Temperature sensitivity of organic carbon decomposition in lake sediments is mediated by chemodiversity

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Abstract
Organic carbon decomposition in lake sediments contributes substantially to the global carbon cycle and is strongly affected by temperature. However, the magnitude of temperature sensitivity (Q10) of decomposition and the underlying factors remain unclear at the continental scale. Carbon quality temperature (CQT) hypothesis asserts that less reactive and more recalcitrant molecules tend to have higher temperature sensitivities, but its support is challenged by complex composition of organic matter and environmental constraints. Here, we quantified Q10 of the sediments across 50 freshwater ecosystems along a 3500 km north–south transect, and characterized the quality of sediment dissolved organic carbon with chemodiversity reflected in molecular richness, functional traits (i.e., molecular weight, bioavailability, etc.) and composition. We further included classic environmental variables, such as climatic, physicochemical and microbial factors, to explore how Q10 is constrained by these factors or carbon quality. We found that Q10 varied greatly across lakes, with the mean value of 1.78 ± 0.62, but showed nonsignificant latitudinal pattern. Q10 was primarily predicted by chemodiversity and showed an increasing trend with the biochemical recalcitrance indicated by traits such as aromaticity and standard Gibb’s Free Energy at both molecular and compositional levels. This suggests that carbon quality is the crucial determinant of Q10 in lakes, supporting the CQT hypothesis. Moreover, Q10 decreased linearly with the increase of molecular richness, implying that the resistance of decomposition to warming is associated with higher molecular diversity. Compared with the structural equation model containing only environmental variables, inclusion of chemodiversity increased 32.8% of the explained variation in Q10, and chemodiversity was the only driver showing direct effects. Collectively, this study illustrates the importance of chemodiversity in shaping the pattern of Q10, and has significant implications for accurately predicting the carbon turnover in lake ecosystems in the context of global warming.

KEYWORDS
carbon quality temperature hypothesis, carbon-climate feedback, chemodiversity, functional traits, geography, global warming, greenhouse gas, lake ecosystems
1 | INTRODUCTION

Global warming is expected to increase decomposition rates ($R_{CO_2}$) of organic carbon in ecosystems and thus CO$_2$ emissions (Gudasz et al., 2010; Johnston et al., 2021), acting as the positive feedback to climate change. Determining how $R_{CO_2}$ responds to warming, termed temperature sensitivity ($Q_{10}$), is necessary to predict accurately carbon-climate feedbacks under future warming scenarios (Davidson & Janssens, 2006; Fan et al., 2022; Su et al., 2022). $Q_{10}$ is quantified as the relative increase in $R_{CO_2}$ with a 10°C rise in temperature, and a value greater than one implies a positive feedback of organic carbon decomposition to warming. Previous studies on the spatial patterns and underlying mechanisms of large-scale variation in $Q_{10}$ focus primarily on terrestrial habitats (Fan et al., 2022; Haaf et al., 2021). For instance, $Q_{10}$ of forest soils ranges from 2.69 to 6.21 in China and shows an increasing trend from warm and wet forests to cold and dry forests (Li et al., 2020). These $Q_{10}$ support projections of strong carbon climate feedbacks from northern soils (Koven et al., 2017). However, few studies of $Q_{10}$ are available for freshwater ecosystems at a large spatial scale, even though lakes and their sediments are major carbon pools and typically net sources of CO$_2$ to the atmosphere (Cole et al., 1994; Holgerson & Raymond, 2016; Raymond et al., 2013). Hence, to better estimate the future carbon budgets and the role of lakes in the global carbon cycle, it is important to reveal the magnitudes, patterns, and drivers of the sensitivity of organic carbon decomposition to climate warming in lake sediments.

The patterns of $Q_{10}$ have been shown to correlate with organic carbon quality and environmental constraints such as climatic, physicochemical and microbial factors (Karhu et al., 2014; Koven et al., 2017; Sobek et al., 2009). According to the Arrhenius function, reactants will be more sensitive to temperature where they are typically less reactive and more recalcitrant, since the activation energy (Arrhenius, 1889; Davidson & Janssens, 2006). Organic compounds with higher activation energies are typically less reactive and more recalcitrant, since the activation energy is frequently related to the barrier for the reaction (Piskulich et al., 2019). Therefore, the carbon quality temperature (CQT) hypothesis suggests that the temperature sensitivity depends on the biochemical recalcitrance of carbon (Davidson & Janssens, 2006). This hypothesis is supported by that the more biogeochemically recalcitrant the organic matter, the greater the $Q_{10}$ of soil respiration (Craine et al., 2010; Wang et al., 2018; Zhou et al., 2018). However, opposite views show that labile and resistant organic matter respond similarly to warming (Fang et al., 2005; Hicks Pries et al., 2017), with climatic factors, mineral protection or microbiome being the key factors affecting $Q_{10}$ (Koven et al., 2017; Qin et al., 2021). For instance, hydrometeorology is considered to be as important as temperature in shaping the spatial pattern of ecosystem carbon turnover (Fan et al., 2022; Koven et al., 2017). A recent study shows that compared with biochemical recalcitrance, mineral protection, substrate quantity and environmental factors, the microbiome explained the largest portion of variation in $Q_{10}$ of soil ecosystems across global scale (Sáez-Sandino et al., 2023). These discrepancies indicated that environmental constraints could affect relationships between carbon quality and $Q_{10}$, whereas the relative contribution of biotic and abiotic factors to the variability of $Q_{10}$ in lakes across large spatial scales remains largely unknown. Above knowledge gaps make it challenging to improve predictions of the fate of aquatic carbon as the climate warms.

