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Combined use of radiocarbon and stable carbon isotope to constrain the sources and cycling of particulate organic carbon in a large freshwater lake, China



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HIGHLIGHTS

G R A P H I C A L A B S T R A C T

- Radiocarbon and stable isotope compositions of POC were measured in Lake Fuxian.
- Contributions of autochthonous, terrestrial, and sediment POC to the bulk POC were 61%, 22%, and 17%, respectively.
- Autochthonous POC plays a dominant role in sustaining large lake ecosystem.
- Algal POC has more persistent impacts on lake ecosystem than terrestrial POC.
- Sediment might have significant influence on aquatic environment and ecosystem.

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ABSTRACT

The concentrations and isotopic compositions of dissolved inorganic carbon (DIC) and particulate organic carbon (POC) were measured in order to better constrain the sources and cycling of POC in Lake Fuxian, the largest deep freshwater lake in China. Model results based on the combined δ^{13} C and Δ^{14} C, showed that the average lake-wide contributions of autochthonous POC, terrestrial POC, and resuspended sediment POC to the bulk POC in Lake Fuxian were 61%, 22%, and 17%, respectively. This indicated autochthonous POC might play a dominant role in sustaining large oligotrophic lake ecosystem. A mean 17% contribution of resuspended sediment POC to the bulk POC to the bulk POC implied that sediment might have more significant influence on aquatic environment and ecosystem than previously recognized in large deep lakes. The contributions of different sources POC to the water-column POC were a function of the initial composition of the source materials, photosynthesis, physical regime of the lake, sediment resuspension, respiration and degradation of organic matter, and were affected indirectly by environmental factors such as light, temperature, DO, wind speed, turbidity, and nutrient concentration.

This study is not only the first systematic investigation on the radiocarbon and stable isotope compositions of POC in large deep freshwater lake in China, but also one of the most extensive radiocarbon studies on the ecosystem of any great lakes in the world. The unique data constrain relative influences of autochthonous POC, terrestrial POC, and resuspended sediment POC, and deepen the understanding of the POC cycling in large freshwater lakes. This study is far from comprehensive, but it serves to highlight the potential of combined radiocarbon and stable carbon isotope for constraining the sources and cycling of POC in large lake system. More radiocarbon investigations on the water-column POC and the aquatic food webs are necessary to illuminate further the fate of autochthonous POC, terrestrial POC, and their eco-environmental effects.

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1. Introduction

Lake carbon cycle is one of the focuses of current lacustrine research, and its significance lies mainly in two aspects. Firstly, lake carbon cycle is one of the key components of global carbon cycle and has important influence on global source and sink of carbon. On the one hand, as important carbon sinks, lakes bury up to 58% of the carbon that oceans do per year even though the combined surface area of lakes is <2% that of the ocean (Dean and Gorham, 1998; Cole et al., 2007; Zigah et al., 2012a). On the other hand, lakes are nonnegligible carbon sources, with an estimated potential global CO₂ emission of 140 Tg C per year, roughly half the annual carbon transport from rivers to the ocean (Cole et al., 1994). Secondly, lake carbon (C) cycle plays important roles in regulating nutrient cycling and within-lake ecosystem. It is well known that nitrogen (N) and phosphorus (P) are the primary nutrients governing the trophic status of lakes. Excessive N and P may cause lake eutrophication, and further result in algae bloom and drinking water crisis (Oin et al., 2010: Paerl et al., 2011: Ho and Michalak, 2015; Hanifzadeh et al., 2017). The migration and transformation of N and P usually take organic matter as the main carrier. The biogeochemical cycles of C, N and P are tightly coupled by lake primary production and organic matter degradation. The growth process of phytoplankton is certainly accompanied by photosynthetic uptake of C, N and P, while the degradation of organic matter releases synchronously C, N and P back to the water body through a more or less complicated network of microbially mediated biochemical reactions (Bratkič et al., 2012). Therefore, a comprehensive understanding on lake carbon cycle not only enriches our knowledge of global carbon cycle, but also helps to clarify the coupling mechanisms of C-N-P biogeochemical cycles and associated eco-environmental effects, thus providing scientific guidance for the prevention and control of lake eutrophication.

Carbon exists in lake water mainly in four species, including dissolved inorganic carbon (DIC), particulate inorganic carbon (PIC), dissolved organic carbon (DOC) and particulate organic carbon (POC). In comparison to DIC and PIC, knowledge of the sources and transformation of DOC and POC in lake water is very limited due to the complexity of the composition of DOC and POC (millions of monomer compounds) and the difficulty in sampling and analysis (Wu and Tanoue, 2001; Kim et al., 2003: Urban et al., 2005: Bianchi, 2007: Li et al., 2008: Wu and Xing, 2010; Zigah et al., 2012a, 2017). POC is normally defined as organic matter that does not pass a filter with sub-micron pore size (normally 0.7 µm, GF/F glass fiber filter), consisting mainly of terrestrial inputs, autochthonous phytoplankton and macrophyte debris in lake water (Zigah et al., 2011; Adams et al., 2015). POC plays a significant role in carbon and energy flow within lacustrine system, and governs to a large extent the transport of the macronutrients N and P, even metals and organic contaminants (Tipping et al., 1997; Foster et al., 2000; Adams et al., 2015). It is very important to constrain the sources and cycling of POC for fully understanding lake C-N-P cycle, functioning of aquatic ecosystems, and migration of contaminants. However, the sources and cycling of POC in large freshwater lakes has not been well delineated until now.

The combined and complementary use of radiocarbon (¹⁴C) and stable carbon isotope (¹³C) is a promising approach to constrain the sources and cycling of OC in surface earth environment (Raymond and Bauer, 2001a, 2001b; Zigah et al., 2012a, 2017). Δ^{14} C has the following advantages in tracing OC sources and migration- transformation processes: (1) the dynamic range of Δ^{14} C (-1000 to +200%) is much greater than that of δ^{13} C in organic carbon (-32 to -12%) (Petsch et al., 2001; Bauer et al., 2012a), thus providing a more sensitive means for differentiating the sources of OC; (2) as a result of the lower susceptibility of Δ^{14} C to degradation or diagenesis of OC, the Δ^{14} C value of given organic matter changes only with time, thus providing unique and reliable information on age and residence time of OC in surface earth environment (Raymond and Bauer, 2001a, 2001b; Zigah

et al., 2011); (3) both δ^{13} C and Δ^{14} C are linear quantities that can be used directly for isotopic mixing models, which is in favor of distinguishing quantitatively the sources of organic carbon (McNichol and Aluwihare, 2007; Zigah et al., 2012b); and (4) Δ^{14} C has the advantage of being the same for consumers and their food source in a modern ecosystem (as the Δ^{14} C calculation corrects for biochemical fractionations), thereby eliminating the need for fractionation correction along trophic levels as is the case for δ^{13} C and δ^{15} N (McNichol and Aluwihare, 2007; Bauer and Bianchi, 2011; Zigah et al., 2012a).

