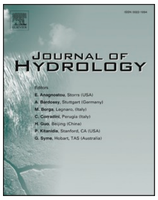
Journal of Hydrology 637 (2024) 131362

Contents lists available at ScienceDirect

Journal of Hydrology

journal homepage: www.elsevier.com/locate/jhydrol



Research papers

Changes in the limiting nutrients and dominant phytoplankton communities of three major European rivers: Response to catchment lithologies and human activities

Sibo Zeng [a,c,1], Hailong Sun [b,1], Zaihua Liu [b,d,*], Nico Goldscheider [e], Simon Frank [e], Nadine Goeppert [e], Min Zhao [b], Haitao Zeng [b], Cuihong Han [b]

[a] Chongqing Key Laboratory of Karst Environment & School of Geographical Sciences, Southwest University, Chongqing 400715, China
[b] State Key Laboratory of Environmental Geochemistry (SKLEG), Institute of Geochemistry, Chinese Academy of Sciences (CAS), 550081 Guiyang, China
[c] Institute of Geological Sciences, Geophysics Section, Freie Universität Berlin, 12249 Berlin, Germany
[d] CAS Center for Excellence in Quaternary Science and Global Change, 710061 Xi'an, China
[e] Institute of Applied Geosciences, Division of Hydrogeology, Karlsruhe Institute of Technology (KIT), 76131 Karlsruhe, Germany

ARTICLE INFO

Keywords:
Limiting nutrients
Dominant phytoplankton
Catchment lithology
Human activity
River eutrophication

ABSTRACT

Catchment lithologies and human activities can cause variations in riverine carbon (C), nitrogen (N), and phosphorus (P) loads, and the ratio of these nutrients may affect the primary productivity of rivers and their phytoplankton communities. We conducted a comparative study of biogeochemical variations in three major European rivers—the Rhine, Danube, and Seine—which reveals the impacts of different carbonate outcrops and human impacts (agricultural activities and sewage input) on the changes in the limiting nutrients and phytoplankton community compositions of flowing water systems. N limitation was observed in the Rhine and Danube owing to their low average NO_3^- loads (4.04–6.45 mg/L). Although the extensive outcrops of carbonate rocks in the Seine catchment result in high average HCO_3^- concentrations of ~ 4.68 mmol/L, the elevated inorganic C input did not match the high average NO_3^- loads (~19.38 mg/L), driven by intensive agricultural activity and urban sewage input, demonstrating a potential C limitation on productivity. Our results show that the productivity of the Seine River, determined by the chlorophyll-a concentration, was significantly related to the dissolved inorganic carbon (DIC) concentration (coefficient of determination: $R^2 = 0.68$, $P < 0.05$). Our results demonstrate that changes in DIC content can significantly alter the dominant phytoplankton species in the water column. The high inputs of DIC and aqueous $CO_{2(aq)}$ to the Seine lead to Bacillariophyta proportions that are 3.96–8.81 % and 19.87–22.56 % higher than those of the Rhine and Danube in the wet and dry seasons, respectively. This can be explained by the difference in the efficiency of carbon concentrating mechanisms (CCMs) among phytoplankton species. Therefore, to mitigate river eutrophication and improve the quality of the aquatic environment, we suggest that future water–carbon management in the flowing water systems with abundant nutrients should consider C-limitation alleviation and its potential effect for reducing the abundance of harmful algae.

1. Introduction

Carbon (C), nitrogen (N), and phosphorus (P) are essential for the primary productivity and carbon sequestration of aquatic ecosystems (Paerl et al., 2015; Hammer et al., 2019; Shao et al., 2023). Generally, N and P have been considered to be the dominant limiting nutrients for algal growth in aquatic ecosystems with low nutrient contents (Schindler, 1974, Schindler et al., 2016; Howarth and Marino, 2006; Paerl et al., 2016). However, C has not been regarded as a limiting element in the conventional view (Sterner, 2008; Schindler et al., 2016). However, recent studies suggested that aquatic photosynthesis can increase the water pH, causing the depletion of aqueous carbon dioxide ($CO_{2(aq)}$). Decreased $CO_{2(aq)}$ in the water column may reduce the productivity of aquatic ecosystems and result in C-limitation because some

---

* Corresponding author at: State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, CAS, Guiyang 550081, China.
E-mail address: liuzaihua@vip.gyig.ac.cn (Z. Liu).

[1] These authors contributed equally.

https://doi.org/10.1016/j.jhydrol.2024.131362
Received 14 April 2023; Received in revised form 2 May 2024; Accepted 3 May 2024

algae cannot utilize HCO_3^- due to the lack of carbon-concentrating mechanisms (CCMs) (Finlay, 2003; Low-Décarie et al., 2014). In this case, the high input of dissolved inorganic carbon (DIC, composed of $CO_{2(aq)}$, HCO_3^- and CO_3^{2-}) can promote the productivity of aquatic plants (Zeng et al., 2019a). Thus, C is currently being regarded as a potential limiting element for aquatic ecosystems (Bao et al., 2022; Shao et al., 2023).

The supply of anthropogenic N and P to aquatic systems has increased globally due to increased agricultural N fertilizer usage and urban-industrial sewage discharge (Tong et al., 2017; Xuan et al., 2019; Yu et al., 2019; Conley et al., 2009; Paerl et al., 2016; Liu et al., 2020). These rising inputs of N and P may promote the productivity aquatic ecosystems and enhance their carbon sequestration, but they can also result in blooms of nuisance algae (such as Cyanophyta) and lead to eutrophication (Paerl et al., 2015, 2016; Huisman et al., 2018). The contamination of water resources due to eutrophication may subsequently threaten human health, ecosystem services, and various ecosystem functions (Tong et al., 2017; Huisman et al., 2018; Chen et al., 2019; Noori et al., 2022; Mahdian et al., 2023; Malekmohammadi et al., 2023). Therefore, reducing N and P loads are major treatments to alleviate eutrophication in aquatic environments. However, removing the anthropogenic N and P from aquatic systems using sustainable methods remains a challenging task in water resource management around the world (Liu et al., 2020; Czajkowski et al., 2021; Dehestaniathar et al., 2021; Goodarzi et al., 2022). Compared to N and P treatments, recent studies have found that the supply of elevated amounts of DIC to aquatic ecosystems can not only increase their productivity and carbon sequestration, but it can also reduce the abundance of nuisance algae (Bao et al., 2022). Hence, the DIC input is currently becoming a new potential water management tool to synchronously enhance the carbon sink and mitigate eutrophication in freshwater ecosystems (Ma and Wang, 2021; Bao et al., 2022; Lai et al., 2023; Shao et al., 2023; Zhang et al., 2023).

Previous studies of nutrient limitation and eutrophication have focused mainly on lakes and reservoirs (Paerl et al., 2011; Smith et al., 2016; Tong et al., 2017; Schindler et al., 2016; Sun et al., 2022). However, flowing freshwater systems such as rivers and streams are vital for nutrient transport from land to sea, and they are also greatly affected by eutrophication (Jarvie et al., 2018). However, the analysis of the major limiting element in these flowing freshwater systems and the evaluation of the influence of elevated DIC input on river eutrophication have lagged behind that for lakes and reservoirs (Lewis et al., 2011; Jarvie et al., 2018; Shao et al., 2023). Precise knowledge of which environmental conditions may cause C, N or P-limitation in rivers, and the impacts of the elevated input of DIC for the phytoplankton community in flowing water bodies, are major research gaps in recent studies. Therefore, to better manage carbon sequestration and prevent the eutrophication of flowing freshwater systems in the future, additional comprehensive studies are needed to detect the relationships between primary productivity and major nutrients in the rivers with different environmental conditions and to explore whether C-limitation alleviation can alter the phytoplankton community compositions.

In this study, we selected three major European rivers—the Rhine, Danube, and Seine— which were impacted by different lithologies (carbonate vs non-carbonate) and human activities (agricultural activities and sewage leakage). These rivers have different carbonate area proportions and land use patterns, which lead to large gradients of the C, N, and P inputs to their phytoplankton communities. From the summer of 2018 to the spring of 2019, we performed a comparative analysis of the nutrient loads (C, N, P), Chlorophyll-*a* (Chl-*a*) concentration, phytoplankton community structure, and stable carbon isotopes of inorganic and organic carbon at different sampling locations. The selected rivers and measured parameters were intended to achieve three major research objectives: (1) Test the assumption that low dissolved N and P loads via catchment management can lead to the N or P limitation of productivity in flowing freshwater systems. (2) Verify that the limiting nutrient of a flowing freshwater system subjected to high dissolved N and P loads, may change to C due to the control of the ecosystem C:N:P stoichiometry. (3) Confirm that C inputs can substantially alter the composition of phytoplankton communities in flowing water bodies, and a higher DIC input may trigger the succession of the phytoplankton community and reduce the abundance of harmful algae.

2. Materials and methods

2.1. Conceptual framework of this research

This study was performed during 2018–2019 on three major European rivers—the Rhine, Danube, and Seine. To achieve our research objectives, we systematically organized the field investigations, water samplings, and in situ and laboratory measurements. To better present the conceptual framework for this research, a schematic diagram of the methodology is shown in Fig. 1. In Sections 2.2–2.5 we give details of the study sites, field investigation, laboratory analysis, and modeling methods.

2.2. Study sites and field sampling

The Rhine River originates in Lake Toma, Switzerland, and flows for 1233 km before discharging into the North Sea. The average discharge is 2300 m^3/s, and the drainage area of the Rhine River Basin is ~ 185,300 km^2, covering major parts of Switzerland, Germany, Luxembourg, France, and the Netherlands, and parts of Western Austria and southeast Belgium (Hartmann et al., 2011; Demirel et al., 2013). The Rhine River Basin lithology ranges from siliciclastic sedimentary rocks to alluvial deposits. Carbonate rocks cover 19.1 % of the drainage area and are distributed mainly in the upper and middle parts of the basin (Hartmann et al., 2007).

The Danube, with a drainage area of 796,250 km^2 and mean discharge of 6,500 m^3/s, is the second largest river in Europe. The Danube flows from the Black Forest Mountains in southwest Germany to the Black Sea, with the total length of 2,857 km. The river can be divided into three sections: the upper 1,066 km, middle 860 km, and lower 931 km (Sommerwerk et al., 2010). In the upper Danube, carbonate rocks cover 24.5 % of the catchment (Hartmann et al., 2007).

The Seine River is 1047 km long, with a drainage area of 67,500 km^2 between the Poses station and the last lock before the estuarine section. Sedimentary rocks comprise up to 97.5 % of the basin, including 78.2 % of various carbonate rocks, such as chalk and limestone (Meybeck, 1998). The Seine River Basin contains a large proportion of cultivated land (75.8 %), and a relatively small urban area (2 %). Intensive agricultural practices and urban wastewater make the Seine River one of the most nitrogen-loaded rivers in the world (Billen et al., 2001, Sebilo et al., 2006).