Uncovering the relationship between carbon quality and temperature sensitivity is also challenging because of the complexity of organic matter (Hu et al., 2024). Dissolved organic matter (DOM) in soils and lake sediments typically consists of thousands of molecules (Ding et al., 2020; Kellerman et al., 2014), and each molecule has unique kinetic properties and thus temperature sensitivity. Using ultrahigh resolution mass spectrometry, molecular formulas for thousands of DOM compounds could be obtained to deduce basic structural features that detail the chemodiversity of DOM (Tanentzap et al., 2019). Therefore, kinetic properties could be quantified at both the levels of individual molecules (molecular level) and entire mixtures of DOM (compositional level). Chemodiversity could be reflected in molecular diversity, functional diversity and chemical composition, and plays a pivotal role in shaping ecological interactions and ecosystem function (Hu, Jang, et al., 2022; Kellerman et al., 2014). Molecular diversity is quantified using conceptually different diversity measures, such as richness or the abundance-based diversity of molecular formulas (Mentges et al., 2017). Functional diversity describes the range and distribution of functional trait values in an assemblage (Lavorel et al., 2008). Functional traits, such as molecular weight, stoichiometry, oxidation state and bioavailability, could reflect the quality of DOM at molecular and compositional levels. The chemical composition of DOM that is a complex mixture of reduced carbon compounds bound to heteroatoms such as oxygen, nitrogen, phosphorus, and sulphur, which could be characterised by the identity and intensity of molecular formulae in a DOM assemblage (Hu, Choi, et al., 2022). Compared to the conventional indicators of carbon quality used to test the CQT hypothesis, such as carbon-to-nitrogen ratios and age of organic carbon (Hicks Pries et al., 2017; Wang et al., 2018), the chemodiversity from molecular-level insight has the potential to prevent misconceptions regarding the correlation between carbon quality and temperature, which may arise due to an imprecise assessment of the overall carbon quality of organic compound mixtures. Exploring chemodiversity is an important contribution to a deeper understanding of the fate and persistence of DOM, as well as the response of carbon cycle to climate change (Dittmar et al., 2021; Kellerman et al., 2015). Currently, site-level studies have linked the molecular diversity and traits of individual molecules, such as their molecular weight, chemical structure and bioavailability, to microbial communities and carbon decomposition (Österholz et al., 2016; Tanentzap et al., 2019). However, the links between chemodiversity and temperature sensitivity, as well as the contribution of chemodiversity to temperature sensitivity are poorly understood.

Here, we examined how organic carbon decomposition in lake sediments responds to climate warming on a continental scale. We collected sediment samples from 50 freshwater ecosystems...
spanning a 31° latitudinal in China. The sediments were incubated anaerobically in the laboratory for 3 days at 20 and 25°C to simulate carbon decomposition under a 5°C warming. $R_{CO_2}$ at both temperatures and $Q_{10}$ were measured along with environmental variables known to affect $R_{CO_2}$ and $Q_{10}$, including climatic, physicochemical and microbial factors. Chemodiversity of sediment DOM was used to characterize carbon quality, and further be combined with environmental variables to explore the driving mechanism of $R_{CO_2}$ and $Q_{10}$. We aimed to determine (1) the magnitude, spatial pattern and main drivers of $R_{CO_2}$ and $Q_{10}$ in lake ecosystems, (2) the generality of the CQT hypothesis at the molecular level and (3) the linkages between chemodiversity, the decomposition function of lakes, and feedbacks between carbon cycling and climate warming. To our knowledge, our study is one of the few to examine the effects of chemodiversity on $R_{CO_2}$ and its $Q_{10}$ at the continental scale.

2 | MATERIALS AND METHODS

2.1 | Experimental sites and field sampling

During July 9–August 18, 2020, we collected 50 freshwater sediments along a 3500 km north–south transect in China for laboratory experiments. These sediments spanned a latitude of 18°48′–49°34′ N and a longitude of 102°51′–129°36′ E (Figure 1a), and a wide range of mean annual temperature (MAT, 2.85–25.65°C) and mean annual precipitation (MAP, 175–2362 mm). The study area contains five climate zones: the mid-temperate semi-humid and mean annual precipitation (MAP, 175–2362 mm). The study area contains five climate zones: the mid-temperate semi-humid zone ($n=8$), the mid-temperate semi-arid zone ($n=2$), the warm-temperate semi-humid zone ($n=13$), the subtropical humid zone ($n=22$), and the tropical humid zone ($n=5$). Samples of sediment and associated overlying water were collected near the lake shore where water depth ranged from 0.5 to 1 m. For each site, three locations were selected, the surface sediment (0–5 cm) and surface water (0–20 cm) samples were collected at these locations, and finally mixed to form one water sample and one sediment sample. All samples were transferred into new, polyethylene terephthalate purified water bottles that had been pre-rinsed with lake water. After refrigeration at 4°C overnight, all samples were placed into insulated containers containing 3–6 ice packs based on the distance between the sampling site and the laboratory, and then transported back to the laboratory within 3 days for further analysis and incubation experiments. It should be noted that we included three sediments from riverine environments due to the difficulties in obtaining lake sediments from these regions. We have kept these three samples in the overall analysis, because those sediments were used for laboratory incubation, and the inclusion of these three riverine samples did not alter the overall spatial patterns of organic carbon decomposition in lake sediments and its temperature sensitivity and also the driving mechanisms.

