in excess and (d) an area where P is limited but Si is in excess.

summer months between April and July, where most ICEP values were closer to zero with more positive ICEP values as outliers.

4. Discussion

4.1. Influences on flow weighted mean DSi concentrations

The highest FWM concentrations of DSi occurred in (i) the chalk and limestone-based catchments and (ii) the calcite-cemented sandstone catchments in southern GB, both of which have high baseflow index (BFI), i.e. a high groundwater contribution to flow. The inputs of DSi from chalk and limestone-based catchments in the south of England (>4.09 mg Si L⁻¹) are largely derived from the siliceous materials that occur as impurities. These are largely nano-quartz spheres crystallized in the marine chalk environment, which flocculate and accumulate on the sea floor (Lindgreen et al. 2011). The source of the nano-quartz is from the dissolution of diatoms and radiolarians. Haines & Lloyd (1985) published a range of DSi values for UK groundwaters and found that those from chalk had high Si concentrations (range: 9.2–26.8 mg-SiO₂ L⁻¹; range 4.23 – 12.32 mg Si L⁻¹). Groundwater samples taken close to the river sampling point used for the River Stour, having the highest concentrations (26.8 mg-SiO₂ L⁻¹; 12.32 mg Si L⁻¹). This was reflected in the

DSi concentrations found in the river Stour (BFI=0.52) being the highest MFW concentration found in the 2017 survey.

High Si in sandstone lithologies is likely derived from the dissolution of silica from quartz particles and secondary precipitates. Haines & Lloyd (1985) reported a range of 10.7–14.7 mg-SiO₂ L⁻¹ (4.92 – 6.76 mg Si L⁻¹) for UK sandstone aquifer groundwater. In addition, silicate minerals such as feldspars found in sedimentary sandstones will release Si from weathering processes. These may be particularly high in the calcite-cemented sedimentary sandstones of southern England, as compared, for example, to the harder silica cemented sandstones in Scotland. The greater porosity of calcite-cemented stones increases the available surface area for weathering reactions to take place. In addition, the waters often have a high pH, which encourages silicate dissolution (Drever, 1994).

DSi concentrations of the 2017 survey were compared to the HMS survey (1978–2013) results. Despite the pool of DSi being measured by ICP-MS in theory being slightly larger than the molybdate-reactive Si assay, a comparison of the 2017 data with the long-term Si data from the HMS, along with data from Neal et al. (2005), suggest that concentrations of the 2017 survey were broadly similar. Between-year variation of riverine DSi could result from fluctuations in the amounts and seasonal intensity of precipitation, diffuse and point sources of macro-nutrients

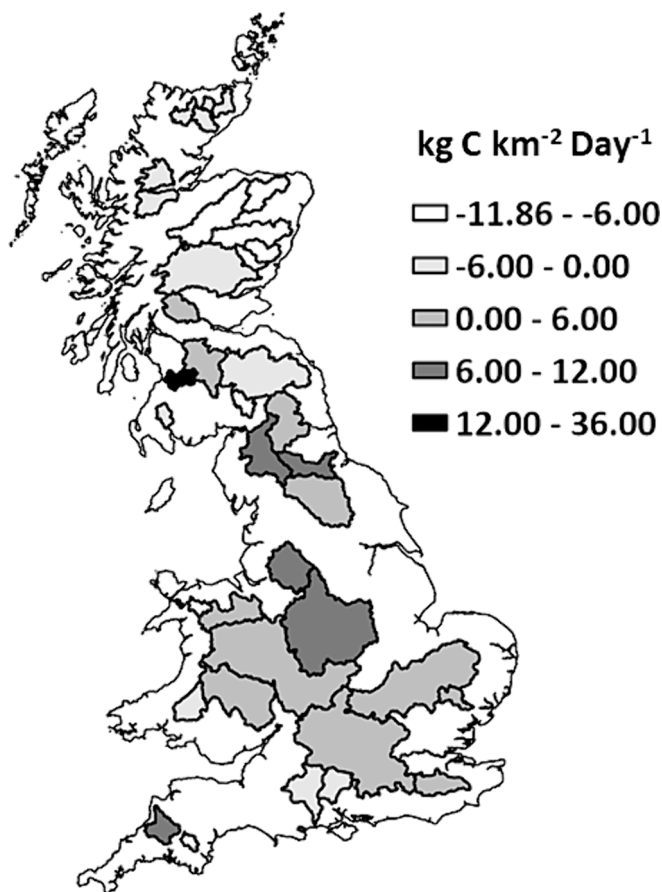


Fig. 8. Map showing catchment annual calculated ICEP values for catchments based on 2017 survey results. Contains Ordnance Survey data (C) Crown Copyright & database right 2019.