Because of the increasing accessibility of accelerator mass spectrometry (AMS) facilities and the decreasing sample size requirement for accurate ¹⁴C measurement, numerous studies using radiocarbon measurements have been conducted in aquatic ecosystems in the past few decades (Raymond and Bauer, 2001a, 2001b; McNichol and Aluwihare, 2007; McCallister and del Giorgio, 2008; Bauer and Bianchi, 2011; Zigah et al., 2011, 2012a, 2017; Marwick et al., 2015; Walker et al., 2016; Xue et al., 2017). However, radiocarbon studies on lacustrine POC are very limited, especially in large freshwater lake. Only few studies used limited Δ^{14} C data to infer lacustrine POC sources (McCallister and del Giorgio, 2008; Zigah et al., 2011, 2012a, 2012b; Kruger et al., 2015; Keaveney et al., 2015; Stimson et al., 2017). More radiocarbon measurements of POC from various lacustrine systems will not only improve our understanding of the global carbon cycle, but also help illuminate the roles of different carbon sources in modern lacustrine ecosystem. To the best of our knowledge, there has not been a radiocarbon study reported to quantitatively identify sources of POC in any large lake of China until now. Therefore, this study attempt to carry out the first systematic investigation on the radiocarbon and stable isotope compositions of POC in Lake Fuxian, the largest deep freshwater lake in China. The objectives of this study are (1) to reveal the spatial-temporal distribution characteristics in radiocarbon and stable isotope compositions of POC; (2) to identify quantitatively the sources of water-column POC; (3) to assess the ages and cycling of lacustrine POC.

Lake Fuxian was selected for this study because (1) as the largest deep freshwater lake in China, Lake Fuxian is the most important freshwater resource in China, accounting for 9.16% of the total volume of China's freshwater lakes (Ai et al., 2010; Dai et al., 2017) and nearly half of the total lake freshwater with average water quality of Class I of the China National Water Quality Standard, thus it is most representative of large freshwater lake in China; (2) plateau lake ecosystem in China is very vulnerable and sensitive to environmental change and human disturbance, due to its strong closeness, species simplification, oligotrophy and simple food chain (Dai et al., 2017). Monitoring data indicated an obvious eutrophication trend as a result of increased N and P concentrations in Lake Fuxian in recent years (Gao et al., 2013; Zhang et al., 2015). In consideration of the correlation between N-P cycle and POC within lacustrine system, a thorough investigation on the sources and cycling of POC will provide scientific basis for the prevention and control of eutrophication in Lake Fuxian.

2. Methods

2.1. Study site

Lake Fuxian ($102^{\circ}49'12''-102^{\circ}57'26''E$, $24^{\circ}21'28''-24^{\circ}38'00''N$), the largest deep freshwater lake in China, is located in the Yunnan-Guizhou Plateau, Southwest China. Its altitude is 1721 m. The lake is 31.5 km long and 6.7 km wide on average and has a mean depth of 89.7 m, a maximum depth of 155.0 m, and a volume of $190 \times 10^8 \text{ m}^3$. It has a water surface area of 212 km^2 , and a long water retention time of 167 years (Wang and Dou, 1998; Liu et al., 2009). The northern basin of the lake is wide and deep, but the south basin is narrow and shallow. It is surrounded on all sides by mountains, receiving water from >20 rivers, of which seven are piedmont rivers flowing through cultivated fields in the northern watershed, with the remainder being intermountain rivers

with short lengths and steep gradients from hilly lands on the east and west (Liu et al., 2014; Zhang et al., 2015). The only exit, the Haikou River, is located at the east bank of the lake.

Lake Fuxian is an oligotrophic lake with average water quality of Class I of the China National Water Quality Standard, but the trophic state has started to shift towards increasing eutrophication. Previous studies showed that the total nitrogen (TN) concentration increased from 100 to 223 μ g L⁻¹, the total phosphorus (TP) concentration increased from 5 to 13 μ g L⁻¹, chlorophyll *a* increased from 0.16 to 1.91 mg m⁻³, and transparency decreased from 7.9 to 4.6 m between 1980 and 2005 (Zeng and Wu, 2007; Liu et al., 2009; Gao et al., 2013; Zhang et al., 2015).

2.2. Sampling

7 representative sites were selected to sample the isothermal water column in January 2015 and the stratified water column in August 2015. At each site, we sampled at different depths corresponding to the epilimnion (5 m), the summer thermocline (30–50 m), and the hypolimnion (60–120 m), respectively. Site locations, water depths, and sampling depths are given in Table 1 and Fig. 1. Water samples from major inflowing rivers (Liangwang River, Dongda River, Maliao River, Niumo River, Jianshan River, Shanchong River, and Shapan River) (Fig. 1) were sampled during high-flow events for particulate organic matter analyses.

At each site, temperature (T), pH, conductivity (EC), and dissolved oxygen (DO) were measured using an automated multi-parameter profiler (model YSI 6600 V2). Waters were sampled from given depths using 10 L Niskin bottle. Dissolved inorganic carbon (DIC) samples were taken directly from the Niskin bottle via precleaned (10% HCl v/v, and ultrapure water [Millipore Milli-Q]) silicone tubing into 250 mL high density polyethylene bottles. These bottles, previously acid-cleaned and oven-dried at lab, were rinsed three times with sample in field and then overflowed with two volumes of the unfiltered water. After creating a 5 mL headspace, the samples were immediately preserved with saturated mercuric chloride (HgCl₂) solution, sealed with parafilm, and stored at low temperature in the dark.