2.2 | Organic Carbon decomposition and $Q_{10}$ calculation

For each sediment, we measured $R_{CO_2}$ and $Q_{10}$ by laboratory microcosms with fresh sediments anaerobically incubated at 20 and 25°C. In total, there were 300 microcosms from 50 sediments at two temperatures with triplicates. In each microcosm, we added 3 g dry-weight fresh sediments in pre-autoclaved 20 mL glass bottle,
and then added autoclaved Milli-Q water to a water level of 4 cm to ensure equal headspace volume. Before incubation, the bottles were purged with nitrogen gas to remove air in the headspace and then sealed for a pre-incubation period of 2 days in the dark at 20°C. Then, the headspace gas in bottles was removed using nitrogen gas and sealed again, and incubated at 20°C or 25°C in the dark for 3 days. Afterwards, headspace samples were collected using 25 mL syringes and stored in aluminum foil sampling bags (Delin Co., China). CO₂ concentrations were analyzed within 2 days by a gas chromatograph (Agilent 7890B; Agilent Corp., USA).

The sediment R_CO₂ was determined based on the amount of CO₂ released per unit mass of sediment in 1 day (µg C ⁻¹ sediment day⁻¹) (Xu et al., 2021). Since R_CO₂ at 20 and 25°C were highly correlated and shared similar patterns and drivers (Figure S1), only the results of R_CO₂ at 20°C were shown below. The Q₁₀ value of R_CO₂ was calculated as:

\[ Q_{10} = \left( \frac{R_{CO_2}^{20}}{R_{CO_2}^{25}} \right)^{10/(T_{20}-T_{25})}, \]

where R_CO₂[T] and R_CO₂[T₀] were the R_CO₂ at temperature T (e.g., 25°C) and temperature T₀ (e.g., 20°C), respectively (Koven et al., 2017).

### 2.3 Climate, physicochemical variables and bacterial community

We examined the effects of climatic, physicochemical and microbial factors on R_CO₂ and Q₁₀. For climatic factors, we collected MAT and MAP of sampling sites from WorldClim Version 2.1 (Fick & Hijmans, 2017). For physicochemical factors, we collected total nitrogen (TN), total phosphorus (TP), pH, electrical conductivity (EC), total organic carbon (TOC) and dissolved organic carbon (DOC) of sediments, and TN, TP, pH and EC of waters. TN and TP were measured by the alkali potassium persulfate digestion-UV spectrophotometric method (Chinese EPA, 2002). pH was measured using a pH meter (Sx-610, China). EC was measured using a COM-100 (HM Digital, USA). TOC and DOC were determined using a solid TOC analyzer (SSM-5000A, Shimadzu, Japan) and a TOC analyzer (Torch, Teledyne Tekmar, USA), respectively.

For microbial communities, sediment DNA was extracted using a DNeasy PowerSoil Pro Kit (QIAGEN, GERMANY) according to the manufacturer’s instructions. Amplification of the bacterial 16S rRNA genes were performed in triplicate using the universal primers [515F, 5′-GTGCTACGGGCTCTGAA-3′] and [806R, 5′-GGACTACNVGG GTWCTCTAA-3′] targeting the V4 region (Wang et al., 2016). 16S rRNA amplicons were sequenced with the Illumina MiSeq platform (2×250bp paired end). The primers for the amplicon datasets were trimmed by cutadapt v3.5 (Martin, 2011). Amplicon sequence variants (ASV) for bacteria were generated using the DADA2 package V1.18 according to the online tutorial (Callahan et al., 2016). To avoid potential bias caused by differences in sequencing depth, the number of sequences in each sample was rarefied to 32,718, using the “rrarefy” function in the R package “vegan” V2.4.6 (Dixon, 2003). The relative abundance of ASVs was calculated by dividing the read counts of ASVs by the sum of all reads within each sample. The sequencing data have been deposited in the National Omics Data Encyclopedia (https://www.biosino.org/node/index) with accession number QEP004545.

We characterized the bacterial communities with two aspects: alpha diversity and community composition. Bacterial alpha diversity was calculated using species richness that counts the total number of ASV observed in each sample (Willis, 2019). Community composition was represented by the first two axes of a non-metric multidimensional scaling (i.e., NMDS1 and NMDS2) ordination of the Bray-Curtis dissimilarity metric (Hu, Choi, et al., 2022), since these axes represent the most important change in species data (Kruskal, 1964).