Due to the local climate, the discharges of the Rhine, Danube (upper) and Seine vary seasonally, enabling division into a wet season (January to June) and a dry season (July to December). To compare the within-stream biogeochemical changes under different hydrological conditions, we collected water samples during low flow conditions in July 2018 in the dry season (Summer) and high flow conditions from March–April 2019 in the wet season (Spring). Water samples were taken from the Rhine at six locations (R-B-1, R-B-2, R-B-3, R-B-4, R-K-1, R-C-1); from the Danube at four locations (D-P-1, D-P-2, D-V-1, D-B-1); and from the Seine at four locations (S-P-1, S-P-2, S-R-1, S-R-2). The sampling locations were selected according to key hydrological points (Rhine: Constance, Karlsruhe, and Cologne; Danube: Passau, Vienna, and Budapest; Seine: Paris and Rouen), as shown in Fig. 2. The use of these locations enabled us to divide the rivers into different sections and to study the differences between the sections. The daily discharges of the Rhine (at Cologne), Danube (at Passau), and Seine (at Paris) (the gauging stations had available data for the sampling sites within the study periods) were obtained from the Global Runoff Data Centre (http

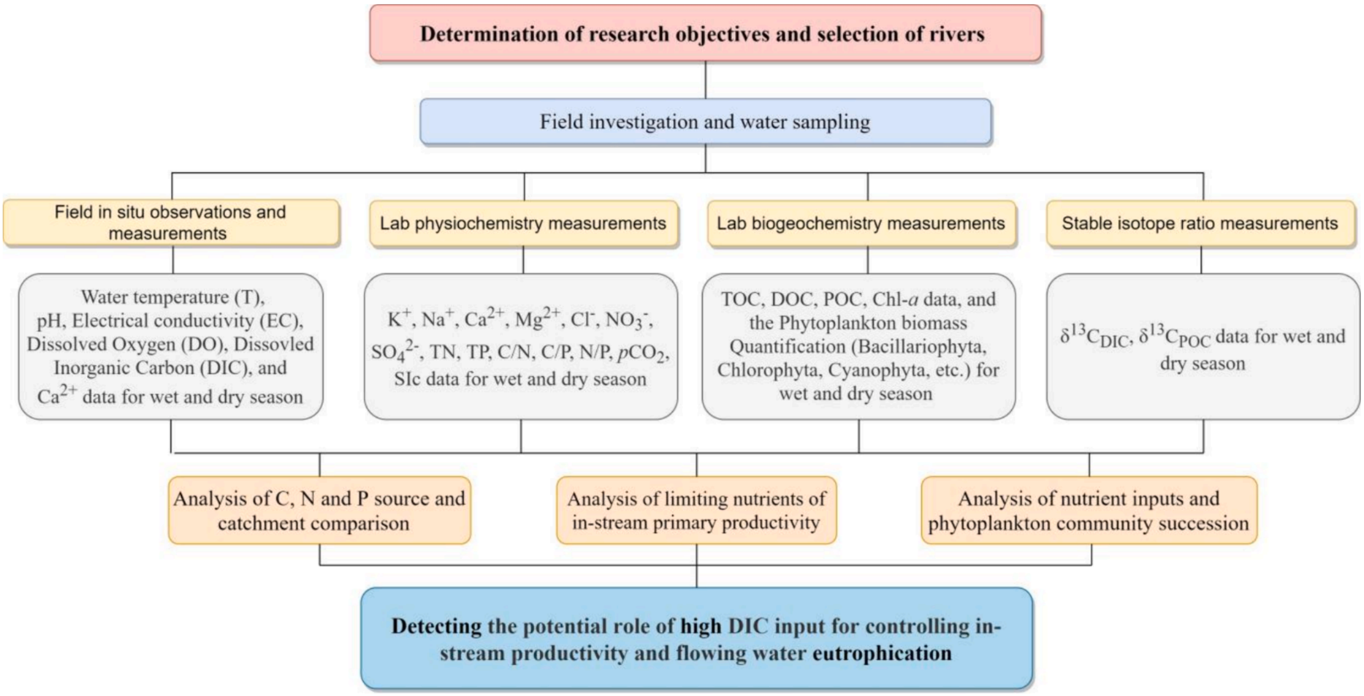


Fig. 1. Schematic diagram of the research methodology used in this study.

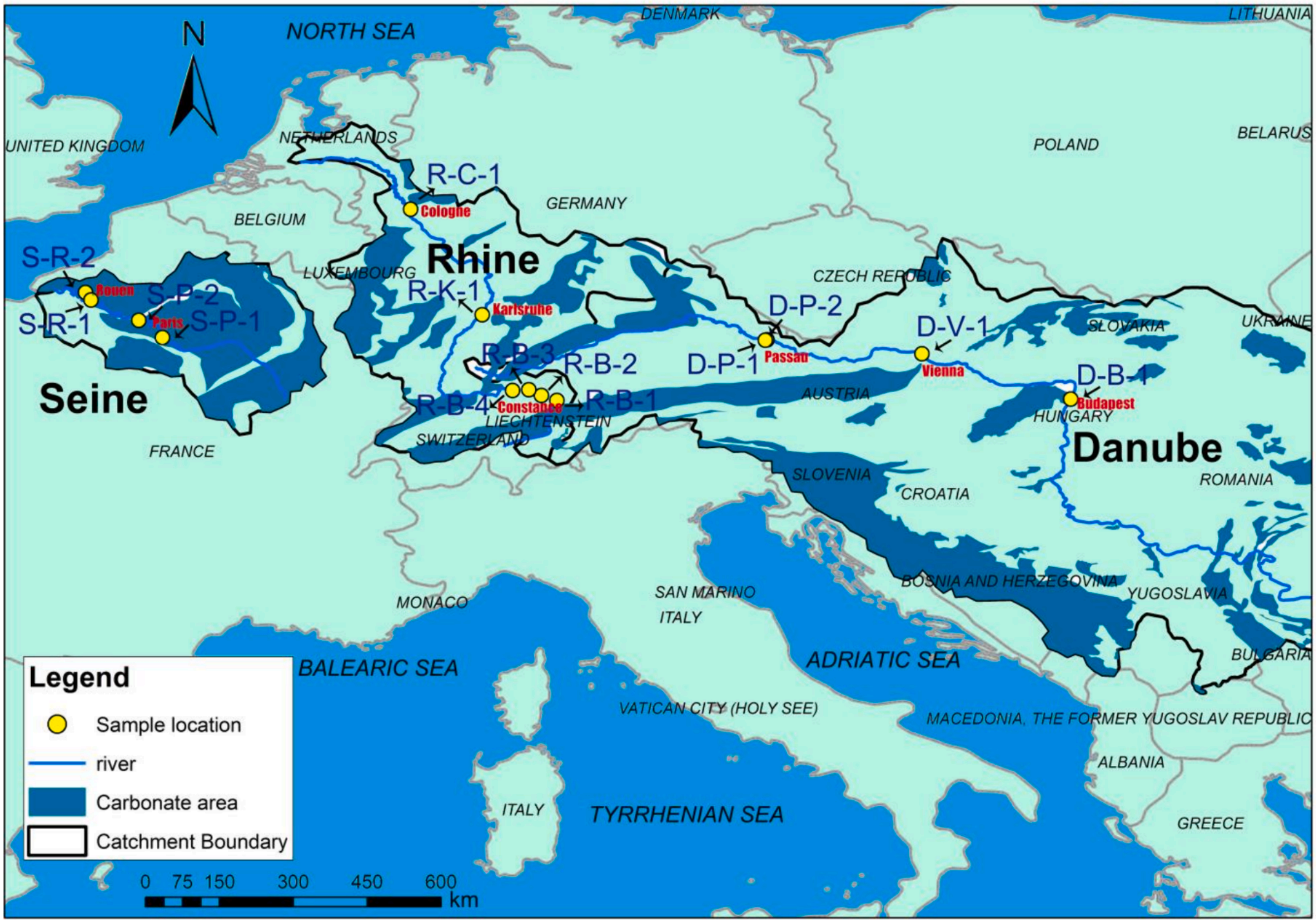


Fig. 2. Location map showing the drainage areas of the Seine, Rhine, and Danube. Sample locations are indicated by a circle and number. The distribution of carbonate terrain follows the global karst aquifer map (Goldscheider et al., 2020).

s://portal.grdc.bafg.de/) and the French Ministry of Ecology, Sustainable Development and Energy (https://www.hydro.eaufrance.fr).

Physicochemical water parameters were measured using a water quality meter (WTW3430, Germany), including water temperature (T), pH, electrical conductivity (EC, 25℃), and dissolved oxygen (DO), with the resolution limits being 0.01 °C, 0.01, 0.1 μS cm^{-1}, and 0.01 mg L^{-1}, respectively. The probes were calibrated using the pH standards of 4.0, 7.0, and 10.0, and the EC standard of 1413 μS cm^{-1}. The DO probe was calibrated using water-saturated air.

Water samples for analysis of major cations and anions were collected in 20 ml acid-washed high-density polyethylene bottles, using 0.45-μm acetate fiber filters. The cationic samples were acidified to a pH below 2.0, with concentrated HNO_3, to prevent precipitation and complexation. Water samples for total nitrogen (TN) and total phosphorus (TP) were stored in 100 ml acid-washed brown glass bottles with Teflon-lined screw caps. Samples for estimating total organic carbon (TOC) were collected in 50 ml brown glass bottles, and heat-treated at 450℃ for a minimum of 4 h to remove residual carbon. The pH of the TOC samples was lowered using hydrochloric acid (37 %, Suprapur) to inhibit bacterial and algal growth and to remove inorganic carbon. Before collecting the experimental samples for analysis, all sample bottles and filters were rinsed and flushed thoroughly with sample water. After sampling, all bottles were transferred to the laboratory, stored in a refrigerator, and analyzed as soon as possible.

Water samples (1 L volume) were collected and filtered through a 47 mm GF/F filter to determine the Chl-*a* concentration. Qualitative phytoplankton samples were collected using a handheld phytoplankton net with a 64 μm mesh size in surface waters, and 1 L water samples were collected for quantitative phytoplankton analysis. Phytoplankton samples were preserved in Lugol's iodine solution with 2 % final concentration.

2.3. Laboratory analyses

Samples of anions, cations, and total organic carbon (TOC) were transported to the Institute of Applied Geosciences, Karlsruhe Institute of Technology, for analysis. The concentrations of potassium (K^+) and sodium (Na^+) were determined using ion chromatography (ICS-1100, Thermo Fisher Scientific), while concentrations of calcium (Ca^{2+}) and magnesium (Mg^{2+}) were determined using flame AAS (Perkin–Elmer 3030B). Concentrations of chloride (Cl^-), sulfate (SO_4^{2-}), and nitrate (NO_3^-) were determined using ion chromatography (ICS-2100, Thermo Fisher Scientific). TOC was determined by oxidative combustion at 850 °C and subsequent determination of carbon dioxide (Vario TOC cube, Elementar Analysesysteme GmbH). Due to their instability, HCO_3^- concentrations were determined in situ using titration with an Aquamerck alkalinity test kit with a resolution of 0.05 mmol/L, and each sample was titrated 2–3 times.