Waters were filtered through pre-combusted Whatman GF/F glass fiber filters (450 °Cfor 4 h; 0.7 μ m nominal pore size) via nitrogen pressurized stainless steel canisters to obtain POC samples (Zigah et al., 2012a, 2012b). After ~15 L lake water had passed through a GF/F filter, the filter with retained particulate matter was removed from the stainless steel holder, folded, placed in pre-combusted aluminum foil and stored under frozen condition until analysis. Sediment cores were collected using a gravity corer with a 58 mm diameter in August 2015. The surface 0–2 cm sediments were used for obtaining sedimentary POC samples. Atmospheric CO₂ samples were collected in the central area of the lake in January 2015. Algae samples were collected via vertical net tows (64 μ m mesh) from 10 m to the water surface. We used the protocol developed by Hamilton et al. (2005) to partition fine

Table 1

Coordinates, sampling depths, and water depths of sites in Lake Fuxian.



Fig. 1. Map of Lake Fuxian showing the sampling sites. The open-lake sites are FX-1 in the northern lake, FX-2 in central lake, and FX-3 in the southern lake. The nearshore sites include FX-4, FX-5, FX-6, and FX-7. The major inflowing rivers include Niumo River (NMR), Jianshan River (JSR), Shanchong River (SCR), Shapan River (SPR), Liangwang River (LWR), Maliao River (MLR), Dongda River (DDR), and Haikou River (HKR).

particulate matter into predominantly algal and detrital components by centrifugation in colloidal silica (Ludox TM-50; density 1.40 g cm^{-3}).

All sampling activities were carried out very carefully to avoid possible ¹⁴C contamination. All plasticware and glassware were cleaned with soap and distilled water, leached with 10% (v/v) HCl in water, and then rinsed with distilled water. Glassware was combusted at 450 °C for >4 h before using (Zigah et al., 2012a, 2012b).

2.3. Measurement of Concentrations of DIC and POC

The lake DIC usually includes H_2CO_3 , HCO_3^- , and CO_3^{2-} components. The pH values of lake water range generally from 8 to 9, so DIC exists

Site name		Site Description	Latitude (N)	Longitude (E)	Sampling depth (m)	Water depth (m)
Lake water	FX-1	Northern lake	24°34′21″	102°54′02″	5,30,70,120	130
	FX-2	Central lake	24°27′27″	102°52′45″	5,30,100	105
	FX-3	Southern lake	24°25′07″	102°51′55″	5,30,80	85
	FX-4	Northern nearshore	24°36′28″	102°54′19″	5,30,40,70	75
	FX-5	Eastern nearshore	24°31′23″	102°54′44″	5,30,60	70
	FX-6	Southern nearshore	24°23′02″	102°51′38″	5,30,50,65	70
	FX-7	Western nearshore	24°30′26″	102°52′16″	5, 30,70	80
Rivers	NMR	Niumo River	24°27′21″	102°51′32″	0.5	*
	JSR	Jianshan River	24°35′20″	102°49′55″	0.5	*
	SCR	Shanchong River	24°37′50″	102°51′38″	0.5	*
	SPR	Shapan River	24°37′59″	102°52′34″	0.5	*
	LWR	Liangwang River	24°37′57″	102°52′59″	0.5	*
	MLR	Maliao River	24°38′3″	102°54′05″	0.5	*
	DDR	Dongda River	24°37′48″	102°55′29″	0.5	*

mainly in the form of HCO_3^- (Pendyala et al., 2017). Thus, the concentration of HCO_3^- was used to represent DIC concentration, and measured by in situ titration using a MColortest alkalinity test kit, with an accuracy of 0.05 mM L⁻¹.

POC samples, algae, and surface sediments were freeze-dried to constant weight and homogenized, fumigated with 12 N HCl overnight to remove carbonates, dried again at 60 °C, and cooled in a desiccator. They were then loaded into tin capsules and analyzed for OC contents on a elemental analyzer (Elementar-vario MACRO). The EA was calibrated with reference standard materials B2150 and AR2026, with a typical measurement precision of 0.2%.

2.4. Measurement of $\delta^{13}{\rm C}$ of DIC and POC

DIC samples were directly hydrolyzed with H₃PO₄. POC samples, including water POC, algae POC, and sedimentary POC, were transferred into a quartz tube filled with CuO. The quartz tube was evacuated on a vacuum line, flame-sealed, and then combusted to CO₂ in a muffle furnace at 850 °C for 4 h (Sofer, 1980). The evolved CO₂ was trapped in a vacuum line, purified cryogenically, and stored in a Pyrex tube. Stable carbon isotope ratios (δ^{13} C) of DIC and POC samples were determined at the State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences using IRMS (MAT 252/253). The measurement result was reported in per mil (‰) relative to Pee Dee Belemnite (PDB), with a measurement precision better than 0.2‰. The δ^{13} C is calculated as: δ^{13} C = (R_{sample}/R_{standard} - 1) × 1000, where $R = {}^{13}$ C/ 12 C.

2.5. Measurement of Δ^{14} C of DIC and POC

Radiocarbon measurements were performed at Xi'an Accelerator Mass Spectrometry Center (XAAMS). The prepared solid samples were mixed with an excess amount of copper oxide and combusted at 850 °C for 2 h under a vacuum. DIC samples were directly hydrolyzed with H₃PO₄. The evolved CO₂ was trapped in a vacuum line, purified cryogenically and reduced to graphite in high vacuum using a reducing system with zinc as the reductant and iron as the catalyst (Zhou et al., 2014). The synthesized graphite was transferred and pressed into a special aluminum holder, which was used for the measurement of ¹⁴C using a 3 MV AMS. Each sample was totally recorded up to about 250,000–300,000 ¹⁴C counts, in order to get a precision of ~3‰. Radiocarbon values are reported as Δ^{14} C, the part per thousand deviation of the sample's ¹⁴C/¹²C ratio relative to a nineteenth century wood standard that has been corrected to the activity it would have had in 1950 and a δ^{13} C of -25%. Δ^{14} C was corrected for fractionation using δ^{13} C of samples according to the convention of (Stuiver and Polach, 1977).

 Δ^{14} C is expressed as: Δ^{14} C = [R_{sample}/R_{standard} - 1] × 1000, where R is 14 C/ 12 C. NBS Oxalic acid II (SRM-4990C) was used as reference sample. Instrumental precision of Δ^{14} C analysis was based on error of standards or multiple analyses on a target and ranged normally from 2‰ to 7‰.