### 2.4 FT-ICR MS analysis of sediment dissolved organic matter

We analyzed the molecular composition of sediment DOM after extraction and purification with an ultrahigh-resolution Fourier-transform ion cyclotron resonance mass spectrometer (FT-ICR MS, Bruker Daltonics, Billerica, MA) following previous methods (Hu, Choi, et al., 2022). Briefly, 0.7 g freeze-dried sediment was sonicated with 30 mL ultrapure water for 2 h, and then centrifuged and filtered through a 0.45 µm Millipore filter and acidified to pH 2 using 1 M HCl. Filtrates were solid-phase extracted with Oasis HLB extraction cartridges after the cartridges were pre-activated with methanol (ULC-MS grade) and acid water (pH = 2). Then, cartridges were rinsed with acid water and dried with N₂ gas. Samples were finally eluted with methanol into precombusted amber glass vials, dried with N₂ gas and stored at −20°C until DOM analysis. The DOM samples were analyzed using a 15 Tesla solariX XR FT-ICR MS coupled with an electrospray ionization source in negative ion mode. The DOM samples were injected at 2 µL min⁻¹ and scanned 100 times over a range of 150−1200 m/z. All FT-ICR mass spectra were internally calibrated using organic matter homologous series separated by 14 Da (-CH₂ groups). Chemical formulae were assigned to peaks (signal to noise ratio >7) using the software Formularity following the Compound Identification Algorithm (Tolic et al., 2017). The mass error was less than 1 ppm for a given chemical formula between the measured mass and the theoretical mass. All formula assignments followed (1) the nitrogen rule, (2) ensured the number of hydrogen atoms was at least 1/3 of carbon and could not exceed 2C + N + 2; (3) the number of nitrogen or oxygen atoms could not exceed the number of carbon atoms; (4) the ratio of O/C was between 0–1, H/C ≥ 0.3, N/C ≤ 1, and double bond equivalents (DBE) ≥ 0 (Hu, Choi, et al., 2022; Koch et al., 2007).

The assigned molecules were categorized into eight compound classes (Hu, Choi, et al., 2022; Kim et al., 2003), which were lignin-like (O/C = 0.1–0.67, H/C = 0.7–1.5), proteins-like (O/C = 0.3–0.55, H/C = 1.5–2.2), lipids-like (O/C = 0–0.3, H/C = 1.5–2.0), condensed aromatics-like (ConHC; O/C = 0–0.67, H/C = 0.2–0.7), tannin-like (O/C = 0.67–1.2, H/C = 0.5–1.5), unsaturated hydrocarbons-like...
(UnsatHC; O/C=0–0.1, H/C=0.7–1.5), amino sugars-like (O/C = 0.55–0.67, H/C=1.5–2.2), and carbohydrates-like (Carb; O/C=0.67–1.2, H/C=1.5–2).

We used chemodiversity of DOM to explore the relationship between carbon quality and temperature sensitivity at the molecular and compositional levels. The chemodiversity was analyzed in three aspects: (1) molecular diversity, (2) functional traits and (3) molecular composition. Molecular diversity of DOM was calculated using a richness index that represented by the total number of assigned formulas in each sample. We calculated 17 functional traits of each molecule, and their weighted means at a compositional level were calculated as the sum of the product of the trait value for each molecule and relative intensity divided by the sum of all intensities (Hu, Choi, et al., 2022). Take DBE as an example:

$$\text{DBE}_{wm} = \frac{\sum DBE \times I_i}{\sum I_i},$$

where $\text{DBE}_{wm}$ was intensity weighted mean value of DBE at compositional level. $I_i$ was relative intensity of molecule $i$.

The 17 traits were mass, the number of carbon (C) atoms, aromaticity index (AI), the modified AI (AI$_{modified}$), DBE, DBE minus oxygen (DBE-O), DBE of molecule after removal of heteroatomic bond (DBE-All) (Koch & Dittmar, 2015), standard Gibb's free energy of carbon oxidation (GFE), nominal oxidation state of carbon (NOSC) (LaRowe & Van Cappellen, 2011), Kendrick defect (kdefect$_{CH2}$) (Hughey, 2001), O/C ratio, H/C ratio, N/C ratio, P/C ratio, N/P ratio, S/C ratio, and carbon use efficiency ($\gamma_m$) (Song et al., 2020). Typically, higher values of AI, AI$_{modified}$ DBE, and GFE and lower H/C indicate a higher recalcitrance of DOM (D’Andrilli et al., 2015; Koch & Dittmar, 2006; LaRowe & Van Cappellen, 2011). DBE-O describes unsaturation by excluding all the possible C=O bonds in carbonyl or carboxyl groups (Antony et al., 2017). DBE-AI is the DBE of the resulting molecular core that obtained by subtracting bonds between carbon and heteroelements from the original molecular formula (Koch & Dittmar, 2015), and therefore represents the unsaturation after the removal of heteroelements (i.e., O, N, P, S). Higher values of kdefect$_{CH2}$, NOSC and O/C indicate a higher degree of oxidation. Low $\gamma_m$ values indicate a higher thermodynamic efficiency of metabolic reaction involved in biomass production (Song et al., 2020).

As for molecular composition of sediment DOM, we first calculated the relative abundance of molecules by normalizing signal intensities of assigned peaks to the sum of all intensities within each sample. To quantify the dissimilarity of molecular composition between pairwise sites, we calculated the Bray–Curtis dissimilarity metric based on the abundance table (Bray & Curtis, 1957), and used the first two axes of NMSD ordination of this dissimilarity metric to represent molecular composition (Hu, Choi, et al., 2022).