Table 4

Model coefficients selected through stepwise regression for a model predicting annual ICEP in river waters from the 2017 survey. Significance codes are *** $P < 0.001$, ** $P < 0.01$, * $P < 0.05$.

Coefficients	Estimate	Std. Error	Pr(> t)
Intercept	0.6307	2.1820	0.7742
Altitude	-0.0191	0.0076	0.0175 *
Sandstone	0.6084	0.1641	0.0007 ***

Multiple R-squared: 0.4307

p-value: 5.232e-05

Residual standard error: 4.637 on 35 degrees of freedom

and diatom growth. With respect to the 2017 survey, annual precipitation was also close to the long-term average (Met Office, 2017). For the UK, an average precipitation of 1106 mm was recorded across the country in 2017, and this represented 95.9 % of the long-term average (1981–2010), suggesting that the 2017 results were not biased towards an extreme dry or wet year. The comparison of the two surveys is worthwhile for two reasons. Firstly, Struyf et al. (2010) and Clymans et al. (2011) have both reported on the long term (>250 years) decrease in silica mobilisation resulting from the conversion of forest to agricultural land, and secondly, more recent studies have suggested possible decreases in plant available Si through the depletion of soil Si via the agricultural removal of straw and grass (Guntzer et al. 2012). This has been linked to reported declines in the soil phytolith pool and the addition of the 'silica loop' in the biogeochemical cycle (Vandevenne et al. 2012; Keller et al. 2012). However, comparison of our data with

the earlier HMS survey does not provide support for a major decrease at a UK scale over the last 40 years. It is possible that DSi concentrations had declined before widespread river monitoring was initiated in the UK.

A regression model was parameterised to identify key variables that may influence DSi concentrations in the rivers studied. However, because of significant covariation of climate, mean altitude, geology, soils, agricultural and urban extent from North to South GB, the variables selected need careful interpretation. The regression model that best explained MFW DSi concentrations using catchment characteristics included two variables with positive coefficients: urban area and BFI. The role of the chalk and sandstone lithologies as sources of DSi concentrations may be accounted for in the BFI variable, as these lithologies result in largely base-flow driven catchments. DSi in groundwaters has been found to reflect mean residence times for recent groundwater (5–100 years) at regional scales (Marcais et al. 2018). Generally, 'urban areas' are not considered by themselves to be a large source of Si within the global Si cycle (Sferratore et al. 2006). Thus, the inclusion of 'population', a possible proxy for urban areas, as a positive coefficient may further identify the sandstone and chalk-based catchments of southern GB, as they also have greater urban areas. In addition, urban areas within catchments also create areas of impermeability to bedrock and soil. In the current study SAAR had a negative coefficient, as the southern chalk and limestone catchments are also dry areas of the country. Finally, the area of both fen and bog and freshwater in the catchments also had negative coefficients in the model. These may both relate to the use of silica by diatoms and wetland plants, reducing DSi concentrations in rivers (Kokfelt et al. 2009; Struyf & Conley, 2009; Struyf et al. 2010). In addition, these variables may also indicate the higher altitude and northern catchments which have lower permeability. Overall, despite the complexity of the geological, geomorphological, climate and ecological interactions that occur in each catchment, the variables selected suggest the importance of silicates and phytolith weathering. The transfer of DSi from weathering depends on the concentration and availability of minerals for weathering, the transport of solutes and volume and residence time of water passing through the system. These will differ for each catchment, and under different environmental conditions (Maher, 2010; Raymond and Hamilton, 2018). For many catchments, particularly those with lower BFI, the principal source of DSi may be via the weathering of soil phytoliths (Farmer et al. 2005).

