

Evidence from isotopic geochemistry as an indicator of eutrophication of Meiliang Bay in Lake Taihu, China

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Abstract In this paper, Lake Taihu, a large shallow freshwater lake in China, is chosen as an example of reconstruction of eutrophication through the comparison between stable isotopes from dissolved nutrients and plants and water column nutrient parameters and integration of multiple proxies in a sediment core from Meiliang Bay including TN, TP, TOC, C/N, $\delta^{15}\text{N}$, $\delta^{13}\text{C}$, etc. Differences in aquatic plant species and trophic status between East Taihu Bay and Meiliang Bay are indicated by their variations in $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of aquatic plants and $\delta^{15}\text{N}$ of NH_4^+ . A significant influence of external nutrient inputs on Meiliang Bay is reflected in temporal changes in $\delta^{15}\text{N}$ of NH_4^+ and hydro-environmental parameters. The synchronous change between $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values of sedimented organic matter (OM) has been attributed to elevated primary production at the beginning of eutrophication between 1950 and 1990, then recent inverse correlation between them has been caused by the uptake of ^{15}N -enriched inorganic nitrogen by phytoplankton grown under eutrophication and subsequent OM decomposition and denitrification in surface sediments, indicating that the lake has suffered from progressive eutrophication since 1990. Based on the use of a combination of stable isotopes and elemental geochemistry, the eutrophication of Meiliang Bay in Lake Taihu could be better traced. These transitions of the lake eutrophication respectively occurring in the 1950s and 1990s have been suggested as a reflection of growing impacts of human activities, which is coincident with the instrumental data.

Keywords: stable carbon isotope of OM, stable nitrogen isotope, eutrophication, Lake Taihu.

Stable carbon and nitrogen isotopes in lake sediments have proven to be useful in studies of tracing paleoenvironmental changes, such as changes in OM sources and aquatic primary production and the utilization and transition of nutrients^[1-5]. Recently, more attention has been paid to the reconstruction of trophic history in lakes due to the aggravation of the eutrophication problem^[5-7]. The stable isotope, however, cannot provide unique solutions because the sediment

records of lakes are controlled by many factors. In order to heighten the reliability of environmental interpretation supported by stable isotopic record and better understand its corresponding processes and mechanism, much more emphasis is put on modern geochemical processes and environmental significance of stable isotopic compositions needs to be confirmed in hydro-environmental parameter data. In this paper, we attempted to reconstruct the eutrophication in Lake

Taihu, a large shallow freshwater lake in China, using stable isotopes in dissolved nutrients, plants of various lake areas and in a sediment core collected from Meiliang Bay together with other associated indexes. Analytical results agreed well with monitoring data. It gave the possibility of further application of stable isotope analysis to reconstructing the history of eutrophication in lakes.

1 Site

Lake Taihu, the third largest fresh water lake in China, is located in the Yangtze River Delta, which is the most advanced economic zone in China. There are several large and medium-sized cities such as Wuxi, Suzhou in Jiangsu Province and Huzhou in Zhejiang Province around the lake ($30^{\circ}56' - 31^{\circ}34'N$, $119^{\circ}54' - 120^{\circ}36'E$; Fig. 1). It is a shallow lake with a surface area of 2425 km^2 , a mean depth of 2.12 m, a volume of $51.4 \times 10^8 \text{ m}^3$, and a catchment area of 36500 km^2 ^[8]. The lake is primarily fed with precipitation as well as surface runoff including the West Tiaoxi River, Changxing River, Zhihu River, Liangxi River, and Yili River, etc. The water retention time in the lake is 309 d. The lake can be divided into two parts with the boundary of Dongjiao Headland of Dongshan Island. Its west is the main part and almost consists of phytoplankton. The east supports a dense population of vascular plants with better water quality, which is actually a bay of the lake^[9]. In the past the majority of the Taihu Basin had been used for agricultural purposes, such as mulberry plantations, fish and rice culture. The land-use pattern in the basin changed greatly due to the development of agriculture and industry, especially the countryside industry expansion, and was characterized by the conversion of agricultural land to urban and industrial uses in the recent decades. As a result of inputs of agricultural runoff, industrial sewage and human waste disposal, increased nutrients like N and P and heavy metal pollutants loading of the lake are understood to be important factors in reduced water quality, enhanced eutrophication and frequent phytoplankton blooms^[10]. Since 1990, research monitoring has documented cyanobacteria blooms in the northwestern part of the lake including Meiliang Bay between May and October, particularly in July and

August^[8]. During 2004 the first cyanobacteria accumulations at the monitored site were noted on June 11.