2.5 Statistical analysis

We first analyzed the Spearman correlations of environmental variables and chemodiversity with $R_{CO_2}$ and $Q_{10}$. In this analysis, functional traits were represented by the first two axes of the principal component analysis (PCA) of 17 traits of DOM (Figure S2). The relationships between all predictor variables and $R_{CO_2}$ or $Q_{10}$ were visualized with linear models. To ensure normality in statistical analyses, we log$_{10}$-transformed $R_{CO_2}$, $Q_{10}$ and all predictive variables except for pH and the first two axes of the PCA and NMSD.

To explore the associations between chemodiversity and $R_{CO_2}$ or $Q_{10}$ at a molecular level, Spearman’s rank correlation coefficient was calculated between $R_{CO_2}$ or $Q_{10}$ and the sum-normalized intensity of each molecule. To reduce type I errors in correlation calculations created by low-occurrence molecules (Hu, Choi, et al., 2022), we retained molecules that were observed in at least 20% of the samples (≥13). Accordingly, we generated subsets of molecules showing significant (p < 0.05) correlations with $R_{CO_2}$ or $Q_{10}$. For each subset, we visualized the molecules in a van Krevelen diagram and further performed statistical analyses of their molecular characteristics. For instance, the compound classes of molecules were identified, and the relative abundance of each compound class was calculated as the ratio of the number of molecules of one compound class relative to total number of molecules. The mean values of 17 traits of each subset were calculated and visualized in scattered plot.

To further evaluate key drivers of $R_{CO_2}$ and $Q_{10}$, we used random forest analysis, variance partitioning analysis (VPA) and structure equation modeling (SEM). First, random forest analyses were conducted to identify the relative influence of climatic, physicochemical, microbial and chemodiversity predictors on $R_{CO_2}$ and $Q_{10}$. The importance of each predictor was determined by evaluating the increase in mean square error between observations and out-of-bag prediction when the data for that predictor were randomly permuted (Hu, Choi, et al., 2022). The accuracy importance measure was computed for each tree and averaged over the 1000 trees. 1000 permutation replicates were run to construct a null distribution and calculate p-values. Details of analyses, such as robustness testing (Figure S3), were described in the Supplementary methods.

Second, to explore the relative contributions and interaction effects of driver categories toward $R_{CO_2}$ and $Q_{10}$, we partitioned explanatory variables into four composite variables in VPA (Peres-Neto et al., 2006): climatic, physicochemical, microbial and chemodiversity. All observed indicators of four composite variables were shown in Table S1. To eliminate irrelevant indicators of composite variables and enhance the explanatory power of the VPA, we initially excluded the indicators with variance inflation factors greater than 10, and constructed linear regression models for each composite variable of $R_{CO_2}$ or $Q_{10}$ with the rest observed indicators. Subsequently, we employed backward selection with stepwise regression to filter out the final set of indicators that were integrated into the VPA (Venables & Ripley, 2002). The stepwise regression was performed using the R package stats V4.0.5 with step function, and the candidate observed indicators were shown in Table S2.

Third, we tested a hypothesis for the direct and indirect effects of environmental drivers and chemodiversity on $R_{CO_2}$ and $Q_{10}$ using the SEM illustrated in Figure S4a. We used composite variables described in Table S1 to account for the collective
effects of climatic, physicochemical, microbial and chemodiversity (Grace et al., 2016). The four composite variables were obtained by stepwise regressions as described above, and their calculation formulae were shown in Table S2. We Z score-transformed the input composite variables to allow cross-comparisons and performed an analysis of variance (ANOVA) to estimate the significance of the standardized path coefficient and the model (Lapiere et al., 2013). Adequate model fits were determined according to a non-significant $\chi^2$ test ($p > .05$), higher comparative fit index (CFI > 0.95) and lower standardized root mean squared residual (SRMR < 0.05). To examine the role of chemodiversity, we also compared the difference of models with and without this composite variable (Figure S4b). The significance of difference in the explanatory power of the $R_{CO}$ or $Q_{10}$ between the two models with and without the composite variable of chemodiversity was estimated based on 1000 permutations and Wilcoxon rank sum tests (Hu, Choi, et al., 2022).

The statistical analyses of diversity and compositions of bacteria and DOM, as well as VPA were performed using the R package vegan V2.4.6 (Dixon, 2003). The PCA was conducted using the R package stats V4.0.5. Random forest analysis was conducted using the R package rPermute V2.5.1 (Archer, 2022). The SEM was estimated using the R package lavaan V0.6-15 (Rosseel, 2012).

3 | RESULTS

We observed right-skewed distributions of $R_{CO}$ and $Q_{10}$ (Figure S5), which varied greatly spatially at the continental scale, but showed non-statistically significant monotonic changes with latitude (Figure 1). Across the 50 sediments, $R_{CO}$ ranged from 0.67 to 25.35 μg C g$^{-1}$ day$^{-1}$ with a mean ± SD of 5.24 ± 4.60 μg C g$^{-1}$ day$^{-1}$ at 20°C (Figure 1b). At 25°C, $R_{CO}$ was, on average, 1.32-fold higher (Figure S6). $Q_{10}$ was generally larger than 1, and ranged from 0.45 to 3.60 with a mean ± SD of 1.78 ± 0.62 (Figure 1b), suggesting that there was a positive feedback of sediment organic carbon decomposition to warming.