2.6. Bayesian isotope mixing model used for identifying multiple sources of POC

A Bayesian isotope mixing model has been implemented in the software package SIAR (Parnell et al., 2010). This model uses a Bayesian framework to determine the probability distribution of the proportional contribution of each source to a mixture. In this study, the contributions of POC sources to a mixture were quantified using the SIAR model (Parnell et al., 2010) as follows:

$$\begin{split} X_{ij} &= \sum^k p_k \big(S_{jk} + C_{jk} \big) + \epsilon_{ij} \\ S_{jk} &\sim N \Big(\mu_{jk}, \omega_{jk}^2 \Big) \end{split}$$

$$\begin{split} & C_{jk} \sim N\!\left(\lambda_{jk}, \tau_{jk}^2\right) \\ & \epsilon_{ij} \sim N\!\left(0, \sigma_j^2\right) \end{split}$$

where X_{ij} is the isotope value j of the mixture i, in which i = 1, 2, 3, ..., Nand j = 1, 2, 3, ..., J; S_{jk} is the source value k on isotope j (k = 1, 2, 3, ..., K) and is normally distributed with mean μ_{jk} and standard deviation ω_{jk} ; p_k is the proportion of source k, which must be estimated using the SIAR model; C_{jk} is the fractionation factor for isotope j on source k and is normally distributed with mean λ_{jk} and standard deviation τ_{jk} ; and ε_{ij} is the residual error representing additional unquantified variation between individual mixtures and is normally distributed with mean 0 and standard deviation σ_j . A detailed description of this model can be found in Moore and Semmens (2008) and Parnell et al. (2010).

3. Results and discussions

3.1. Variations in temperature and dissolved oxygen in the water column

The vertical profiles of water temperature and DO (Fig. 2) showed that the water column was well mixed between 0 and 60 m in January 2015. In contrast, a significant thermal stratification occurred in August 2015, with the thermocline lying at the depth of 20–40 m (Fig. 2). The water temperature decreased rapidly from ~19.5 °C at the top of thermocline to <11 °C at the bottom of thermocline. Similar decreasing trend of DO concentrations with depth was observed, but an obvious trough existed in the thermocline. Due to O₂ mass transfer from the atmosphere into the lake water, there should be higher DO concentrations in the epilimnion than in the hypolimnion. The DO trough probably resulted from the oxygen consumption by non-photosynthetic aquatic species and degradation of easily degradable organic matter in the thermocline. Because of the difference in density between the top and the bottom of the thermocline, POC, especially algae organic matter, settled very slowly and stayed for a longer time in the thermocline. Thus, most of the easily degradable organic matter could be degraded in the thermocline, leading to lower DO concentrations there.

3.2. Variations in concentrations of DIC and POC

The DIC concentrations in the lake ranged from 35.4 to 40.8 mg L⁻¹ with the most frequently observed values between 37 and 38 mg L⁻¹ (Fig. 4A). In general, the DIC concentrations were nearly homogenous both vertically in the water column and laterally across the lake throughout the year (Fig. 3A and B), indicating the absence of significant localized DIC input. A slight decrease in the DIC concentrations with depth (an average of 39.1 mg L⁻¹ in the epilimnion versus 36.9 mg L⁻¹ in the hypolimnion) during winter mixing in January (Fig. 3A) could be observed. This was most likely due to higher CO₂ solubility in cool surface water (Kelts and Hsu, 1978; Chen and Wan, 2002) in winter.

The POC concentrations varied from 0.042 to 0.142 mg L⁻¹, and 0.06 to 0.10 mg L⁻¹ were the most commonly observed values (Fig. 4B). Concentrations of POC were more variable than that of DIC both vertically in the water column and laterally across the lake (Fig. 3C and D). Generally speaking, surface water usually had higher POC concentrations than deep water as would be expected by increased aquatic in situ primary production in the epilimnion and degradation of POC in the hypolimnion (Zigah et al., 2011). The highest POC concentration was found at the FX-4 site representing the northern nearshore province of the lake (Fig. 1 and Table 1), where several rivers inflow into the lake (Fig. 1), possibly indicating considerable inputs of allochthonous terrestrial POC from the northern rivers (Liu et al., 2014; Zhang et al., 2015).



Fig. 2. Seasonal variations of water temperature and dissolved oxygen in the water column of Lake Fuxian.

3.3. Variations in stable carbon isotopic compositions of DIC and POC

The stable carbon isotopic compositions of DIC and POC in the water column were closely coupled to the physical regime of Lake Fuxian. During winter mixing (isothermal condition) in January, the $\delta^{13}C$ of DIC ($\delta^{13}C_{\text{DIC}}$) were almost homogenous vertically in the water column and laterally across the lake, with a mean of -1.7% (Fig. 5A). In contrast, the $\delta^{13}C_{\text{DIC}}$ displayed considerable fluctuations (Fig. 5B) vertically during thermal stratification in August, with mean values decreasing from 0.2‰ in the epilimnion to -1.8% in the hypolimnion. Likewise, the $\delta^{13}C$ of POC ($\delta^{13}C_{\text{POC}}$) were spatially (vertically and laterally) uniform with a mean of -28.6% in January (Fig. 5C), while, during thermal stratification in August, the $\delta^{13}C_{\text{POC}}$ averaged -25.7% in the epilimnion (Fig. 5D).

The depth variations of $\delta^{13}C_{DIC}$ and $\delta^{13}C_{POC}$ during stratification were most likely to be a combined result of (1) photosynthesis in the epilimnion, which caused more positive $\delta^{13}C$ in surface DIC pool through isotopic fractionation (Falkowski and Raven, 1997; Chen et al., 2008), and was affected by the environmental factors such as light, temperature, turbidity, and nutrient concentration in lake water; (2) degradation and remineralization of organic carbon in deep water, which produced ¹³C-depleted DIC (Parker et al., 2010); and (3) sediment resuspension, which brought ¹³C-depleted sedimentary POC to the hypolimnion, as described hereinafter. Although the aforementioned processes also existed in winter, the water column was well mixed and the influences of photosynthesis, microbial activity, degradation and remineralization on $\delta^{13}C_{DIC}$ and $\delta^{13}C_{POC}$ are smoothed. Thus, the $\delta^{13}C_{DIC}$ and $\delta^{13}C_{POC}$ were homogenous in the water column in winter.