The water samples for TN and TP determination were digested with alkaline potassium persulfate and neutral potassium persulfate, respectively, and then analyzed using ultraviolet spectrophotometry (Ebina et al., 1983).

Water samples for $\delta^{13}C_{DIC}$ measurements were injected into precleaned 100 mL glass vials with no air bubbles or headspace. The samples were stored at 4 °C until analysis after adding one drop of saturated $HgCl_2$ solution to prevent microbial activity. The preserved samples for $\delta^{13}C_{DIC}$ analyses were acidified with pure phosphoric acid, and the extracted CO_2 was purified using a vacuum line after cryogenic removal of H_2O using a liquid nitrogen-ethanol trap. The POC samples were captured on Whatman GF/F filters and combusted with CuO powder in evacuated 9 mm quartz tubes at 850 °C. The yields of CO_2 on a vacuum extraction line were used for the $\delta^{13}C$ measurements.

Chl-*a* was concentrated from the water sample by vacuum filtration and then extracted using an acetone 90 % solution. Chl-*a* concentrations were determined using an ultraviolet spectrometer according to the standard methods established by the Ministry of Environmental Protection of China.

The preserved phytoplankton samples were concentrated to a volume of 30 ml. After mixing, 0.1 ml of the concentrated samples was used for counting and identifying the phytoplankton species using a phytoplankton counting chamber at 400 × magnification.

2.4. Calculation of CO_2 partial pressure, $CO_{2(aq)}$ concentration, and saturation index of calcite

The CO_2 partial pressure (pCO_2), $CO_{2(aq)}$ concentration, and the saturation index of calcite (SI_C) of river water were calculated using PHREEQC Interactive 3.4.0 (Parkhurst and Appelo, 1999). The measured pH, water temperature, and the concentrations of K^+, Na^+, Ca^{2+}, Mg^{2+}, HCO_3^-, Cl^-, SO_4^{2-}, and NO_3^-, were used as the inputs.

pCO_2, assumed to be in equilibrium with the sampled water, was calculated as:

$$pCO_2 = \frac{(HCO_3^-)(H^+)}{K_H K_1}$$

where the parentheses denote species activity in mol·L^{-1}, which is related to concentrations by the activity coefficient γ, and K_H and K_1 are the temperature-dependent Henry's Law and first dissociation constants for CO_2 gas in water, respectively.

SI_C was calculated as:

$$SI_C = \log_{10}\left[\frac{(Ca^{2+})(CO_3^{2-})}{K_C}\right]$$

where K_C is the temperature-dependent equilibrium constant for calcite (Drever, 1988; Stumm and Morgan, 1981). If $SI > 0$, the water is oversaturated for the mineral; if $SI < 0$, the water still has a calcite corrosion capacity; and if $SI = 0$, equilibrium is reached.

2.5. Stable carbon isotopes

The $\delta^{13}C$ values of DIC and POC ($\delta^{13}C_{DIC}$ and $\delta^{13}C_{POC}$) were analyzed using a MAT-252/253 (Thermo Fisher Scientific) mass spectrometer at the Institute of Geochemistry, Chinese Academy of Sciences. The data on carbon isotope ratios were measured and reported per mil relative to the international standard Vienna Peedee Belemnite (VPDB). The instrumental accuracy of the $\delta^{13}C$ measurements was greater than 0.06 ‰. $\delta^{13}C$ was calculated as $\delta^{13}C_{sample} = (R_{sample}/R_{standard}\text{-}1) \times 1000$, where R is the $^{13}C/^{12}C$ ratio of the sample or standard.

3. Results

3.1. Physiochemical and stable carbon isotope characteristics of the river water samples

The basic physicochemical and isotopic parameters of the three European rivers studied were different (Supplementary data Table. 1). The water temperature of the three rivers ranged from 5.3 °C to 24.7 °C, with the lowest and highest values occurring in the Rhine in spring and in the Danube in summer, respectively. The Seine River had the lowest mean water pH value of 7.98 and DO concentration of 103.0 %, while the mean pH of the Rhine (8.18) and the mean DO concentration of the Danube (114.8 %) were the highest. The HCO_3^- concentrations of the three rivers were 131.2–305.0 mg/L during spring and summer. The highest mean HCO_3^- concentrations (285.6 mg/L) occurred in the Seine and the lowest (156.6 mg/L) in the Rhine. The mean pCO_2 and $CO_{2(aq)}$ of the Seine were ~ 2914 ppmv and ~ 115 μmol/L, respectively, and were almost 2–3 times higher than those of the other two rivers. Relatively high nitrate concentrations, ranging from 18.6 mg/L to 21.1 mg/L, were observed in the Seine; these values are similar to those reported in a previous study which found that the NO_3^- concentration of the Seine was ~ 20 mg/L (Brion and Billen, 2000a). The lowest nitrate concentration was detected in the Danube River ($\sim$4 mg/L), and such a low content was also detected by Hartman et al (2007). The Seine also had the highest PO_4^{3-} concentrations among the three rivers (20–132.7 μg/L), while the Rhine had the lowest (19.9–87.5 μg/L).

The $\delta^{13}C_{DIC}$ values of the Rhine, Danube, and Seine ranged from −10.42 ‰ to −5.69 ‰, from −11.75 ‰ to −9.34 ‰, and from −12.72 ‰ to −11.66 ‰, respectively. Previous studies reported $\delta^{13}C_{DIC}$ values of the Rhine and Danube of $\sim$ -10 ± 2 ‰, which are similar to the results of this study (Pawellek et al., 2002; Hartmann et al., 2007). The $\delta^{13}C_{POC}$ values of the Rhine, Danube, and Seine ranged from –33.64 ‰ to −25.91 ‰, from –33.63 ‰ to −29.23 ‰, and from –33.91 ‰ to −27.13 ‰, respectively. The discharges of these three rivers were higher in spring and lower in summer, demonstrating clear seasonal variations (Supplementary data Fig. 1).

3.2. Spatial variation of physiochemical parameters, nutrients, and stable carbon isotopes

The physiochemical parameters of these three rivers showed different spatial patterns along their courses. For the Rhine, the concentrations of HCO_3^-, Ca^{2+}, NO_3^-, TN, and TP from the upper part of the catchment at the Lake Constance outlet to downstream near Cologne showed increasing trends in both the summer and spring seasons (Fig. 3a). Additionally, the concentrations of DO and PO_4^{3-} were inconsistent along its course. PO_4^{3-} close to the outlet of Lake Constance reached nearly 80–90 μg/L, which was almost two times higher than that at the downstream sites. As shown in Fig. 3b, the evolution of the physiochemical characteristics of the Danube can be divided into two sections: above and below Passau. Most parameters showed significant changes below Passau, except for pH and DO, where two tributaries (the Inn and Ilz Rivers) enter the Danube downstream of Passau. From sites D-P-2 to D-B (Fig. 2), the pH, SIc, DO, and $CO_{2(aq)}$ showed different spatial patterns. pH, water temperature, DO, SIc, and NO_3^- of the Danube showed increasing trends in the section between Passau and Budapest, especially in the summer season, whereas pCO_2, $CO_{2(aq)}$, PO_4^{3-}, TN, and TP showed decreasing trends in summer along this section, with no apparent spatial changes in spring. In the Seine, decreases in pH, DO, and SIc were evident from upstream of Paris to the downstream part in Rouen, during the two seasons (Fig. 3c). Steep decreases in pH and DO along the Seine were also observed in many previous studies (Brion and Billen, 2000a,b; Cébron et al., 2003). pCO_2, CO_2, and TP showed increasing trends along the course of the Seine. The spatial patterns of HCO_3^-, NO_3^-, and PO_4^{3-} of the Seine are different to those of the Rhine and Danube. The anions showed substantial increases between the upper part of the catchment to downstream of Paris followed by decreases in the Rouen section. $\delta^{13}C_{DIC}$ and $\delta^{13}C_{POC}$ of the Rhine showed the substantial differences of 1.83 ‰ and 3.89 ‰ in the two sampling periods, and differences in $\delta^{13}C_{DIC}$ and $\delta^{13}C_{POC}$ between the two seasons were also detected for the Danube and Seine.

3.3. Dynamics of within-stream primary productivity and phytoplankton community composition

The Chl-*a* concentrations of the three rivers were 0.19–13.49 μg/L, with both the highest and lowest values occurring in the Seine (summer average = 7.55 μg/L, spring average = 0.65 μg/L). The Chl-*a* concentrations of the Danube and Seine were higher in summer than in spring, whereas the Rhine had low Chl-*a* concentrations of 0.71–1.07 μg/L in both seasons and did not show consistent spatial patterns. During the summer, the Chl-*a* concentration increased significantly in the Seine and Danube and increased by around 4–10 times from the upstream section to the downstream section. Similar increases in the Chl-*a* concentration were reported in previous studies of the same section (Passau-Vienna-Budapest) of the Danube (Winter et al., 2007). However, the spatial changes in the Chl-a concentrations of these two rivers were smaller in the spring (Fig. 3). To reveal the potential limiting nutrients of the within-stream primary productivity, we employed regression analysis to analyze the relationships between the Chl-*a* concentrations and different nutrients in the three rivers. As shown in Fig. 4a and Fig. 4b, the Chl-*a* concentrations of the Rhine and Danube all show positive correlations with their N loads (NO_3^- or TN). The Chl-*a* concentrations of the Seine are significantly correlated with the concentration of aqueous CO_2 (coefficient of determination: $R^2 = 0.68$, $P < 0.05$) in the water column (Fig. 4c), but there were no significant correlations with the N or P loads. In addition, TOC showed increasing trends along the courses of the Rhine and Danube, and no seasonal differences were observed. In summer, the TOC increased significantly from upstream of Paris to downstream of the city, followed by a decrease in the Rouen section. The