The primary factors explaining spatial variation in $R_{CO}$ were the physicochemical properties of sediments, followed by chemodiversity. Specifically, $R_{CO}$ showed high spearman correlations with physicochemical factors and chemodiversity, such as TOC ($\rho = 0.70$), TN ($\rho = 0.72$) and pH ($\rho = -0.72$) of sediment, and molecular richness ($\rho = 0.70$) and NMDS1 of molecular composition ($\rho = -0.74$, Figure 2a). This result is consistent with the observation that $R_{CO}$ was mostly predicted by sediment pH, TOC and TN, as well as chemodiversity as revealed by random forest model (Figure 2b).

The effects of chemodiversity were further supported at both molecular level (Figure 3) and compositional level (Figure S7a). For instance, a total of 2480 molecules significantly correlated with $R_{CO}$ ($p < .05$, Figure 3a), and almost all molecules classified as proteins-like (96.8%), tannins-like (98.1%) and carbohydrates-like (93.5%), which are bioavailable showed positive correlation with $R_{CO}$ (Figure 3b). In comparison to molecules negatively correlated with $R_{CO}$ ($n = 353$), positively correlated molecules ($n = 2127$) exhibited significantly lower mean values of functional traits such as GFE, AI and H/C, while higher values of O/C and Mass ($p < .001$, Figure 3c). Surprisingly, $R_{CO}$ was less directly affected by climatic and bacterial factors as revealed by VPA (Figure S8a) and SEM (Figure 4a,b; Table S3), while there was a strong indirect effect of climate through mediated physicochemical factors and chemodiversity (Table S4). In total, 73.3% of the variance in $R_{CO}$ was accounted for by environmental variables, with main contribution from sediment physicochemical factors (Figure 4a; Table S4). The inclusion of chemodiversity into the SEM increased the explained $R_{CO}$ variance to a lesser extent (77.6%), but was still a statistically significant increase ($p < .001$, Figure 4b).

In contrast, $Q_{10}$ was primarily predicted by chemodiversity (Figure 2c). Specifically, $Q_{10}$ decreased with increasing molecular richness ($R^2 = 0.13$, $p = .011$, Figure 2d), as opposed to $R_{CO}$. In addition, $Q_{10}$ was positively associated with functional traits such as AI$_{wm}$, GFE$_{wm}$ and DBE-O$_{wm}$ (Figure S7b), which signify the recalcitrance of DOM at the composition level. Consistent with that at the molecular level, molecules positively correlated with $Q_{10}$ were predominantly composed of lipid-like (47.2%), lignin-like (33.2%) and unsaturated hydrocarbons-like compounds (8.4%, Figure 3d,e). Such molecules exhibited significantly ($p < .001$, Wilcoxon rank sum tests) higher mean values of DBE-O, AI and GFE compared to molecules negatively correlated with $Q_{10}$ (Figure 3f). The above results suggested that less reactive and more recalcitrant molecules tend to have higher temperature sensitivities, supporting the CQT hypothesis.

The variance in $Q_{10}$ of lake ecosystems was mainly explained by sediment chemodiversity, with relatively lower contributions from classic environmental variables such as climatic, physicochemical and bacterial factors (Figure 4d; Table S4). Moreover, these environmental variables act mainly through interactions with chemodiversity. For instance, only 27.1% of the variance in $Q_{10}$ was accounted for by environmental variables as revealed by SEM (Figure 4e). However, the predictive power was significantly ($p < .001$) increased to 36.0% when chemodiversity was incorporated in the model (Figure 4d), and all the direct path coefficients of environmental variables on $Q_{10}$ were non-significant, which was consistent with the results of VPA (Figure S8b).

Collectively, chemodiversity was identified as the most important and direct driver regulating the variation of $Q_{10}$.

4 | DISCUSSION

Accurately estimating the carbon-climate feedback in lake ecosystems is crucial due to the large role of lakes in the global carbon cycle (Drake et al., 2018; Mendonca et al., 2017). In this study, we explored spatial patterns of sediment organic carbon decomposition in lake ecosystems and their sensitivity to temperature at a continental scale. We found that $R_{CO}$ and $Q_{10}$ varied greatly across lakes, and neither showed a significant latitudinal pattern. The variance of $R_{CO}$ was dominated by sediment physicochemical variables, while $Q_{10}$ was primarily influenced by chemodiversity, showing that more
Recalcitrant molecules exhibit greater temperature sensitivities, which provides support for CQT hypothesis.