4.2. Influences on DSi yield

Yields of DSi ($t\ km^2/yr$) in GB were found to be between 0.2 and 2.62 $t\ km^2/yr$ (0.43 – 5.60 $t\ km^2/yr$ as SiO_2). These are relatively low yields compared to global estimates. Beusen et al. (2009) reviewed global river DSi yields. Rates exceeding $> 8\ t\ km^2/yr$ (as SiO_2) are typically found in the tropics (high rainfall), and catchments with high areas of volcanic rocks, along with Arctic regions (both have fresh silicate mineral supply). The regression modelling undertaken by Beusen et al. (2009) identified the proportion of volcanic rocks in a catchment, annual precipitation, soil bulk density (as a negative variable describing the role of vegetation) and catchment slope angle as a proxy for relief and erosion, to be key variables. In the 2017 GB survey, the DSi yield was relatively low and with relatively little variation across the country. This may suggest that Si in the form of phytoliths act as the major source of DSi (Derry et al. 2005; Farmer et al. 2005). In addition, the gradient of precipitation across the country, the aquifer recharge and runoff produced, likely results in offsetting the higher DSi concentrations in the south of GB. DSi yields were higher in many of the catchments on the western side of GB where higher SAAR leads to higher runoff. Many of the wetland/peat-based catchments of GB such as the Halladale had low yields of DSi. The model accounted for less variance than the one describing DSi concentrations, with a relatively low R^2 of 0.49. However, the model selected Two negative variables which were the areas of

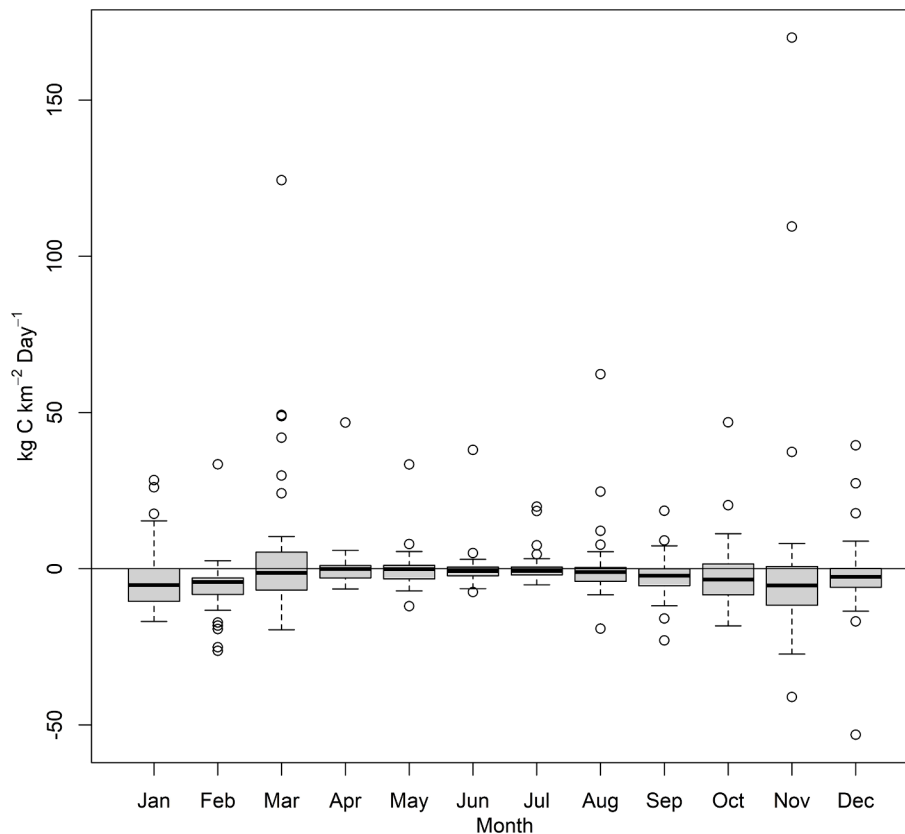


Fig. 9. Range of calculated ICEP values for the 39 rivers of the 2017 survey produced for the day of sampling. The whiskers represent the 5th and 95th percentiles, and the box represents the 25th, 50th and 75th percentiles.