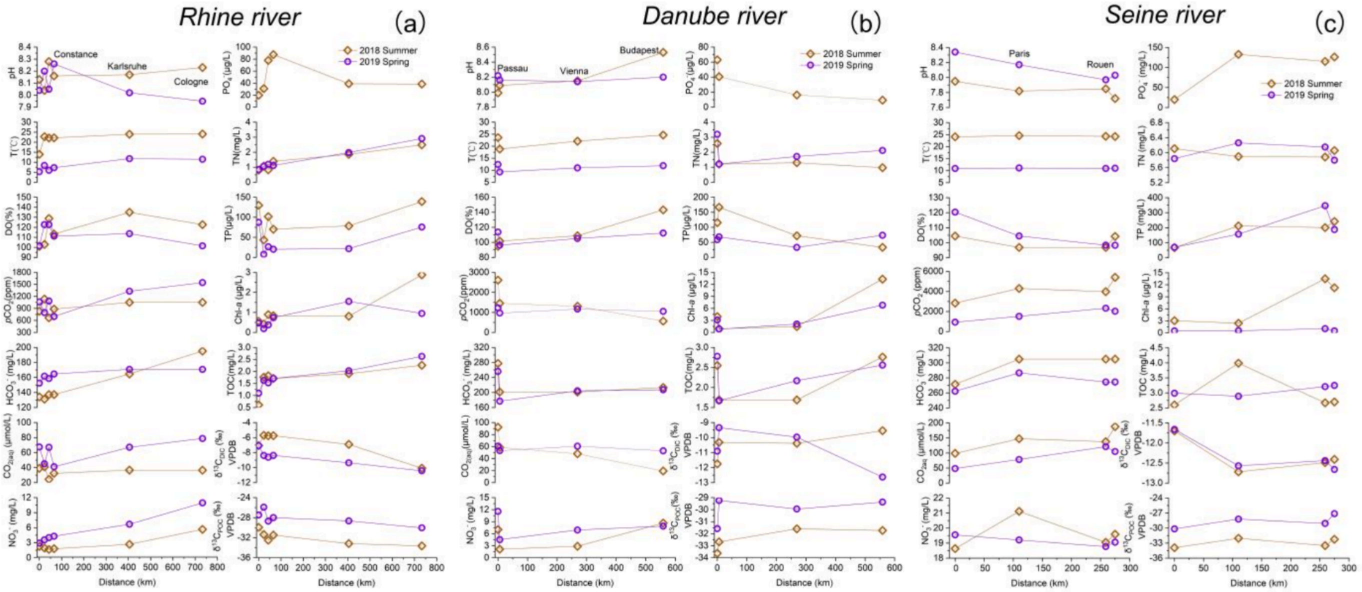


Fig. 3. Downstream evolution of physiochemical parameters and biological characteristics of the Rhine (a), Danube (b), and Seine (c) in summer (July) 2018, spring (March to April) 2019. Green circles = wet season; purple diamonds = dry season. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

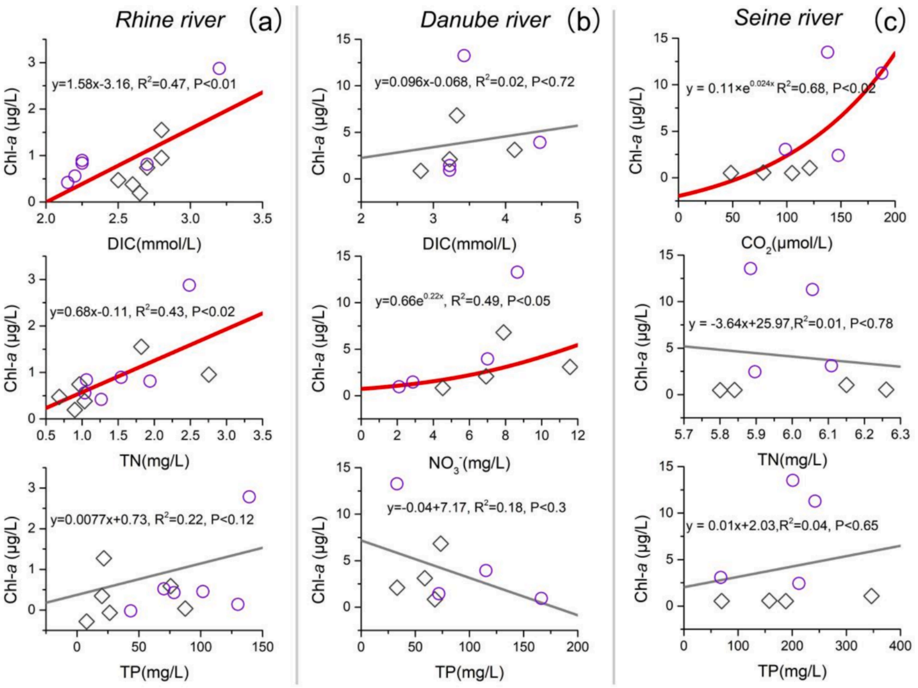


Fig. 4. Relationships between major nutrient concentrations (C, N, P) and Chl-*a* for the Rhine (a), Danube (b) and Seine (c). Violet circles denote the summer (July) 2018 data, and grey diamonds denote the spring (March to April) 2019 data. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Seine samples had the highest mean TOC (2.99–3.09 mg/L) during the two study seasons.

As shown in Fig. 5, these three rivers clearly demonstrate changes in phytoplankton community composition between the two sampling seasons, as well as different spatial patterns along their courses. Among the three rivers, the Rhine had the highest abundance of Cyanobacteria and Chlorophyta (10–64 %, average of 34 %. The quantity of Bacillariophyta was highest in the Seine (47–100 %, average of 78 %), followed by the Danube (average of 66 %). All three rivers showed a higher proportion of Bacillariophyta in spring, whereas Cyanobacteria and Chlorophyta increased significantly in summer. In the Rhine, the phytoplankton community was dominated by Cyanobacteria and Chlorophyta at the outlet of Lake Constance (site R-B-4). Along the course to below Cologne, the major phytoplankton species in the water column were replaced by Bacillariophyta, which increased from 35 % to 81 % in summer, with changes also occurring during spring. In the upper section of the Danube, above Passau, the relative abundances of Cyanobacteria and Chlorophyta were lower than those of Bacillariophyta in summer; however, Cyanobacteria and Chlorophyta were the dominant phytoplankton species in the Vienna section. Bacillariophyta abundance decreased to ∼ 33 %, while Chlorophyta increased from nearly 28 % to 46 % between Vienna and Budapest. The phytoplankton community composition in the Seine demonstrated another spatiotemporal pattern. In summer, Bacillariophyta accounted for 63 % of the total phytoplankton biomass above Paris, while Cyanobacteria and Chlorophyta dominated the phytoplankton community within the section flowing through Paris, while Bacillariophyta increased from 56 % to 93 % along the Rouen section. In contrast, Bacillariophyta dominated the

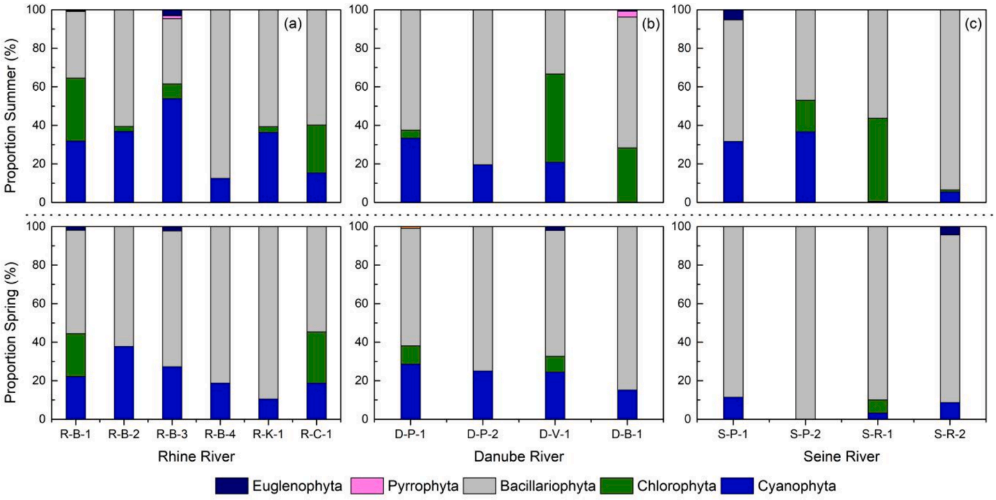


Fig. 5. Downstream evolution of dominant phytoplankton community compositions in the Rhine (a), Danube (b), and Seine (c) in summer (July) 2018 and spring (March-April) 2019.

phytoplankton community structure in spring at all sampling sites in the Seine (Fig. 5).

4. Discussion

4.1. Natural and anthropogenic sources of DIC

The most important factors determining the geochemical fluxes of water bodies on land are the catchment lithology, climate, and land use (Meybeck, 1987; Bluth and Kump, 1994; Gislason et al., 2009; Zeng et al., 2019b). The major ions in river water are controlled mainly by continental weathering processes. River water with high HCO_3^- loads is primarily in areas with carbonate lithologies (Meybeck, 1987). The HCO_3^- concentration ($[HCO_3^-]$) in a carbonate-dominated catchment may be several times higher than that of silicate-dominated catchment (Gaillardet et al., 1999). The differences in $[HCO_3^-]$ among the Rhine, Danube, and Seine rivers and their spatial patterns are examples of such a lithological control. The Seine has an extensive area of carbonate outcrops in its upper drainage area (Fig. 2). Nearly 78.2 % of the carbonate area resulted in the highest observed $[HCO_3^-]$ (285.5 mg/L) among the three rivers. A previous study found that the $[HCO_3^-]$ in the Seine has a single source, and that the carbonate weathering rate is 20 times faster than that of silicate (Roy et al., 1999). However, this high $[HCO_3^-]$ may not be driven solely by natural weathering processes; for instance, previous studies have demonstrated that oxidative nitrogenous fertilizer derived from agricultural activities was responsible for a substantial proportion of the carbonate dissolution in the Garonne River in southwestern France (Perrin et al., 2008). However, among the three rivers in this study, the observed $\delta^{13}C_{DIC}$ values of the Seine suggest that most of the HCO_3^- in the Seine is derived from dissolution by carbonic acid rather than by nitric/sulfuric acid. The most negative $\delta^{13}C_{DIC}$ values in the Seine can be attributed to the stronger soil respiration in the upstream part of the drainage area. The drainage area around the Paris section, from sites S-P-1 to S-R-2, is the most productive agricultural region in Europe. Higher soil CO_2 input and more ^{13}C-depleted signals from C_3 plant metabolism have resulted in the lowest $\delta^{13}C_{DIC}$ values observed in the Seine water column. The more positive $\delta^{13}C_{DIC}$ values observed in the Rhine and Danube can be explained by the major control of carbonate weathering within these silicate-dominated catchments. Although carbonate rocks are less extensive than silicate rocks in the Rhine and Danube drainage areas than in the Seine, these two rivers still exhibit considerable HCO_3^- loads, which can be attributed to the ubiquitous occurrence of carbonate minerals in silicate rocks, or to the calcareous soils within areas of silicate terrain due to the faster kinetics of carbonate weathering compared to silicate weathering (Liu et al., 2011; Zeng et al., 2022). The dominant influence of carbonate weathering on DIC concentrations in rivers in silicate terrain is suggested by the carbon isotope signals. Previous studies found that the high $\delta^{13}C_{DIC}$ values of the Rhine and Danube may be the result of the 1:1 mixture of carbonate rock and bacterially-derived carbon (Pawellek et al., 2002; Hartmann et al., 2007). Carbonate weathering can lead to the occurrence of ^{13}C-enriched DIC in river systems, which is caused by the dominant influence of minor carbonates on $\delta^{13}C_{DIC}$ in silicate catchments (Barth et al., 2003), because carbonate dissolution may generate most of the alkalinity load in areas of silicate terrain. Higher elevation and lower vegetation productivity, soil respiration within the thin soil layer, and the C_3/C_4 vegetation balance in the drainage area, could also lead to positive $\delta^{13}C_{DIC}$ values. The significant control of lithology, soil respiration, and vegetation productivity of HCO_3^- loads and $\delta^{13}C_{DIC}$ is observed in the Rhine and Danube (Fig. 3a and 3b). The Rhine originates in the Swiss Alps, where the $\delta^{13}C_{DIC}$ values (R-B-1 to R-B-4) are higher and close to those indicative of a carbonate weathering origin. Two reasons may account for this $\delta^{13}C_{DIC}$ enrichment. Along the course of the upper Rhine, carbonate outcrops are widely distributed in this alpine area, which causes the ^{13}C enrichment of DIC. Additionally, from sites R-B-1 to R-C-1, the depleted $\delta^{13}C_{DIC}$ may be attributed to the increase in vegetation productivity and soil respiration from the alpine area to the area downstream, and/or to the increasing area of silicate rocks. The $[Ca^{2+}]$ and $[HCO_3^-]$ values upstream of Passau (site D-P-1) (which is the confluence of the mainstream and the Inn and Ilz tributaries) were several times higher than downstream (site D-P-2). As shown in Fig. 3, the high alkalinity loads in the upper Danube can be attributed to the dissolution of Mesozoic carbonates (Pawellek and Veizer, 1994; Pawellek et al., 2002). The drainage area upstream of Passau, a fertile plain region in Germany, is mostly occupied by forests and cultivated land; thus, this drainage area generates high DIC loads and lower $\delta^{13}C_{DIC}$ values before the mainstream joins with the Inn and Ilz. The upper Inn River originates in the Alps and contributes a large volume of water to the mainstream. The higher altitude and lower soil respiration and carbonate dissolution in the Alps lead to more positive $\delta^{13}C_{DIC}$ in the Inn, resulting in $\delta^{13}C_{DIC}$ enrichment downstream of Passau (D-P-2). In summary, the DIC loads and carbon isotopes in these three major European Rivers reflect the controls of lithology, land use, and geomorphology. Additionally, our results confirm the previous conclusion that high DIC inputs can be attributed to chemical weathering–derived loads due to the large area of carbonate rocks within the drainage areas.