Notably, the $\delta^{13}C_{POC}$ shifted by 2.9% towards more ¹³C-enriched values in the epilimnion during the transition from isothermal to

stratified conditions in the lake (Fig. 5C and D). The mean $\delta^{13}C_{POC}$ values (-26.1%) of all water samples in the lake during stratification in August were 2.4‰ more positive than that (-28.5%) during isothermal conditions in January (Tables 2 and 3). The shift of $\delta^{13}C_{DIC}$ in the epilimnion reached 1.7‰ between isothermal and stratified conditions. These shifts reflected the important influence of primary production on the stable carbon isotopic compositions of DIC and POC. Taken all together, the distribution of $\delta^{13}C_{DIC}$ and $\delta^{13}C_{POC}$ in the water column was dominated by the physical regime of the lake, hydrophyte photosynthesis, degradation of organic matter, microbial activity, and sediment resuspension, and was affected indirectly by environmental factors such as light, temperature, DO, wind speed, turbidity, and nutrient concentration.

3.4. Δ^{14} C within atmospheric CO₂ and water-column DIC

Distribution of $\Delta^{14}C_{DIC}$ was almost homogeneous (Fig. 6A and B) across the entire lake throughout the year, with only small or negligible variations at the current precision of accelerator mass spectrometry of 2–7‰. This could be attributed to (1) the lake's large surface area is in favor of effective CO₂ exchange between atmosphere and the in-lake DIC pool; (2) as monomictic lake, the water column is homogenized through mixing vertically once a year; and (3) although photosynthesis and respiration change significantly $\delta^{13}C_{DIC}$ through isotope fractionation, they have no influence on $\Delta^{14}C$ of DIC in the lake water because the $\Delta^{14}C$ calculation has corrected for biochemical fractionations, as described before. The mean value of $\Delta^{14}C_{DIC}$ was slightly higher in January (44‰) than in August (41‰). This most likely resulted from decreasing atmospheric $\Delta^{14}C$ with time (a decline of ~5‰/yr), as described later.

We determined the radiocarbon value of atmospheric CO_2 collected in the central area of Lake Fuxian the same year in order to provide



Fig. 3. Spatial distributions of the concentrations of DIC (A) and POC (C) during winter mixing in January 2015, and the concentrations of DIC (B) and POC (D) during summer stratification in August 2015.

regional ¹⁴C background. The measured Δ^{14} C value of atmospheric CO₂ is 15‰. We do not think there would be considerable differences in atmospheric ¹⁴C across the lake because atmospheric ¹⁴C fluctuations occur normally at large spatial scale. The remoteness of Lake Fuxian from big cities and the uniformity of Δ^{14} C_{DIC} across the entire lake suggest little regional variation in atmospheric ¹⁴C across the lake. It has been reported that the Δ^{14} C value of atmospheric CO₂ decreased from 66‰ in 2004, to 38‰ in 2009, and to 25‰ in 2012, corresponding to a decline rate of ~5‰/yr (Zigah et al., 2017), according to which the Δ^{14} C value of atmospheric CO₂ around Lake Fuxian.

The $\Delta^{14}C_{DIC}$ values (mean 41–44‰) in the lake were significantly higher than that of co-occurring atmospheric CO₂ (15‰). This offset was most likely due to the time of exchange for the in-lake DIC pool with the atmosphere, which was affected by water column stratification and the extent of water column mixing (Alin and Johnson, 2007; Zigah et al., 2017). Zigah et al. (2017) reported that DIC was consistently ¹⁴Cenriched by ~20‰ relative to co-occurring atmospheric CO₂ from 2004 to 2014 in Lake Superior. In Lake Fuxian, DIC was ¹⁴C-enriched by ~26‰ relative to atmospheric CO₂. On the one hand, this proved the absence of significant input of localized groundwater or ¹⁴C-dead carbon from carbonate in the catchment, and thus affirmed the feasibility of Δ^{14} C in identifying carbon sources in the lake. On the other hand, it indicated a carbon isotope equilibration time of ~5–6 years between the DIC and atmospheric CO₂ in Lake Fuxian.

3.5. Δ^{14} C within water-column POC

Measured $\Delta^{14}C_{POC}$ values in the isothermal lake ranged from -2% to -68% (Fig. 6C), corresponding to 17–568 yrs B.P. The $\Delta^{14}C_{POC}$ values

displayed larger fluctuations (Fig. 6D) during thermal stratification in August, ranging from 20% to -125% (modern to 1071 yrs B.P.). The $\Delta^{14}C_{POC}$ in the epilimnion averaged 2‰, and decreased vertically to a mean - 76‰ (Fig. 7B) in the hypolimnion in August. An intriguing contrast was that all the $\Delta^{14}C_{POC}$ values of POC across the entire lake were negative in January (Fig. 6C), while most of surface POC in August had modern (post 1950) ¹⁴C signals (mean Δ^{14} C of 2‰) and negative $\Delta^{14}C_{POC}$ values existed mostly in deep water (Fig. 6D). This could be attributed to increased aquatic in situ primary production in the warmer epilimnetic water in August, which produced more ¹⁴C-enriched algal POC, resulting in higher percentage algal POC among the total POC, and thus causing a shift towards more positive $\Delta^{14}C_{POC}$ values in the epilimnion during stratification. Previous investigation on the vertical distribution and seasonal variation of cell density of phytoplankton in Lake Fuxian has demonstrated higher algae production during August and September, and revealed that the cell density of phytoplankton decreased from the epilimnion to the hypolimnion in the water column (Liu et al., 2003).

The most likely explanations for larger variation range of watercolumn $\Delta^{14}C_{POC}$ in August than January are (1) stratification reduced the homogenization of ¹⁴C of water-column POC in August; (2) increased primary production in the warmer epilimnetic water produced abundant ¹⁴C-enriched algal POC, resulting in more positive $\Delta^{14}C_{POC}$ value up to 20‰; and (3) ¹⁴C-depleted sedimentary POC accounted for higher percentage in hypolimnetic POC during stratification, thus with more negative $\Delta^{14}C_{POC}$ value occurring in the hypolimnion. Above inference also explained why the $\Delta^{14}C_{POC}$ decreased vertically from the epilimnion to the hypolimnion in August. The oldest POC ($\Delta^{14}C = -125\%$, corresponding to 1071 yrs B.P.) was seen at the bottom of the water column at the FX-4 site, possibly indicating a significant contribution of resuspended sediment POC in this lake province.