fens and bog and broadleaf woodland (Table 2). The selection of fens and bogs suggest that these may act as potential DSi sink habitats (Bernard et al. 2010; Struyf & Conley, 2009; Struyf et al. 2010) or that geologically they are areas of low silicate weathering. Peat environments are potentially major DSi sink habitats but although included as a potential explanatory variable in the model it was not selected within the stepwise regression. This may be because this mapped geological variable includes both wet and dry (drained) peatland, with the latter not acting as an active wetland DSi sink. In addition, catchments with high peat coverage may decrease the amount of precipitation that comes into contact with mineral soils and bedrock thus decreasing mineral weathering. The inclusion of the Broadleaf Woodland coefficient suggests that this may relate to a decrease in runoff in heavily wooded catchments through increased evapotranspiration or precipitation interception. Overall, results demonstrated that the concentration and yield rates of DSi for the catchments surveyed in this paper were largely controlled by the interactions of geological, ecological and geomorphological properties, along with south westerly prevailing winds and precipitation patterns.

4.3. River nutrient concentrations and stoichiometry

Current interactions between DSi and macronutrients across GB reflect changes over a range of different spatial and temporal scales. Firstly, the concentrations and stoichiometry of DSi and macro-nutrients found in the 2017 survey result from changes in the long-term management of land and nutrients of many GB catchments. For DSi, results in comparison to the HMS survey suggest that any decreases in terrestrial Si sources (e.g. Struyf et al. 2010) may have occurred prior to river monitoring taking place. For macronutrients, modelling has shown how many catchments have changed from being N and P poor, to conditions of excess N and P since ~ 1750, reaching peak excess between 1980 and

2000 (Bell et al. 2021). However, current yields of TP in the 2017 survey were in a similar range to those reported by Worrall et al. (2016) for the period 1990 to 2012. Reported ranges were between 0.05 – 0.49 t P km⁻² yr⁻¹. Yields of TN from the 2017 survey ranged between 0.24 – 5.20 t N km⁻² yr⁻¹, compared to the 1990–2012 national dataset range of up to 8 t N Km² yr⁻¹ (Worrall et al. 2012).

Whilst underlying controls on riverine DSi concentrations and yields have been identified in this study, annual in-river processes also impact DSi and can be strongly related to macro-nutrient concentrations (Neal et al. 2005). The major in-river process of note was the decline in DSi concentrations, probably due to diatom uptake in the spring (Neal et al. 2005). In the current survey, decreases in river DSi concentrations were found in April 2017 (Fig. 2). Riverine diatom blooms in GB typically occur from March to early June, usually peaking in April, and as the bloom peaks, Si is often depleted (Moorhouse et al. 2018; Snell et al. 2018; Johnson et al. 2024). However, the range of DSi concentrations found in April were similar to other months suggesting that some more northerly, or less eutrophic rivers experienced less significant diatom blooms. This reduction in DSi was most pronounced in the Stour catchment which is highly eutrophic (SI:10 & 11). In winter it showed the highest MFW DSi concentrations, whilst in April 2017 it showed the lowest MFW concentration of 0.03 mg L⁻¹. Further variation in the yearly cycle in concentrations of DSi, N and P in the rivers sampled will be determined by (i) source and amount in the catchment; (ii) mobilization through weathering, erosion or biogeochemical processing; (iii) the transport of the macro-nutrients from the catchment to the waters. These can be influenced by human activities in the catchment, along with the natural catchment characteristics. In addition, temporal shifts in water quality can be influenced by streamflow, precipitation, and air temperature (Guo et al. 2018). These will change the inputs of point and diffuse sources of N and P (Bowes et al. 2008).

Further spatial and temporal variations in DSi and macro-nutrients

concentrations (Si:10–11) will influence nutrient stoichiometry (Si:12–14) along the length of individual rivers. It has been demonstrated that changes in the concentrations of nutrients in relation to each other vary along river systems which will also shift the elemental stoichiometry and, potentially the limiting nutrient. For example, Leong et al. (2014) and Carey et al. (2019) both demonstrated a decrease in DSI concentrations with distance from the headwaters, whilst N and P concentrations increased as greater diffuse and point sources contributed to the river waters in the Mississippi catchment. However, whilst the management of N and P through river systems may be manageable and may decrease through improvements in the management of point and diffuse sources (Bell et al. 2021; Peacock et al. 2022) or rebalancing stoichiometry through reconnection to wetland environments (Stutter et al. 2018), DSI remains intrinsic to each catchment and therefore not possible to easily change through management.