4.2. Sources of N and P

Rivers with high N and P loads are typically influenced by urban sewage or intensive agricultural activity within their drainage areas (Meybeck, 1987; Garnier et al., 2006; Seitzinger et al., 2006), while river catchments with relatively low human populations typically have lower nutrient loads (Depetris et al., 2005). The three major European rivers monitored in this study had large differences in their N and P loads, reflecting different intensities of human activities in their drainage areas. The mainstream of the Seine flows through the metropolitan area of Paris, and the central part of its catchment contains some of the most productive agricultural land in the world. Thus, the N and P levels of the Seine river water are controlled by the intensity of agricultural activity and volume of urban wastewater, particularly in the downstream area (Billen et al., 2007; Sebilo et al., 2006). A previous study found that the major form of dissolved inorganic N in the upstream part of the Seine was NO_3^- (~20 mg/L), while ammonium (NH_4^+) comprised only a minor proportion (Brion and Billen, 2000a). In the lower Seine, downstream of Paris, most of the ammonium released from arable soils and wastewater is rapidly nitrified and there is no evidence of denitrification in the water column, as indicated by the results of analyses of ammonium and nitrate isotopes (Sebilo et al., 2006). In the Seine, the large-scale conversion of NH_4^+ to NO_3^- via nitrification results in a downstream decrease in dissolved oxygen levels (Brion and Billen, 2000a,b; Cébron et al., 2003). Our results reveal similarly high NO_3^--N concentrations in the water body and a rapid decline in DO along the Seine, indicating that the N loads ($NO_3^- + NH_4^+$) are still maintained at a high level. In addition, we detected a significant increase in PO_4^{3-} and TP between sites S-P-1 and S-P-2 in the summer season, indicating that the high P loads in the Seine are most likely derived from industrial and domestic sewage in the urban areas. Although it has been concluded that the dissolved nitrogen species and orthophosphate in the Rhine and Danube are mainly derived from anthropogenic sources such as agricultural fertilizers, communal wastewater, and sewage (Hartmann et al., 2011; Pawellek et al., 2002), these rivers exhibit considerably lower NO_3^-, PO_4^{3-}, TN, and TP loads than the Seine, indicating that the influence of human activities may be less than for the Seine. The relatively low N and P inputs in these two rivers can be attributed to historical water quality regulation, sewage treatment, and the smaller area of cultivated land. For example, less N fertilizer usage and the construction of sewage treatment plants from the 1980 s to the 1990 s (the Rhine Action Plan) have reduced the riverine dissolved inorganic nitrogen (DIN), PO_4^{3-}, and TP loads in the Rhine (Radach and Patsch, 2007; Hartmann et al., 2007,2011). Catchment management and sewage treatment have also reduced the NO_3^- and PO_4^- loads of the Danube (Hartmann et al., 2007). Despite these control policies, anthropogenic N inputs to these two rivers remain significant. We detected a trend of increasing NO_3^- downstream, whereas the PO_4^- concentration declined rapidly. This may indicate that sewage controls were successful, despite high N-fertilizer usage throughout the Danube catchment. The N and P inputs into these three rivers may be derived different anthropogenic sources, and their variations confirm that the nutrient inputs to flowing water systems respond sensitively to human activities.

4.3. Influence of C, N, and P on planktonic algal productivity

As is well-documented, river nutrient loads may be affected by land use changes, sewage leakage, and atmospheric deposition from the surrounding drainage area. Chlorophyll-a (Chl-*a*) has frequently been used as a proxy for productivity (photosynthesis) and algal abundance in freshwater ecosystems (Balch et al., 1992; Chowdhury et al., 2017). Variations in riverine Chl-*a* concentration can respond sensitively to nutrient inputs such as C, N, and P (Howarth and Marino, 2006; Schindler et al., 2016; Sun et al., 2022). In addition, C-N-P is assimilated by phytoplankton in stoichiometric ratios, and C:N:P ratios have been frequently used to detect the major limiting nutrients for primary productivity in aquatic ecosystems (Elser et al., 2007). In these three major European rivers, maximum Chl-*a* concentrations occurred in summer, which can be attributed to the high temperature, low water turbidity, and elevated light penetration during this low flow period. Moreover, the seasonal differences indicate that phytoplankton activity in the water column is sensitive to external environmental perturbations. The regression analysis results (Fig. 4a) show that Chl-*a* concentrations in the Rhine River are better correlated with TN and DIC than with TP. Changes in TN/TP and DIC/P did not influence Chl-*a*, and this phenomenon suggests that while rising TN and DIC inputs may both trigger increases in Chl-*a*, N may be the limiting nutrient for within-stream primary production in the Rhine. Similarly, Chl-*a* in the upper Danube showed a significant positive relationship with NO_3^- loads, rather than with DIC or TP, which can also be attributed to the role of N limitation (Fig. 4b). N limitation occurring in the rivers with low basic DIC contents is observed not only in the Danube but also in low-alkalinity streams in the UK (Jarvie et al., 2018). We suggest that the N limitation in these rivers can primarily be attributed to the removal of anthropogenic N and P via water treatment and the resulting reduction in nutrient loads over the last century (Hartmann et al., 2007). In contrast, although the Seine had the highest riverine DIC (CO_2) load among the three rivers, this elevated carbon supply does not match the large NO_3^- loads caused by agricultural activities, inducing a carbon limitation for within-stream primary productivity. Owing to the high proportion of Bacillariophyta (mainly CO_2 users), the Chl-*a* in the Seine River is strongly correlated with DIC (CO_2) rather than with N and P (Fig. 4c). In addition, the C/N ratio indicated that the available carbon was the highest in the Seine River (2.7–3.7 times higher than that in the other two rivers; Supplementary data Table.1). Therefore, our results show that within-stream productivity and its limiting nutrients vary in response to changes in the ratios of C, N, and P inputs, which can be related to catchment properties such as lithology, human activity, land use, and sewage treatment. In summary, in the Rhine and Danube (which are relatively unpolluted) the major within-stream limiting nutrient for aquatic photosynthesis is N—in contrast to the relatively polluted Seine River, where the limiting nutrient is C. Therefore, the observed differences in the major limiting nutrients in these three major European rivers verify our assumption that the low dissolved N or P loads achieved by catchment management can lead to N or P limitations on productivity, while C may limit the productivity in rivers with high dissolved N and P loads.

4.4. Phytoplankton community succession due to changes in nutrient inputs

Recent studies have shown that different levels of C, N, and P input can alter the major phytoplankton species in slow-flowing water bodies such as artificial ponds and reservoirs (Bao et al., 2020; Sun et al., 2022). However, for flowing water bodies such as rivers, the mechanisms of the response of the phytoplankton community structure to different C-N-P inputs are unclear. The results of this study show that changes in C (DIC-CO_2) and N (TN-NO_3^-) loads may significantly alter the dominant phytoplankton species in these three European rivers, indicating the control of C or N limitation. Previous studies have suggested that Cyanophyta and Chlorophyta may have more efficient CCMs than other algae at low DIC($CO_{2(aq)}$), but a high NO_3^- input may increase the abundance of these two phytoplankton types. For instance, in summer, the abundance of Chlorophyta and Cyanophyta rapidly increased in the section of the Seine that flows through Paris, accompanied by a trend of increasing NO_3^- load. Subsequently, in the section downstream of Paris to Rouen, the Bacillariophyta abundance increased as NO_3^- decreased. Indeed, a high input of DIC and lower pH may favor the blooming of Bacillariophyta, which prefers to use $CO_{2(aq)}$. As shown in Fig. 6, our results for these three major European rivers suggest that a higher DIC ($CO_{2(aq)}$) supply favors the blooming of Bacillariophyta in different seasons, indicating that phytoplankton with low-efficiency CCMs may benefit from increases in DIC($CO_{2(aq)}$).