Our results indicated that $R_{CO2}$ in lake ecosystems was mainly regulated by sediment properties, such as pH, carbon quantity and quality (e.g., chemodiversity). $R_{CO2}$ was promoted at lower pH (Figure 2a), likely because the lower pH facilitates acid-catalyzed organic carbon decomposition (AminiTabrizi et al., 2023), as well as the release or dissolution of mineral-protected organic matter (Ding et al., 2020; Groeneveld et al., 2020). $R_{CO2}$ was greater in the organic carbon rich sediments (Figure 2a; Figure S7a), which was consistent with results from riverine (Comer-Warner et al., 2018; Stegen et al., 2023) and terrestrial forest ecosystems (Li et al., 2020). This result could be attributed to higher organic carbon quantities providing ample energy for microbial respiration. The significant relationships between $R_{CO2}$ and functional traits further reveal the important role of carbon quality in the process of organic carbon decomposition. The higher $R_{CO2}$ was associated with higher bioavailability and reactivity of DOM (i.e., lower values of GFE and AI; Figure 3c; Figure S7a). In addition, $R_{CO2}$ was positively correlated with molecular richness, but was weakly affected by bacterial richness (Figures 2a and 4b; Table S2). This suggests the presence of functional redundancy among bacterial communities in lake sediments, and the decomposition is carried out by a diverse range of microbes (Bardgett & van der Putten, 2014; Qin et al., 2021).
As an indicator of sensitivity of $R_{CO_2}$ to warming, $Q_{10}$ was found to be strongly associated with chemodiversity (Figures 2 and 4d). At the molecular level, $Q_{10}$ was positively correlated with recalcitrant molecules (Figure 3d,f) having traits like smaller O/C, K_{defect}CH2 and Mass, and larger AI and GFE (Hu, Choi, et al., 2022). At the compositional level, $Q_{10}$ exhibited significant correlations with reactivity-related traits of DOM, including negative correlations with O/C_{wm}, K_{defect}CH2_{wm}, and Y_{met,wm} as well as positive correlations with AI_{wm} and GFE_{wm} (Figure S7b). These results at both molecular and compositional levels are consistent with the CQT hypothesis, which asserts that less reactive and more recalcitrant molecules tend to have higher temperature sensitivities (Davidson & Janssens, 2006). This is further supported by the decreased pattern of $Q_{10}$ with increasing $R_{CO_2}$ (Figure S9), which was not always hold when other biotic or abiotic factors were dominant. For instance, at an incubation temperature of 25–35°C, $R_{CO_2}$ and $Q_{10}$ were higher in Arctic soils than in tropical soils (Wang et al., 2021), probably due to the higher organic carbon content and temperature sensitivity of microbes of northern soils. Compared to the traditional characterization of organic carbon as a whole (Li et al., 2020; Wang et al., 2018), the approach based on functional traits of individual molecule can effectively mitigate the inaccuracies in assessing the carbon quality of organic compound mixtures with diverse kinetic characteristics. Consequently, the molecular-level insight uncovers the underlying mechanistic relationships between carbon quality and temperature sensitivity with greater clarity, and definitively supporting the CQT hypothesis.

The strong effects of chemodiversity on $R_{CO_2}$ and $Q_{10}$ were also reflected by the links between molecular diversity and ecosystem function and stability of decomposition. We found that $R_{CO_2}$ and $Q_{10}$ were significantly influenced by molecular richness, but were not directly affected by bacterial richness (Figure 4; Table S2). This is consistent with the fact that molecular diversity could increase the activity of microbial communities without necessitating an increase in their diversity, and thus enhance ecosystem function of organic carbon decomposition (Tanentzap et al., 2019). Moreover, the observed negative effect of molecular richness on $Q_{10}$ suggests that higher molecular diversity reduces temperature sensitivity of decomposition, thereby stabilizing the response of sediment organic carbon.

FIGURE 3 Composition and traits of molecules correlated with $R_{CO_2}$ (a–c) and $Q_{10}$ (d–f). (a, d) Spearman’s rank correlation $\rho$ between $R_{CO_2}$ or $Q_{10}$ and the relative abundance of DOM molecules. Only molecules with statistically significant ($p < 0.05$) correlations were shown. Lines indicate compound classes of (1) Lignin-like, (2) ConHC: condensed aromatics-like, (3) proteins-like, (4) lipids-like, (5) tannin-like, (6) UnsatHC: unsaturated hydrocarbons-like, (7) amino sugars-like and (8) Carb: carbohydrates-like. (b, e) Proportion of compound classes correlated to $R_{CO_2}$ or $Q_{10}$. (c, f) Mean ± standard error values for the chemical characteristics (traits) of molecular formulae that correlated with $R_{CO_2}$ or $Q_{10}$. Each trait was standardized to zero mean and unit variance. Traits differed between molecules that correlated positively versus negatively with $R_{CO_2}$ or $Q_{10}$ according to t-tests ($p < 0.05$), except for traits of C and DBE in panel (c) and traits of DBE, H/C, N/P and Y_{met} in panel (f).
Carbon decomposition to warming in lakes. This may be because molecular diversity was significantly and positively correlated with both the quantity and quality of sediment organic carbon, that is, both TOC and DOM bioavailability (characterized as functional traits of Mass, AI$_{mod}$, GFE and Y$_{met}$) increased with increasing molecular diversity (Figure S10). This implies that higher molecular diversity provides more labile carbon (lower temperature sensitivity), and short-term warming is not sufficiently expensive for microorganisms to utilize recalcitrant carbon (higher temperature sensitivity), resulting in lower temperature sensitivity with higher molecular diversity. In addition, higher molecular diversity provides a more diverse carbon source for microbial metabolism, resulting in greater stability and resistance of microbial communities to disturbances (e.g., warming) (Gammon, 2023; Qin et al., 2021; Xu et al., 2021). Therefore, we emphasize the importance of chemodiversity (i.e., molecular diversity and functional traits) in exploring the stability of organic carbon burial in lake ecosystems.