Fig. 4. Frequency distribution of DIC concentrations (A) and POC concentrations (B) in Lake Fuxian.

3.6. Sources of POC

Sources of lacustrine POC generally include autochthonous POC, terrestrial POC, resuspended sediment POC, and bacterial POC (Zigah et al., 2012a, 2017). In order to identify quantitatively sources of watercolumn POC, we probed firstly into the characteristics of various sources POC in Lake Fuxian. Autochthonous POC is derived from recent withinlake primary production, mainly including algae and macrophyte. It is well known that DIC is incorporated into algal/macrophyte biomass during biosynthesis in the lake water. Thus, the Δ^{14} C within autochthonous POC is consistent with the lake $\Delta^{14}C_{DIC}$ (McCallister et al., 2004; McCarthy et al., 2011; Zigah et al., 2012a, 2012b). In this study, we used the mean $\Delta^{14}C_{\text{DIC}}$ value of $44 \pm 3\%$ (n = 16) in January and 41 \pm 3‰ (n = 10) in August as the endmember values of Δ ¹⁴C for autochthonous POC during the corresponding periods, respectively. Measured δ^{13} C values of algae sampled in the lake in January and August had a mean of $-28.2 \pm 1.2\%$ and $-25.3 \pm 1.2\%$ which were used as the endmember values of δ^{13} C for autochthonous POC during isothermal mixing and stratification, respectively. This was accordant with the more positive $\delta^{13}C_{DIC}$ in the epilimnetic water in August than January.

Terrestrial POC consists mainly of a mixture of terrestrial plant debris and soil organic matter, containing both "old" and "modern" terrestrial OC components. As for a specific lake basin, POC collected in inflowing rivers during high flow conditions was supposed to be representative and a good approximation of terrestrial POC, because most terrestrial influx in rivers occurred during storm flows (Zigah et al., 2011, 2012b). Here, the measured mean values of δ^{13} C and Δ^{14} C of riverine POC from major inflowing rivers (Liangwang River, Dongda River, Maliao River, Niumo River, Jianshao River, Shanchong River, and Shapan River) (Fig. 1) during high-flow events were used as the endmember values for terrestrial POC, which were $-27.2 \pm 1.2\%$ and $-152 \pm 59\%$, respectively.

Resuspended sediment POC refers to POC resuspended from surface sediments due to strong bottom currents, which could be further brought to the upper waters by density-driven vertical mixing of the water column and turbulent flow. Based on the observed relationship between POC and total suspended particles in Lake Superior, a considerable amount of water-column POC was supposed to originate from sediment resuspension (Urban et al., 2005; Zigah et al., 2012a). It has been reported that as much as 35% of sinking POC from several open-ocean sites was derived from resuspended sediments (Hwang et al., 2010). In Lake Fuxian, the presence of old POC in both surface and deep water during isothermal conditions, in combination with the decreasing $\Delta^{14}C_{POC}$ with depth during stratification, suggested a nonnegligible contribution of sediment resuspension to water-column POC. The spatialtemporal variations of $\Delta^{14}C_{POC}$ (Fig. 6C and D) indicated that the influence of sediment resuspension on water-column POC was mostly confined to the hypolimnion during stratification, while extending to the whole water column during isothermal conditions. The mean δ^{13} C and Δ^{14} C values of POC in the surface sediment (0–2 cm) samples of Lake Fuxian were $-28.6 \pm 0.8\%$ (*n* = 7) and $-203 \pm 50\%$ (*n* = 7), which were used as the endmember values of $\delta^{13} C$ and $\Delta^{14} C$ for resuspended sediment POC, respectively.

Bacterial POC might be another identifiable component of POC in large lake, where microbial food web may play important role in carbon processing, similar to oceanic systems (Cotner et al., 2004; Zigah et al., 2012b). The average contributions of bacterial POC to the bulk POM were only 3% in Lake Superior (Cotner et al., 2004; Zigah et al., 2012a, 2012b). Considering smaller surface area of Lake Fuxian than Lake Superior, we believe that the contribution of bacterial POC to the bulk POC is negligible in Lake Fuxian.

From the above discussions, it can be expected that major sources of water-column POC include autochthonous POC, terrestrial POC, and resuspended sediment POC in Lake Fuxian. The endmember values of δ^{13} C and Δ^{14} C for different sources POC, as described before, were displayed in Fig. 8, according of which the contribution percentages of different sources to water column POC could be quantitatively estimated using a Bayesian isotope mixing model (Moore and Semmens, 2008; Parnell et al., 2010), which was described before. In the model, two isotopes (Δ^{14} C and δ^{13} C) and three potential POC sources (autochthonous POC, terrestrial POC, and resuspended sediment POC) were applied. All of the data analyses were performed using Sigmaplot 10.0.

The model results show that the average lake-wide contributions of autochthonous POC, terrestrial POC, and resuspended sediment POC to the water column POC in Lake Fuxian were 61%, 22%, and 17%, respectively. The mean contribution of autochthonous POC to the bulk POC varied from 50% (42–57%) at the FX-2 site during winter mixing to 80% (77–83%) at the FX-2 site during summer stratification (Tables 2 and 3). The mean contribution of terrestrial carbon to the bulk POC ranged from 13% (11–16%) at FX-2 site to 28% (18–39%) at the FX-7 site during summer stratification. The mean contribution of resuspended sediment POC to the bulk POC varied from a mean of 7% (6–7%) during stratification at the FX-2 site to 24% (20–27%) during winter mixing at the FX-5 site.

From Fig. 9, we can see significant different contribution percentages of autochthonous POC, terrestrial POC, and resuspended sediment POC to the bulk POC during winter mixing and summer stratification. Firstly, the contributions of autochthonous POC were almost constant both vertically in the water column and laterally across the lake during winter mixing (Fig. 9A), while displaying greater contribution in the epilimnion (mean 76%) than in the hypolimnion (mean 43%) during summer stratification (Fig. 9B). Secondly, the contributions of terrestrial POC



Fig. 5. Depth profiles of the mean δ^{13} C values of DIC (A) and POC (C) during winter mixing in January 2015, and of mean δ^{13} C values of DIC (B) and POC (D) during summer stratification in August 2015. Box represents the 25th and 75th percentiles, the solid line within the box represents the median value, and the dash line within the box represents the mean value.

were nearly invariable with only small fluctuation between 16% and 29% during winter mixing (Fig. 9A), while it had a mean of 12% in the hypolimnion, much lower than the mean of 31% in the epilimnion during summer stratification (Fig. 9B). Thirdly, resuspended sediment POC has very low contributions (mean 9%) in the epilimnion during summer stratification, while it has much higher contributions in the hypolimnion during summer stratification (mean 25%), and throughout the whole water column during winter mixing (mean 18%). The relative contributions of autochthonous POC, terrestrial POC, and resuspended sediment POC to the bulk POC in the water column were widely variable at different sites and in different seasons. Basically, the relative contributions of different sources POC to the bulk POC were a function of the initial composition of the source materials, photosynthesis, physical regime of the lake, sediment resuspension, respiration and degradation of organic matter, and were affected indirectly by environmental factors such as light, temperature, DO, wind speed, turbidity, and nutrient concentration.