The strong control of catchment lithology–driven DIC($CO_{2(aq)}$) input on the phytoplankton community structure is also indicated by the $\delta^{13}C_{DIC}$ values (Fig. 7a and Fig. 7b). Higher vegetation productivity, soil respiration, and carbonate dissolution lead to higher DIC and $\delta^{13}C_{DIC}$ values that reflect the 1:1 mixing of soil CO_2 and carbonate rock (~-13 ‰). Thus, the proportion of Chlorophyta + Cyanophyta and the lower $\delta^{13}C_{DIC}$ in the Seine can partly be ascribed to the greater input of the carbonate weathering–derived load. However, due to the smaller contribution of the carbonate weathering load, the higher $\delta^{13}C_{DIC}$ in the other two rivers can be attributed to the influence of other processes, due to the lower $\delta^{13}C_{DIC}$ supply (from weathering-driven DIC), such as CO_2 exchange (degassing and atmospheric CO_2 invasion), and the smaller catchment size (Finlay, 2003). Furthermore, we detected large differences in the within-stream phytoplankton community structure in these two seasons, which can be attributed to the greater influences of water temperature, flow rate, light intensity, and water turbidity. The Chlorophyta and Cyanophyta abundance of these three rivers significantly increased in the summer season when the temperature exceeded 10℃, indicating that warm temperatures may trigger blooms of Chlorophyta and Cyanophyta (Paerl and Huisman, 2009; Huisman et al., 2018). It is worth noting that the proportion of Bacillariophyta in the Seine was the highest in the two sampling seasons (average = 78 %), regardless of the temperature (Fig. 6). River POC may directly originate from the erosion of soil litter and soil organic matter from the catchment area (allochthonous source) and may also be generated by the within-stream biota (phytoplankton and submerged macrophyte); thus, the isotopic signals of river POC are mixed. As shown in Fig. 7c and 7d, our results suggest that the $\delta^{13}C$ of POC in all three rivers was enriched during the spring wet season and depleted during the summer dry season. At the same time, phytoplankton productivity changed significantly (Chl-*a* as a proxy) between the two periods. In the spring season, due to the high-water flow and low light penetration, the allochthonous source of POC (from the erosion of catchment-derived soil litter and soil organic matter) dominated the $\delta^{13}C_{POC}$ in the water column. The discharges of the Rhine, Danube and Seine in the spring season were respectively + 49 %, +38 % and + 203 % higher than in summer (Supplementary data Fig. 1). As shown in Fig. 7c and Fig. 7d, the $\delta^{13}C_{POC}$ values in these rivers were all close to a more negative value of ~ -28.91 ‰, indicating that the POC originates mainly from plant-derived organic matter. In contrast, the high water flow in the wet season can reduce the DIC uptake by algae and enhance the allochthonous POC transport ability, because water turbidity is higher during the high-water stage and there is more organic debris derived from vegetation and soils in upland areas (Finlay, 2003; West et al., 2011; Clark et al., 2013). For example, Leithold et al. (2006) reported that riverine POC in highly turbid rivers is

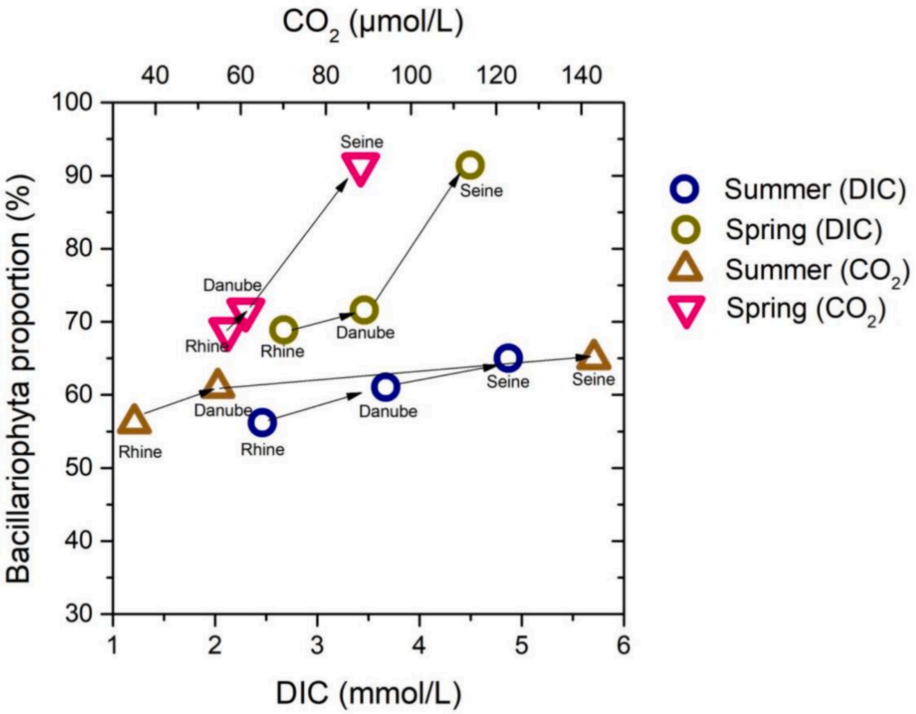


Fig. 6. Relationships between DIC($CO_{2(aq)}$) and the proportion of Bacillariophyta in the three major European rivers in summer (July) 2018 and spring (March to April) 2019.

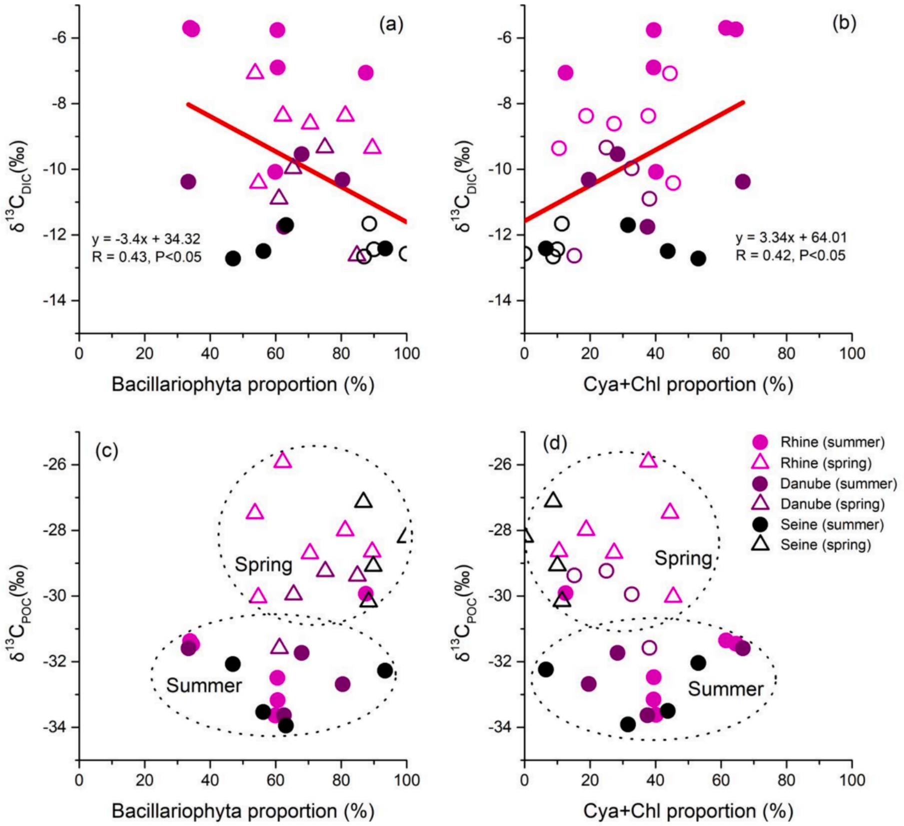


Fig. 7. Relationships between ($\delta^{13}C_{DIC}$ or $\delta^{13}C_{POC}$) and the proportion of different phytoplankton communities in the Rhine, Danube, and Seine rivers. (a) Bacillariophyta proportion versus $\delta^{13}C_{DIC}$ (with the linear regression line); (b) Cyanophyta + Chlorophyta proportion versus $\delta^{13}C_{DIC}$ (with the linear regression line); (c) Bacillariophyta proportion versus $\delta^{13}C_{POC}$; (d) Cyanophyta + Chlorophyta proportion versus $\delta^{13}C_{POC}$. Solid circles = summer (July) 2018, open circles = spring (March to April) 2019.

generally allochthonous during the wet season; whereas the low-flow period corresponded with periods of high algal productivity and biomass (Power, 1992). Rivers with a Mediterranean climate influence may have higher rates of within-stream algal production due to the warm summer with low rainfall (Finlay, 2003). Indeed, our results suggest that the $\delta^{13}C_{POC}$ values of the three European rivers (mainly with a Mediterranean climatic influence) were more negative during the dry season (summer), with an average of –32.39 ‰. The ^{13}C-depleted POC of the three rivers (-3.48 ‰) from spring to summer may reflect the greater input of autochthonous POC produced by aquatic photosynthesis. $\delta^{13}C_{POC}$ will become more negative and deviate from the soil endmember with decreasing turbidity and enhanced light penetration during the dry season, which promotes algal growth (Zhao et al., 2022). Thus, we conclude that the $\delta^{13}C_{POC}$ of these three rivers represents seasonal changes in aquatic photosynthesis intensity and autochthonous organic carbon (AOC) productivity, which are related to temperature, water flow, and light penetration.

Cyanophyta are generally thought to be the major cause of freshwater eutrophication; hence, blooms of Bacillariophyta can improve water quality and potentially mitigate eutrophication. Our results reveal that the high inputs of DIC and aqueous $CO_{2(aq)}$ in the Seine led to Bacillariophyta proportions that were 3.96–8.81 % and 19.87–22.56 % higher than in the Rhine and Danube in the wet and dry seasons, respectively. This can be explained by differences in the efficiency of carbon concentrating mechanisms (CCMs) among species. Based on this finding, we suggest that reducing the C limitation in these river systems may drive the succession of phytoplankton from Cyanophyta and Chlorophyta to Bacillariophyta, thus potentially improving the quality of the aquatic environment. Moreover, all the evidence for these three European rivers highlights the following key findings: the potential role of an elevated DIC input (driven by carbonate weathering) in controlling carbon sequestration and eutrophication in flowing water.

4.5. Implications for future river water quality management and carbon sequestration

In past decades, excessive concentrations of P and/or N were the most common cause of eutrophication in inland waters. Thus, restricting the anthropogenic release of N and P to freshwater is a major means of maintaining a healthy aquatic environment. Indeed, the results of this study suggest that long-term catchment management projects for the Rhine and Danube have significantly lowered their N and P loads. However, we found that these treatments may also constrain their within-stream productivity and carbon sequestration. The Chl-*a* and TOC concentrations in the Rhine and Danube were considerably lower than those in the Seine, which had the highest DIC load. The productivity of the Seine was even C limited rather than N or P limited. More importantly, the elevated DIC input in the Seine has led to the lowest proportion of Cyanophyta in the water column than in the other two rivers, although its nutrients loads were the highest. The most significant implication of this study is that controlling the DIC input is a potential water management strategy in flowing water bodies that synchronously enhances the carbon sink and mitigates eutrophication. Additionally, our results indicated that the regulation of carbon sequestration and eutrophication in streams and rivers should consider the catchment lithologies and human activities. To manage river quality and eutrophication problems in flowing water bodies, consideration of the potential co-limitation of C, N, and P is needed to reduce anthropogenic nutrient export and toxic algal growth. We suggest that considering these implications can assist local authorities and management agencies to develop management strategies for major rivers that reduce anthropogenic nutrient loads, enhance carbon sequestration, and control river eutrophication in the future. Furthermore, our results reveal that the C:N:P stoichiometry of aquatic ecosystems determines the dominant limiting nutrients of these three major rivers, yet the accurate thresholds of C:N:P stoichiometry that lead to shifts in the major limiting nutrients have not been rigorously quantified. To determine these thresholds and the limiting concentrations of nutrients for large river systems according to their specific hydro-chemical backgrounds, it is essential to adopt more sophisticated laboratory experiments and modeling work in future research.