We further found that the response of organic carbon decomposition to warming was weaker in freshwater ecosystems compared to terrestrial ecosystems. Across our 50 study sediments spanning a 3500 km north–south transect, Q$_{10}$ ranged from 0.45 to 3.60, with a mean ± SD of 1.78 ± 0.62 (Figure 1b), which is smaller than a global Q$_{10}$ of 2.26 ± 0.35 in soils (Johnston et al., 2021). For similar short-term culture experiments, the values of Q$_{10}$ were 2.69–5.21 for forest soils in China (Li et al., 2020), 3.0–3.5 for grassland soils in New Zealand (Moinet et al., 2021), 5.7–8.0 for permafrost in Tibetan Plateau (Qin et al., 2021), and 2.0–6.6 for surface soils in 28 sites ranging from Alaska to Puerto Rico in North America (Craine et al., 2010). These results indicate that the response of CO$_2$ release from lake sediment decomposition to climate warming may be weaker compared to that of terrestrial soil ecosystems. This highlights the stability of organic carbon in lakes under global warming. Nevertheless, the turnover rate of organic carbon in freshwater can reach 28.8 times and 292 times that of terrestrial soil and the
marine water column, respectively (Catalán et al., 2016), so freshwater may be much larger absolute hotspots of CO₂ release (Raymond et al., 2013). Under the most stringent scenario (SSP1-2.6) and worst-case scenario (SSP5-8.5) of global warming, the annual mean lake surface water temperature of China will increase by 1.0 and 2.2°C, respectively, during the period 2071–2100 compared to the reference period of 1980–2009 (Wang et al., 2023). As a result, CO₂ emissions from lake sediments are preliminary estimated to increase by 5.4 ± 3.8% and 12.4 ± 8.7%, respectively, according to the obtained Q₁₀ and the assumption that the surface sediment temperature in shallow lakes is the same as the surface water temperature.

Although our results indicate that chemodiversity enhances the interpretation of variation in Q₁₀, there are still large uncertainties (Figure 4d) that should be addressed in future studies to more accurately predict the feedback of lake carbon cycle to warming. Firstly, Q₁₀ is expected to vary with changes in temperature (Davidson & Janssens, 2006), so the exploration of Q₁₀ along a temperature gradient could further reveal the response characteristics of decomposition to warming under fluctuating background temperatures. Secondly, only bacterial communities were considered in this study, whereas fungi may have a stronger effect than bacteria in utilizing refractory organic carbon (e.g., lignocellulloses and humus) by producing a wide range of extracellular enzymes (Alster et al., 2018; Peay et al., 2008; Yang et al., 2022). Therefore, we encourage the incorporation of multiple microbial taxonomic groups into studies of carbon decomposition and its temperature sensitivity. Thirdly, future studies could examine the long-term responses of sediment organic carbon decomposition to warming, due in part to changes in substrates and microbial communities over time (Craine et al., 2010), while short-term incubation may limit microbial adaptation.

In conclusion, our study with large-scale lake sampling depicted spatial patterns, magnitudes and drivers of response of lake sediment organic carbon decomposition to warming. We observed that both RCO₂ and Q₁₀ exhibited substantial variation across China’s lakes, yet neither showed a discernible latitudinal pattern. RCO₂ was mainly predicted by sediment properties such as pH and carbon quantity, while Q₁₀ was mostly predicted by chemodiversity of sediment DOM. At both molecular and compositional levels, functional traits of DOM revealed the positive correlation between Q₁₀ and biochemical recalcitrance, thus supporting the carbon quality temperature hypothesis. Moreover, molecular diversity has a positive effect on stability of ecosystem function of organic carbon decomposition, as revealed by Q₁₀ decreased with molecular diversity, which was previously unrecognized. Therefore, we highlight the robust linkage between chemodiversity, ecosystem function and climate change. These findings have important implications for understanding lake ecosystem function and complex carbon-climate feedbacks in a warming world.

AUTHOR CONTRIBUTIONS

Shuailong Wen: Data curation; formal analysis; visualization; writing – original draft. Ang Hu: Data curation; methodology; validation; writing – review and editing. Shuyu Jiang: Data curation; investigation; methodology. Lei Han: Data curation; investigation. Kyoung-Soon Jang: Data curation; methodology. Andrew J. Tanentzap: Validation; writing – review and editing. Jicheng Zhong: Data curation; methodology. Jianjun Wang: Conceptualization; funding acquisition; methodology; project administration; resources; supervision; validation; writing – review and editing.

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CONFLICT OF INTEREST STATEMENT

The authors declare no competing interests.

DATA AVAILABILITY STATEMENT

The database that supports the findings of this study is available at the National Omics Data Encyclopedia (https://www.biosino.org/node/index) with accession number OEP004545, and https://doi.org/10.5281/zenodo.10479064.

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