The average lake-wide contribution of autochthonous POC to the bulk POC reached 61%, which indicated that photosynthesis has the most

Table 2

Concentrations, $\delta^{13}C$ and $\Delta^{14}C$ of DIC and POC, and mean contribution percentages of autochthonous POC, terrestrial POC, and resuspended sediment POC to the bulk POC in the water column of Lake Fuxian in January 2015.

Sample No.	Depth (m)	DIC (mg L ⁻¹)	δ ¹³ C _{DIC} (‰)	$\Delta^{14}C_{DIC}$ (‰)	POC (mg L ⁻¹)	δ ¹³ C _{POC} (‰)	$\Delta^{14}C_{POC}$ (‰)	Autoch POC (%)	Terre POC (%)	Resus POC (%)
FX-1-1	5	39.6	*	45 ± 3	0.104	-28.8	-13 ± 4	67	19	14
FX-1-2	30	37.2	-1.6	41 ± 3	0.103	-28.7	-12 ± 3	67	19	14
FX-1-3	70	36.6	*	*	0.105	-28.5	-12 ± 2	67	20	13
FX-1-4	120	36.6	-1.6	38 ± 4	0.087	-28.6	-25 ± 3	60	22	18
FX-2-1	5	39.6	-1.9	49 ± 3	0.074	-28.0	-29 ± 3	57	25	18
FX-2-2	30	37.2	-1.8	44 ± 3	**	**	-72 ± 3	42	29	29
FX-2-3	100	36.0	-1.8	46 ± 3	0.071	-28.4	-45 ± 4	51	25	23
FX-3-1	5	39.6	-1.9	46 ± 3	0.075	-28.7	-3 ± 2	72	16	11
FX-3-2	30	37.2	-1.7	45 ± 3	0.059	-28.7	-6 ± 3	71	17	12
FX-3-3	80	37.8	-1.6	*	0.065	-28.7	-35 ± 6	56	23	21
FX-4-1	5	40.8	-1.5	41 ± 3	0.142	-28.1	-68 ± 3	43	29	28
FX-4-2	40	36.0	-1.6	45 ± 3	0.120	-28.1	-19 ± 3	62	23	15
FX-5-1	5	36.0	-1.8	41 ± 3	0.079	-29.1	-52 ± 4	50	23	27
FX-5-2	50	37.2	-1.6	46 ± 3	0.056	-28.7	-30 ± 3	58	22	20
FX-6-1	5	39.6	**	49 ± 3	0.073	-28.5	-7 ± 3	70	18	12
FX-6-2	30	40.2	-1.5	43 ± 3	0.070	-28.6	-34 ± 3	57	23	20
FX-6-3	65	37.2	-1.6	47 ± 3	0.068	-28.7	-32 ± 3	58	22	20
FX-7-1	5	38.4	-1.8	43 ± 3	0.094	-28.3	-14 ± 3	65	21	14
FX-7-2	70	37.2	-1.4	41 ± 4	0.092	-28.4	-2 ± 4	72	17	11

Table 3

Concentrations, δ^{13} C and Δ^{14} C of DIC and POC, and mean contribution percentages of autochthonous POC, terrestrial POC, and resuspended sediment POC to the bulk POC in the water column of Lake Fuxian in August 2015.

Sample no.	Depth (m)	DIC (mg L ⁻¹)	δ ¹³ C _{DIC} (‰)	$\Delta^{14}C_{DIC}$ (‰)	POC (mg L ⁻¹)	δ ¹³ C _{POC} (‰)	$\Delta^{14}C_{POC}$ (‰)	Autoch POC (%)	Terre POC (%)	Resus POC (%)
FX-1-1	5	35.4	0.1	41 ± 4	0.110	-24.8	-3 ± 3	75	15	9
FX-1-2	30	36.0	0.2	42 ± 3	0.094	-25.0	20 ± 3	87	8	5
FX-1-3	120	37.8	-1.5	41 ± 3	0.103	-26.3	-90 ± 3	39	33	28
FX-2-1	5	36.0	0.3	*	0.089	-25.7	16 ± 4	83	11	6
FX-2-2	30	37.2	0.1	*	0.113	-25.7	12 ± 2	81	12	7
FX-2-3	100	38.4	-1.5	*	0.115	-27.0	11 ± 3	77	16	7
FX-3-1	5	40.8	0.2	37 ± 3	0.104	-25.7	4 ± 3	76	16	8
FX-3-2	30	40.8	0.0	37 ± 3	0.071	-26.4	-109 ± 3	34	35	31
FX-3-3	80	39.6	-2.2	*	0.072	-28.2	-27 ± 3	51	29	20
FX-4-1	5	36.0	0.1	45 ± 3	0.071	-25.4	5 ± 3	78	14	8
FX-4-2	30	37.2	0.1	43 ± 3	0.123	-25.7	6 ± 3	78	14	8
FX-4-3	80	37.8	-2.5	42 ± 3	0.069	-27.2	-125 ± 2	27	35	38
FX-5-1	5	36.0	0.2	*	0.099	-25.3	4 ± 3	53	28	19
FX-5-2	30	37.8	0.1	39 ± 3	0.094	-26.2	-44 ± 4	78	14	8
FX-5-3	65	37.2	-1.1	*	0.051	-26.6	-122 ± 2	30	36	34
FX-6-1	5	39.0	0.1	40 ± 3	0.077	-26.3	-9 ± 3	67	21	12
FX-6-2	50	36.1	-0.9	*	0.065	-26.1	-60 ± 4	48	30	22
FX-7-1	5	38.4	0.2	*	0.069	-26.1	-2 ± 4	72	18	10
FX-7-2	30	37.2	0.0	*	0.042	-25.7	-47 ± 4	54	28	18
FX-7-3	80	37.8	-2.2	48 ± 3	0.048	-26.1	-120 ± 3	32	39	29