5. Conclusions

We have explored the changes in major limiting nutrients for within-stream productivity and the compositions of the phytoplankton communities in three major European rivers (the Rhine, Danube, and Seine), with different lithologies and land use backgrounds. We found that the lower N and P contents in the Rhine and Danube, resulting in potential N-limitation along their courses. The Chl-*a* concentrations in the Rhine and Danube were more limited by N inputs (NO_3^- or TN) than by P (TP). In contrast, the widespread distribution of carbonate rocks and cultivated land within the Seine drainage area has resulted in the highest DIC and NO_3^- loads among these three rivers. The Chl-*a* concentrations in the Seine were significantly related to DIC rather than to the N or P loads, indicating the major control of C limitation. For the Rhine, Danube, and Seine, the decrease in DIC availability was accompanied by an increase in Chlorophyta and Cyanophyta and a decrease in Bacillariophyta, due to their different CCM efficiencies. In contrast, the high riverine DIC-$CO_{2(aq)}$ load of the Seine led to a higher abundance of Bacillariophyta among the three rivers. This indicates that changes in nutrient load may result in the successional changes of the dominant phytoplankton communities, and that controlling the DIC input is a potential strategy for controlling the carbon sequestration and eutrophication of flowing water bodies. Therefore, we emphasize that the future control of eutrophication and carbon sequestration in rivers should consider both catchment geology and human activities, and that consideration should also be given to the potential co-limitation of C, N, and P. We also suggest that accurate knowledge of C:N:P thresholds that lead to shifts in the major limiting nutrients is needed to develop more effective river water-carbon management strategies. To determine these thresholds and the concentrations for large river systems, more sophisticated laboratory experiments and modeling research are needed in future research.

CRediT authorship contribution statement

Sibo Zeng: Conceptualization, Formal analysis, Investigation, Methodology, Software, Visualization, Writing – original draft, Writing – review & editing. **Hailong Sun:** Data curation, Formal analysis, Investigation, Methodology, Writing – original draft, Writing – review & editing. **Zaihua Liu:** Conceptualization, Funding acquisition, Methodology, Project administration, Supervision, Writing – review & editing. **Nico Goldscheider:** Resources, Validation, Writing – review & editing. **Simon Frank:** Resources, Validation, Writing – review & editing. **Nadine Goeppert:** Conceptualization, Resources, Validation, Writing – review & editing. **Min Zhao:** Investigation, Validation. **Haitao Zeng:** Investigation, Validation. **Cuihong Han:** Investigation, Validation.

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.

Acknowledgments

This work was supported by the Fundamental Research Funds for the

Central Universities (SWU-KR22021), the National Natural Science Foundation of China (42130501, 42141008, 41921004 and 41977298), the Chongqing's Scholars with Overseas Experience fund (2204012978152018), and the Chongqing Municipal Science and Technology Commission Fellowship Fund (CSTC2020yszx-jcyjX0006, CSTC2021yszx-jcyjX0005).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jhydrol.2024.131362.

References

Balch, W., Evans, R., Brown, J., Feldman, G., McClain, C., Esaias, W., 1992. The remote sensing of ocean primary productivity: use of a new data compilation to test satellite algorithms. J. Geophys. Res. Oceans 97, 2279–2293.

Bao, Q., Liu, Z., Zhao, M., Hu, Y., Li, D., Han, C., Wei, Y., Ma, S., 2020. Primary productivity and seasonal dynamics of planktonic algae species composition in karst surface waters under different land uses. J. Hydrol. 591, 125295.

Bao, Q., Liu, Z., Zhao, M., Hu, Y., Li, D., Han, C., Zeng, C., Chen, B., Wei, Y., Ma, S., Wu, Y., 2022. Role of carbon and nutrient exports from different land uses in the aquatic carbon sequestration and eutrophication process. Sci. Total Environ. 813, 151917.

Barth, J.A.C., Cronin, A.A., Dunlop, J., Kalin, R.M., 2003. Influence of carbonates on the riverine carbon cycle in an anthropogenically dominated catchment basin: evidence from major elements and stable carbon isotopes in the Lagan River (N. Ireland). Chem. Geol. 200, 203–216.

Billen, G., Garnier, J., Ficht, A., Cun, C., 2001. Modelling the response of water quality in the Seine Estuary to human activity in its watershed over the last 50 years. Estuaries 24, 977–993.

Billen, G., Garnier, J., Némery, J., Sebilo, M., Sferratore, A., Barles, S., Benoit, P., Benoît, M., 2007. A long-term view of nutrient transfers through the Seine River continuum. Sci. Total Environ. 375, 80–97.

Bluth, G.J.S., Kump, L.R., 1994. Lithologic and climatologic controls of river chemistry. Geochim. Cosmochim. Acta 58, 2341–2359.

Brion, N., Billen, G., 2000. Wastewater as a source of nitrifying bacteria in river systems: the case of the river Seine downstream from Paris. Water Res. 34, 3213–3221.

Brion, N., Billen, G., Guezennec, L., Ficht, A., Guezennec, L., Ficht, A., 2000. Distribution of nitrifying activity in the Seine River (France) from Paris to the estuary. Estuaries 23, 669–682.

Cébron, A., Berthe, T., Gamier, J., 2003. Nitrification and nitrifying bacteria in the lower Seine River and estuary (France). Appl. Environ. Microbiol. 69, 7091–7100.

Chen, B., Wang, M., Duan, M., Ma, X., Hong, J., Xie, F., Zhang, R., Li, X., 2019. In search of key: protecting human health and the ecosystem from water pollution in China. J. Clean. Prod. 228, 101–111.

Chowdhury, M., Hardikar, R., Kesavan, H.C., Thomas, J., Mitra, A., Rokade, M.A., Naidu, V.S., Sukumaran, S., 2017. Nutrient stoichiometry and freshwater flow in shaping of phytoplankton population in a tropical monsoonal estuary (Kundalika Estuary). Estuarine, Coastal Shelf Sci. 198, 73–91.

Clark, K.E., Hilton, R.G., West, A.J., Malhi, Y., GrÖcke, D.R., Bryant, C.L., Ascough, P.L., Robles, C.A., New, M., 2013. New views on old carbon in the Amazon River: insight from the source of organic carbon eroded from the Perucian Andes. Geochem. Geophys. Geosyst. 14, 1644–1659.

Conley, D.J., Paerl, H.W., Howarth, R.W., Boesch, D.F., Seitzinger, S.P., Havens, K.E., Lancelot, C., Likens, G.E., 2009. Controlling eutrophication: nitrogen and phosphorus. Science 323, 1014–1015.

Czajkowski, M., Andersen, H.E., Blicher-Mathiesen, G., Budzinski, W., Elofsson, K., Hagemejer, J., Hasler, B., Humborg, C., Smart, J.C.R., Smedberg, E., Thodsen, H., Was, A., Wilamowski, M., Zylicz, T., Hanley, N., 2021. Increasing the cost-effectiveness of nutrient reduction targets using different spatial scales. Sci. Total Environ. 790, 147824.

Dehestaniathar, S., Nesari, S., Borzooei, S., Abolfathi, S., 2021. Application of natural biodegradable fiber as biofilm medium and carbon source in DEnitrifying AMmonium OXidation (DEAMOX) process for nitrogen removal from wastewater. J. Taiwan Inst. of Chem. e. 119, 108–114.

Demirel, M.C., Booij, M.J., Hoekstra, A.Y., 2013. Identification of appropriate lags and temporal resolutions for low flow indicators in the River Rhine to forecast low flows with different lead times. Hydrol. Processes 27, 2742–2758.

Depetris, P.J., Gaiero, D.M., Probst, J.L., Hartmann, J., Kempe, S., 2005. Biogeochemical output and typology of rivers draining Patagonia's Atlantic seaboard. J Coastal Res. 214, 835–844.

Drever, J.I., 1988. The Geochemistry of Natural Waters, second ed. Prentice-Hall.

Ebina, J., Tsutsui, T., Shirai, T., 1983. Simultaneous determination of total nitrogen and total phosphorus in water using peroxodisulfate oxidation. Water Res. 17, 1721–1726.

Elser, J.J., Bracken, M.E.S., Cleland, E.E., Gruner, D.S., Harpole, W.S., Hillebrand, H., Ngai, J.T., Seabloom, E.W., Shurin, J.B., Smith, J.E., 2007. Global analysis of nitrogen and phosphorus limitation of primary producers in freshwater, marine and terrestrial ecosystems. Ecol. Lett. 10, 1135–1142.

Finlay, J., 2003. Controls of streamwater dissolved inorganic carbon dynamics in a forested watershed. Biogeochemistry 62, 231–252.

Gaillardet, J., Dupré, B., Louvat, P., Allègre, C.J., 1999. Global silicate weathering and CO_2 consumption rates deduced from the chemistry of large rivers. Chemi. Geol. 159, 3–30.

Garnier, J., Sferratore, A., Meybeck, M., Billen, G., Dürr, H.H., 2006. Modelling silica transfer processes in river catchments. In: Ittekkot, V. (Ed.), Role of Silica in Land-Sea Interactions. Island Press, Washington DC, pp. 139–162.

Gislason, S.R., Oelkers, E.H., Eiriksdottir, E.S., Kardjilov, M.I., Gisladottir, G., Sigfusson, B., Snorrason, A., Elefsen, S., Hardardottir, J., Torssander, P., Oskarsson, N., 2009. Direct evidence of the feedback between climate and weathering. Earth Planet. Sci. Lett. 277, 213–222.

Goldscheider, N., Chen, Z., Auler, A.S., Bakalowicz, M., Broda, S., Drew, D., Hartmann, J., Jiang, G., Moosdorf, N., Stevanovic, Z., Veni, G., 2020. Global distribution of carbonate rocks and karst water resources. Hydrogeol. J. 28, 1661–1677.

Goodarzi, D., Mohammadian, A., Pearson, J., Abolfathi, S., 2022. Numerical modelling of hydraulic efficiency and pollution transport in waste stabilization ponds. Ecol. Eng. 182, 106702.

Hammer, K.J., Kragh, T., Sand-Jensen, K., 2019. Inorganic carbon promotes photosynthesis, growth, and maximum biomass of phytoplankton in eutrophic water bodies. Freshwater Biol. 64, 1956–1970.

Hartmann, J., Jansen, N., Kempe, S., Dürr, H.H., 2007. Geochemistry of the river Rhine and the upper Danube: recent trends and lithological influence on baselines. Journal of Environmental Science for Sustainable Society 1, 39–46.

Hartmann, J., Levy, J., Kempe, S., 2011. Increasing dissolved silica trends in the Rhine River: an effect of recovery from high P loads? Limnology 12, 63–73.

Howarth, R.W., Marino, R., 2006. Nitrogen as the limiting nutrient for eutrophication in coastal marine ecosystems: evolving views over three decades. Limnol. Oceanogr. 51, 364–376.

Huisman, J., Codd, G.A., Paerl, H.W., Ibelings, B.W., Verspagen, J.M.H., Visser, P.M., 2018. Cyanobacterial blooms. Nat. Rev. Microbiol. 16, 417.