Due to the controls on river DSI concentrations and yields previously described, the perturbation of the N cycle is of particular importance because of the magnitude of the loads involved. Turner et al. (1998) described the Si:N ratio of 1:1 as a pivot point. Based on yield (Table 3), only 12 of the 39 rivers investigated had mean annual molar Si:N ratios (range 0.25–2.5) > 1:1. When considering individual sampling events, most rivers had occasions when Si:N < 1:1 (Si:12). A significant ‘power’ relationship ($R^2 = 0.63$; $P < 0.001$) between annual Si:N based on yield and estimated catchment population was found (Fig. 10). This relationship is similar to that reported for major global rivers (Turner et al., 2003) where molar Si:N (range 0.1–12) correlated with the percentage of developed land (urban and agricultural) in catchments, suggesting diffuse (e.g. agricultural) and point sources (e.g. wastewater treatment works) as a major source of N. In the current study similar relationships were also found between Si:N and catchment areas of arable ($R^2 = 0.27$) and improved grassland ($R^2 = 0.54$) agriculture suggesting fertiliser use was another likely source of catchment N enrichment. These relationships were not as strong as that found for catchment population, but results point to the intensification of human activity within the catchments as the source of N.

In this study, some general patterns were evident in the molar Si:N, Si:P and N:P nutrient ratios. Firstly, those rivers with lower concentrations of TN and TP have greater temporal variation in their nutrient ratios (SI Figures 11–14). This likely results from lower buffering of these nutrients in river waters making them more susceptible to changes in the relative magnitude of P and N inputs from point and diffuse sources caused by precipitation and other events. For rivers where TP and TN concentrations were higher (e.g. Mersey, Great Ouse, Medway, Stour) more consistent and lower ratios of Si:N and Si:P were found throughout the year demonstrating that point and diffuse sources of N and P buffer these ratios. For the N:P ratio, greater variation appeared to occur in the first part of the year and may reflect the changing nature of

N and P inputs. Reasons for the variation in TN concentrations may include: (i) for smaller chalk based catchments such as the Stour, Avon and Test, and to a degree the sandstone catchment of the Trent, concentrations of TN were high at the beginning of year and this may be associated with higher BFI and contributions of $\text{NO}_3\text{-N}$ from groundwater; (ii) the application of N fertilisers during the spring and summer to crops and grassland; and (iii) the impacts of precipitation on the concentration of diffuse and point sources of N and P. Based on the molar ratio it was determined that the Si:N ratio dropped below 1:1 at a threshold concentration of $\sim 1.8 \text{ mg TN L}^{-1}$. This is higher than the 0.1 mg TN L^{-1} given as the threshold concentration for the world’s major river basins (Turner et al. 2003). This much higher threshold concentration for GB rivers could result from the catchments being much smaller, with less opportunity for DSI to enter ‘sinks’ such as reservoirs and uptake by diatoms, thus helping to maintain DSI concentrations as diffuse N and P enter the rivers (Justić et al. 1995). In addition, many of the GB rivers with high concentrations of N and P also have relatively high DSI concentrations sourced from their lithology.

4.4. Marine eutrophication and ICEP values

Coastal eutrophication is a recognised problem around the world leading to dissolved oxygen depletion (hypoxia and anoxia), loss of critical habitats (e.g. seagrass beds and coral reefs), changes in ecological structure and biodiversity, along with algal blooms (Howarth et al. 2011). For the UK, Maier et al. (2008) reported significant reductions in N and P in rivers due to the EU’s urban Wastewater Treatment Directive, although less change had resulted in N loads to estuaries. This reported general decrease in N and P has continued (Axe et al. 2022) although analysis of the HMS data for N suggests that this may be a consequence of reductions of NH_4^+ from wastewater treatment works but with a remaining large NO_3^- legacy from agricultural land (NEA, 2011). Results from the 2017 survey demonstrated the recent extent of nutrient enrichment entering GB estuaries, and particularly the degree of continued N enrichment. Nutrient ratios determined for the ICEP analysis and based on annual yields were typical values for temperate European and North American rivers where eutrophication regularly occurs (Billen & Garnier, 2007). The range of annual ICEP values reported for the 2017 survey were between -119 to $35.8 \text{ kg C km}^{-2} \text{ day}^{-1}$. However, most positive values of ICEP found in the 2017 survey, particularly for rivers in southern GB were $< 12 \text{ kg C km}^{-2} \text{ day}^{-1}$. This figure is similar to published values in a Europe wide assessment of ICEP values examining the extent of eutrophication of the North Sea (Howarth et al. 2011). The stepwise regression model ($R^2 = 0.43$) was not particularly strong but confirms the likely macro-nutrient status of the catchments as important factors in determining ICEP values. The identification of altitude as a negative variable indicates the