important influence on the water column POC. The highest contribution of autochthonous POC to the bulk POC, up to 87%, was seen in the epilimnetic water at the FX-1 site during winter mixing. Lower contribution in the hypolimnion (mean 43%) during summer stratification should be attributed to the hypolimnetic respiration and degradation of organic matter, and increasing influence of sediment resuspension. The highest contribution of resuspended sediment POC to the bulk POC, up to 38%,

was seen in the hypolimnion at the FX-4 site during summer stratification. This was accordant with the oldest POC ($\Delta^{14}C = -125\%$, corresponding to 1071 yrs. B.P.) at the bottom of the water column at the FX-4 site (Table 3).

The almost invariable contributions of autochthonous POC, terrestrial POC, and resuspended sediment POC to the bulk POC in the water column in winter suggested that the density-driven vertical mixing was



Fig. 6. Spatial distributions of the Δ^{14} C values of DIC (A) and POC (C) during winter mixing, and of the Δ^{14} C values of DIC(B) and POC (D) during summer stratification.



Fig. 7. Depth profiles of the mean values of Δ^{14} C of POC during winter mixing (A) and summer stratification (B). Box represents the 25th and 75th percentiles, the solid line within the box represents the median value, and the dash line within the box represents the mean value.

strong enough to homogenize the whole water column both in the nearshore region and in the open-water region.

Algal POC played a dominant role in sustaining the lake ecosystem. Firstly, it provided ~61% of the water-column POC. Secondly, higher contributions of terrestrial POC, along with lower contributions of autochthonous POC, in the hypolimnion than the epilimnion during summer stratification (Fig. 9B) indicated that terrestrial POC sank more rapidly from the epilimnion to the hypolimnion than autochthonous POC. This suggested that algal POC stayed longer in surface water and had more persistent influence, which was supported by normally higher POC concentrations in the epilimnetic water than the hypolimnetic water (Fig. 3C and D).

3.7. Implications of resuspension for environment and ecosystem

The average lake-wide contributions of resuspended sediment POC to the bulk POC in Lake Fuxian were 17%, and the highest contribution, up to 38%, was seen at the FX-4 site during summer stratification. This implied that sediment might have more significant influence on aquatic environment and ecosystem than previously recognized in large deep oligotrophic lakes, similar to Lake Fuxian (Zhao et al., 2012; Chen et al., 2017). Firstly, this study proves that sediment resuspension do transport a considerable amount of POC from sediments to the overlying water, along with which numerous nutrients (N and P), heavy metals and organic



Fig. 8. The endmember values of Δ^{14} C and δ^{13} C for autochthonous POC, terrestrial POC, and resuspended sediment POC in Fuxian Lake. The values are expressed by mean values with error bars.

pollutants must have been released concurrently (Tipping et al., 1997; Foster et al., 2000; Adams et al., 2015) and brought to the upper water, increasing risks of algal bloom and water quality deterioration (Ho and Michalak, 2015; Hanifzadeh et al., 2017). Because of the strong closeness and long water retention time, these lakes are difficult to restore to clearwater state once their sediments are heavily polluted. Secondly, if resuspended sediments, along with terrestrial POC, do support aquatic food webs by zooplankton directly feeding on resuspended POC and/or



Fig. 9. Relative contribution percentages of autochthonous POC, terrestrial POC, and resuspended sediment POC to water-column POC in different sites during winter mixing (A) and summer stratification (B).

feeding on heterotrophic organisms that consume resuspended POC, the response of lacustrine ecosystem to yearly variations in primary productivity would be buffered (Zigah et al., 2011). Many studies have demonstrated that resuspended sediment POC and/or terrestrial POC supported bacterial, zooplankton, and fish production (Brett et al., 2009; Berggren et al., 2010). More radiocarbon investigations on the watercolumn POC and the aquatic food webs are necessary to illuminate further the fate of autochthonous POC, terrestrial POC, and resuspended sediment POC, and their eco-environmental effects in large freshwater lakes.

4. Conclusions

In this study, the radiocarbon and stable isotope compositions of DIC and POC were systematically investigated in order to better constrain the sources and cycling of POC in Lake Fuxian. The main findings of this study are:

- DIC was ¹⁴C–enriched by ~26‰ relative to atmospheric CO₂, which proved the absence of significant input of localized groundwater or ¹⁴C–dead carbon from carbonate in the catchment, and thus affirmed the feasibility of Δ¹⁴C in identifying carbon sources in Lake Fuxian.
- The average lake-wide contribution of autochthonous POC to the bulk POC in Lake Fuxian was 61%. This indicated Lake Fuxian was net autotrophic with a high balance of autochthony to allochthony. Autochthonous POC might play a dominant role in sustaining large oligotrophic lake ecosystem.
- Terrestrial POC sank more rapidly from the epilimnion to the hypolimnion than autochthonous POC, suggesting that algal stayed longer in surface water and had more persistent impacts on the lake ecosystem than terrestrial POC.
- The average lake-wide contributions of resuspended sediment POC to the bulk POC were 17%, with the highest contribution up to 38%. This implied that sediment might have more significant influence on aquatic environment and ecosystem than previously recognized in large deep oligotrophic lakes, similar to Lake Fuxian.
- The relative contributions of autochthonous POC, terrestrial POC, and resuspended sediment POC to the water-column POC were a function of the initial composition of the source materials, photosynthesis, physical regime of the lake, sediment resuspension, respiration and degradation of organic matter, and were affected indirectly by environmental factors such as light, temperature, DO, wind speed, turbidity, and nutrient concentration.

This study is not only the first systematic investigation on the radiocarbon and stable isotope compositions of POC in large deep freshwater lake in China, but also one of the most extensive radiocarbon studies on the ecosystem of any great lakes in the world. The unique data constrain relative influences of autochthonous POC, terrestrial POC, and resuspended sediment POC, and deepen the understanding of the POC cycling in large freshwater lakes. This lays scientific basis for further revealing the reason and mechanisms of eutrophication, and thus providing helpful guidance for the prevention and control of eutrophication.

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