Jarvie, H.P., Smith, D.R., Norton, L.R., Edwards, F.K., Bowes, M.J., King, S.M., Scarlett, P., Davies, S., Dils, R.M., Bachiller-Jareno, N., 2018. Phosphorus and nitrogen limitation and impairment of headwater streams relative to rivers in Great Britain: a national perspective on eutrophication. Sci. Total Environ. 621, 849–862.

Lai, C., Ma, Z., Liu, Z., Sun, H., Yu, Q., Xia, F., He, X., Bao, Q., Han, Y., Liu, X., He, H., 2023. Alleviating eutrophication by reducing the abundance of Cyanophyta due to dissolved inorganic carbon fertilization: Insights from Erhai Lake, China. J. Environ. Sci. 131, 68–83.

Leithold, E.L., Blair, N.E., Perkey, D.W., 2006. Geomorphologic controls on the age of particulate organic carbon from small mountainous and upland rivers. Glob Biogeochem. Cy 20, GB3022, n/a–n/a.

Lewis Jr, W.M., Wurtsbaugh, W.A., Paerl, H.W., 2011. Rationale for control of anthropogenic nitrogen and phosphorus to reduce eutrophication of inland waters. Environ. Sci. Tech 45, 10300–10305.

Liu, Z., Dreybrodt, W., Liu, H., 2011. Atmospheric CO2 sink: silicate weathering or carbonate weathering? Appl. Geochem. 26, S292–S294.

Liu, B., Liu, L., Li, W., 2020. Effective removal of phosphorus from eutrophic water by using cement. Environ. Res. 183, 109218.

Low-Décarie, E., Fussmann, G.F., Bell, G., 2014. Aquatic primary production in a high-CO_2 world. Trends Ecol. Evol. 29, 223–232.

Ma, J., Wang, P., 2021. Effects of rising atmospheric CO_2 levels on physiological response of cyanobacteria and cyanobacterial bloom development: a review. Sci. Total Environ. 754, 141889.

Mahdian, M., Hosseinzadeh, M., Siadatmousavi, S.M., Chalipa, Z., Delavar, M., Guo, M., Abolfathi, S., Noori, R., 2023. Modelling impacts of climate change and anthropogenic activities on inflows and sediment loads of wetlands: case study of the Anzali wetland. Sci. Rep. 13, 5399.

Malekmohammadi, B., Uvo, C.B., Moghadam, N.T., Noori, R., Abolfathi, S., 2023. Environmental risk assessment of wetland ecosystems using bayesian belief networks. Hydrology 10, 16.

Meybeck, M., 1987. Global chemical weathering of surficial rocks estimated from river dissolved loads. American J. Science 287, 401–428.

Meybeck, M., 1998. Man and river interface: multiple impacts on water and particulates chemistry illustrated in the Seine River basin. Hydrobiologia 373, 1–20.

Noori, R., Farahani, F., Jun, C., Aradpour, S., Bateni, S.M., Ghazban, F., Hosseinzadeh, M., Maghrebi, M., Vesali Naseh, M.R., Abolfathi, S., 2022. A non-threshold model to estimate carcinogenic risk of nitrate-nitrite in drinking water. J. Clean. Prod. 363, 132432.

Paerl, H.W., Huisman, J., 2009. Climate change: a catalyst for global expansion of harmful cyanobacterial blooms. Environ. Microbiol. Rep. 1, 27–37.

Paerl, H.W., Xu, H., McCarthy, M.J., Zhu, G., Qin, B., Li, Y., Gardner, W.S., 2011. Controlling harmful cyanobacterial blooms in a hyper-eutrophic lake (Lake Taihu, China): the need for a dual nutrient (N & P) management strategy. Water Res. 45, 1973–1983.

Paerl, H.W., Xu, H., Hall, N.S., Rossignol, K.L., Joyner, A.R., Zhu, G., Qin, B., 2015. Nutrient limitation dynamics examined on a multi-annual scale in Lake Taihu, China: implications for controlling eutrophication and harmful algal blooms. J. Freshwater Ecol. 30, 5–24.

Paerl, H.W., Scott, J.T., McCarthy, M.J., Newell, S.E., Gardner, W.S., Havens, K.E., Hoffman, D.K., Wilhelm, S.W., Wurtsbaugh, W.A., 2016. It Takes two to tango: when and where dual nutrient (N & P) reductions are needed to protect lakes and downstream ecosystems. Environ. Sci. Technol. 50, 10805–10813.

Parkhurst, D.L., Appelo, C.A.J., 1999. In: U.S. Geological Survey Water Resources Investigations Report, User's Guide to PHREEQC, second version-A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. U.S. Geological Survey, p. 99–4259.

Pawellek, F., Frauenstein, F., Veizer, J., 2002. Hydrochemistry and isotope geochemistry of the upper Danube River. Geochim. Cosmochim. Acta 66, 3839–3853.

Pawellek, F., Veizer, J., 1994. Carbon cycle in the upper Danube and its tributaries: $^{13}C_{DIC}$ constraints. Isr. J. Earth Sci. 43, 187–194.

Perrin, A.S., Probst, A., Probst, J.L., 2008. Impact of nitrogenous fertilizers on carbonate dissolution in small agricultural catchments: implications for weathering CO_2 uptake at regional and global scales. Geochim. Cosmochim. Acta 72, 3105–3123.

Power, M.E., 1992. Hydrologic and trophic controls of seasonal algal blooms in northern California rivers. Archiv. Hydrobiol. 125, 385–410.

Radach, G., Patsch, J., 2007. Variability of continental riverine freshwater and nutrient inputs into the North Sea for the years 1977–2000 and its consequences for the assessment of eutrophication. Estuar. Coasts 30, 66–81.

Roy, S., Gaillardet, J., Allégre, C.J., 1999. Geochemistry of dissolved and suspended loads of the Seine River, France: anthropogenic impact, carbonate and silicate weathering. Geochim. Cosmochim. Acta 63, 1277–1292.

Schindler, D.W., 1974. Eutrophication and recovery in experimental lakes: implications for lake management. Science 184, 897–899.

Schindler, D.W., Carpenter, S.R., Chapra, S.C., Hecky, R.E., Orihel, D.M., 2016. Reducing phosphorus to curb lake eutrophication is a success. Environ. Sci. Technol. 50, 8923–8929.

Sebilo, M., Billen, G., Mayer, B., Billiou, D., Grably, M., Garnier, J., Mariotti, A., 2006. Assessing nitrification and denitrification in the Seine River and estuary using chemical and isotopic techniques. Ecosystems 9, 564–577.

Shao, M., Liu, Z., Sun, H., Lai., Ch., Ma, Zh., He, X., Fang, Y., Chai, Q., 2023. C-N-P driven changes to phytoplankton community structure and gross primary productivity in river-fed reservoir ecosystems on the Chinese Loess Plateau. J. Hydrol. 616, 128781.

Smith, V., Wood, S., McBride, C., Atalah, J., Hamilton, D., 2016. Phosphorus and nitrogen loading restraints are essential for successful eutrophication control of Lake Rotorua, New Zealand. Inland Waters 6, 273–283.

Sommerwerk, N., Bloesch, J., Paunović, M., Baumgartner, C., Venohr, M., Schneider-Jacoby, M., Hein, T., Tockner, K., 2010. Managing the world's most international river: the Danube River Basin. Mar. Freshwater Res. 61, 736–748.

Sterner, R.W., 2008. On the phosphorus limitation paradigm for lakes. Int. Rev. Hydrobiol. 93, 433–445.

Stumm, W., Morgan, J.J., 1981, Aquatic Chemistry, second ed. Wiley-Interscience, pp. 357–364.

Sun, H., Han, C., Liu, Z., Wei, Y., Ma, S., Bao, Q., Zhang, Y., Yan, H., 2022. The nutrient limitation on primary productivity and phosphorus removal by biological pump in river-dammed reservoirs: implications for carbon sink and eutrophication control. J. Hydrol. 607, 127480.

Tong, Y., Zhang, W., Wang, X., Couture, R.-M., Larssen, T., Zhao, Y., Li, J., Liang, H., Liu, X., Bu, X., He, W., Zhang, Q., Lin, Y., 2017. Decline in Chinese lake phosphorus concentration accompanied by shift in sources since 2006. Nature Geosci. 10, 507–511.

West, A.J., Lin, C., Lin, T., Hilton, R.G., Tanaka, M., Chang, C., Lin, K., Galy, A., Sparkes, R., Hovius, N., 2011. Mobilization and transport of coarse woody debris by large storms. Limnol. Oceanogr. 56, 77–85.

Winter, C., Hein, T., Kavka, G., Mach, R.L., Farnleitner, A.H., 2007. Longitudinal changes in the bacterial community composition of the danube river: a whole-river approach. Appl. Environ. Microbiol. 73, 421–431.

Xuan, Y., Tang, C., Cao, Y., Li, R., Jiang, T., 2019. Isotopic evidence for seasonal and long-term C and N cycling in a subtropical basin of southern China. J. Hydrol. 577, 123926.

Yu, C., Huang, X., Chen, H., Godfray, H.C.J., Wright, J.S., Hall, J.W., Gong, P., Ni, S., Qiao, S., Huang, G., Xiao, Y., Zhang, J., Feng, Z., Ju, X., Ciais, P., Stenseth, N.C., Hessen, D.O., Sun, Z., Yu, L., Cai, W., Fu, H., Huang, XiaoMeng, Zhang, C., Liu, H., Taylor, J., 2019. Managing nitrogen to restore water quality in China. Nature 567, 516–520.

Zeng, S., Liu, H., Liu, Z., Kaufmann, G., Zeng, Q., Chen, B., 2019a. Seasonal and diurnal variations in DIC, NO_3^- and TOC concentrations in spring-pond ecosystems under different land-uses at the Shawan Karst Test Site, SW China: carbon limitation of aquatic photosynthesis. J. Hydrol. 574, 811–821.

Zeng, S., Liu, Z., Kaufmann, G., 2019b. Sensitivity of the global carbonate weathering carbon-sink flux to climate and land-use changes. Nat. Commun. 10 (1), 5749.

Zeng, S., Liu, Z., Groves, C., 2022. Large-scale CO_2 removal by enhanced carbonate weathering from changes in land-use practices. Earth-Sci. Rev. 225, 103915.

Zhang, Y., Liu, Z., Wu, Y., Ma, S., Cao, W., Lai, Ch., Bao, Q., Xia, F., Sun, H., Hu, Y., Liu, X., He, H., 2023. Relationships between biomass of phytoplankton and submerged macrophytes and physicochemical variables of water in Lake Caohai, China: implication for mitigation of cyanobacteria blooms by CO2 fertilization. J. Hydrol. 617, 129111.

Zhao, M., Sun, H., Liu, Z., Bao, Q., Chen, B., Yang, M., Yan, H., Li, D., He, H., Wei, Y., Cai, G., 2022. Organic carbon source tracing and the BCP effect in the Yangtze River and the Yellow River: insights from hydrochemistry, carbon isotope, and lipid biomarker analyses. Sci. Total Environ. 812, 152429.