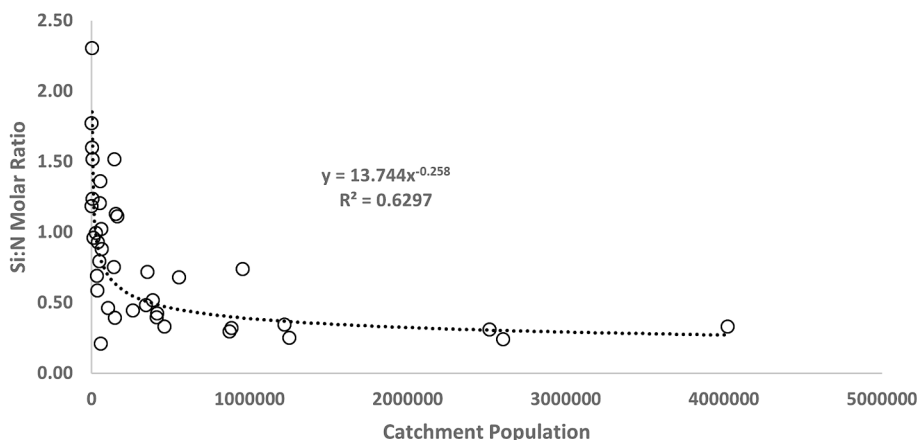


Fig. 10. Relationship between annual mean molar Si:N ratio for rivers and catchment population.

intensification of agriculture at lower altitudes and greater human populations leading to an increase in treated wastewater entering rivers (Neal et al. 2010). Soils formed from sandstone geology are also likely to be agriculturally productive, where past leaching of $\text{NO}_3\text{-N}$ to the aquifers results in high groundwater concentrations which may be exported to rivers via BFI (Wang et al. 2013).

Whilst the annual ICEP values calculated suggest that DSi concentrations are sufficiently high that conditions for non-siliceous algal blooms are generally not favoured, ICEP yield rates calculated for the day of collection, suggest greater occurrences where $\text{ICEP} > 0$. During the summer months the values of ICEP for the 39 rivers included in this analysis were more constrained around zero. These more constrained ICEP values likely result from higher evapotranspiration and lower weathering producing DSi whilst TN concentrations from point sources such as wastewater treatment works may remain similar or increase in concentration because of lower river flows. Incidences where $\text{ICEP} \gg 0$ appeared to be related to storm events and increases in point and diffuse sources of N and P entering the rivers. Nutrient loading models for rivers in England suggest that concentrations of N and P decrease with increasing flow due to dilution of a relatively constant input, whilst concentrations of N and P from diffuse sources usually increase with increasing flow (Bowes et al. 2008; Bowes et al. 2014). These incidences suggest that further work is needed to investigate the frequency and duration of these events to build an improved picture of their impacts within riverine and estuarine systems. Whilst the results from this survey are based on samples taken at the tidal limits of the rivers, these are often above many cities (e.g. London) and inputs from wastewater treatment works may occur below this point. These lower points of discharge, in addition to the input of river nutrients, will help determine the presence of estuarine algal blooms, and will also reflect the residence time of waters within the estuary.

4.5. Wider implications

In future, catchment concentrations and export of DSi may be accelerated by climate change, driven by higher temperatures and more extreme precipitation events (Met Office, 2019), in similar ways to those that may potentially influence the riverine DIC cycle (Tye et al. 2022). This study has demonstrated the role of SAAR in DSi concentrations and fluxes, particularly in the wetter western side of GB. In addition, warming may increase the temperature of groundwater (Hemmerle & Bayer, 2020) and this may lead to increased silicate mineral weathering of catchment bedrock, increasing DSi loss via base flow. However, the impacts of climate change on groundwater temperature is presently largely unclear (Egidio et al. 2024). However, greater impacts on DSi fluxes may arise from efforts to mitigate rising atmospheric CO_2 through the application of crushed basalt rock to agricultural land (a process referred to as ‘Enhanced Rock Weathering’), used to mimic the natural drawdown of CO_2 via silicate weathering processes (Beerling et al. 2020). Signals representing the application of liming materials have previously been found in DIC behaviour in river waters (Oh et al. 2006), so it is likely that applications of basalt will impact river DSi concentrations. However, much may depend on the distribution of application (likely to be focused on arable land) and application rate (up to 100 t/ha; Harrington et al. 2023; Buckingham et al. 2022) which suggests that not all catchments will be equally affected (Kantzas et al. 2022). This study provides a valuable baseline against which to monitor and verify changes in the terrestrial to ocean pathway of DSi and will support the assessment of biogeochemical or ecological impacts of this practice.

5. Conclusions

Results from this study have demonstrated how riverine DSi across GB is strongly influenced by the interactions of a range of geological, geomorphological, precipitation and landcover variables. Examination of data from the 2017 survey suggests that riverine DSi concentrations

are within the range of the long-term HMS dataset, and there was no indication of recent decreases in DSi concentration through the so-called ‘silica loop’. This may be a result of major land-use change in GB having taken place over many centuries. Whilst these factors will largely determine concentrations and yields of DSi from catchments, its ecological importance is in maintaining the stoichiometric safe operating ranges of aquatic systems in which biological processes can effectively self-regulate, and beyond which detrimental impacts, such as algal blooms may occur. For GB, results have shown that the impacts of eutrophication in many rivers and estuaries are partly offset by catchments with lithologies that supply high concentrations of DSi. However, the management of riverine macro-nutrients to improve stoichiometry is complex and currently focuses heavily on source control of N and P. Stutter et al. (2018) suggest that this emphasis on source controls, including the management of legacy P (Jarvie et al. 2013) and N (Wang et al. 2013; Ascott et al. 2021) has dominated ‘eutrophication management’ to the possible detriment of considering how the biological regulation of nutrients, such as reconnecting rivers with sources of allochthonous DOC via linking to wetlands and riparian forests, could help decrease N and P concentrations. However, results from the current study have demonstrated the importance of monitoring DSi, along with N and P, when considering ‘biological regulation’ as many wetland-based schemes may involve potential DSi ‘sink’ habitats.

CRedit authorship contribution statement

Andrew M. Tye: Writing – review & editing, Writing – original draft, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Helen P. Jarvie:** Writing – review & editing, Conceptualization. **Bryan M. Spears:** Writing – review & editing, Funding acquisition, Conceptualization. **Nancy B. Dise:** Writing – review & editing. **Jennifer L. Williamson:** Writing – review & editing, Investigation. **Dan J. Lapworth:** Writing – review & editing, Methodology. **Don Monteith:** Writing – review & editing. **Richard Sanders:** Methodology, Investigation, Funding acquisition, Conceptualization. **Daniel J. Mayor:** Writing – review & editing, Project administration, Investigation, Funding acquisition, Conceptualization. **Michael J. Bowes:** Writing – review & editing, Investigation. **Michael Bowes:** Writing – review & editing, Investigation. **Annette Burden:** Investigation. **Nathan Callaghan:** Investigation. **Gareth Farr:** Investigation. **Stacey Felgate:** Investigation. **Stuart Gibb:** Investigation, Funding acquisition. **Pete Gilbert:** Investigation. **Geoff Hargreaves:** Investigation. **Olivier S. Humphrey:** Investigation. **Patrick Keenan:** Investigation. **Vassilis Kitidis:** Investigation, Conceptualization. **Monika D. Jürgens:** Writing – review & editing, Investigation. **Adrian Martin:** Investigation, Data curation. **Monty Pearson:** Investigation. **Philip D. Nightingale:** Investigation, Conceptualization. **M. Gloria Pereira:** Investigation. **Justyna Olszewska:** Investigation. **Amy Pickard:** Investigation. **Andrew P. Rees:** Writing – review & editing, Investigation, Conceptualization. **Mark Stinchcombe:** Investigation. **Fred Worral:** Writing – review & editing, Investigation. **Chris D. Evans:** Writing – review & editing, Project administration, Investigation, Funding acquisition, Conceptualization.

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.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jhydrol.2024.131738>.

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