2 Materials and methods

2.1 Sampling

A 52-cm gravity core named ML was collected from Meiliang Bay in Lake Taihu in March 2004, which was preserved perfectly and free of disturbance. Core ML was extruded *in situ* and sections sliced off at 0.5 cm intervals on the top 20 cm depth and at 1 cm intervals on the rest of the core and sealed in plastic bags. 5 L water samples were collected at three sites in Meiliang Bay and one site in East Taihu Bay between May and September in 2004 (Fig. 1). At each site water was sampled from the lake surface and below a depth of 1 m. 20–40 mg/L HgCl_2 was added to each sample to suppress microbial activity^[11]. Aquatic plants samples were collected in the same four sites between July and August in 2004 and algae samples were mostly composed of cyanobacteria accumulations. *Trapa bispinosa* was planted in a waterproof polyethylene enclosure near 863 project base in Meiliang Bay.

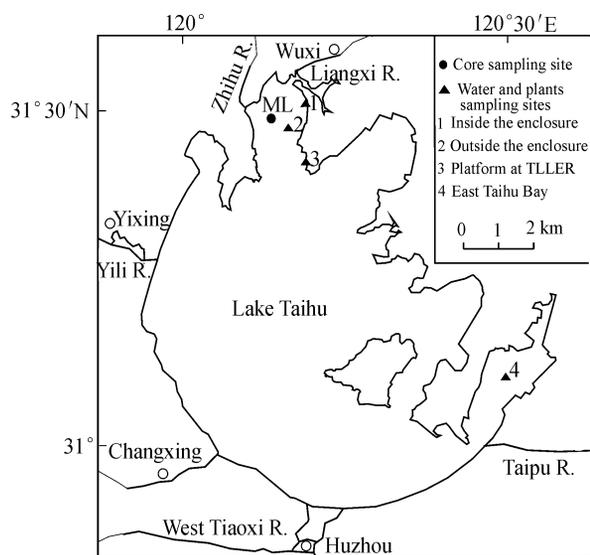


Fig. 1. Map of Lake Taihu showing the sampling locations.

2.2 Analytical methods

(i) Analyses of sediment and aquatic plants samples. After the sediment samples were dried at 40°C and aquatic plants samples were washed with deionized

water and freeze-dried, all samples were ground finely to pass through 100 mesh.

5% dilute hydrochloric acid was added in the appropriate sample amount. The mixture reacted for 24 h to dissolve carbonate and rinsed till neutrality with distilled water to remove remaining chloride, dried, and ground finely to pass through 150 mesh. An appropriate sample amount was taken and put into a high-temperature vacuum reaction furnace fixed with copper oxide and silver wires. It was burnt fully for 15 min at the constant temperature of 800°C and high purity oxygen, and the pure CO₂ gas was collected with liquid nitrogen and cool liquid. The $\delta^{13}\text{C}$ value of the produced CO₂ gas was determined by MAT-251 mass spectrometer. The result was expressed in the permil notation relative to the international PDB standard, with a precision of less than 0.05‰.

Stable nitrogen isotopic composition of samples was analyzed using Kjeldahl digestion with sulfuric acid and mixed catalyst^[12]. Cooled digestates were treated with NaOH, then steam-distilled and trapped in dilute H₂SO₄ solution. Distillates were evaporated dryness on a water bath. Under vacuum conditions, the N₂ was released by reacting samples with NaBrO and the $\delta^{15}\text{N}$ value was determined by MAT-251 mass spectrometer. Analytical precision is within 0.05‰.

Total organic carbon (TOC) was measured by oxidation with a mixture of potassium dichromate-sulfuric acid (oil bath) followed by titration with ferrous sulfate. Standard Kjeldahl procedure was employed for the analysis of total nitrogen (TN) followed by a strong acid digestion of the sample with sulphuric acid and potassium dichromate^[13]. The grain size analysis was conducted by using a Mastersizer-2000 laser grain size instrument. Concentrations of elements including total phosphorus (TP) were determined by ICP-AES.

(ii) Analyses of water samples. Water samples were filtered through 0.45 μm mixed cellulose ester membrane and passed through prefilled cation exchange resin columns. Sample ammonium was desorbed with 2 mol/L hydrochloric acid. The eluate was water steam distilled using a Kjeldahl distillation apparatus and trapped in a solution of sulfuric acid then evaporated over a water bath before the measurement of nitrogen isotopic composition on the mass spectrometer. The determination of TN, TP and chlorophyll

a (Chl-a) concentration followed the methods of Jin Xiangcan and Tu Qingying^[13].

3 Results

3.1 Core lithology, grain size and chronology

Core ML was composed of dun mud with shell fragments mixed at a depth of 23–7 cm (Fig. 2). The particles of silt size (16–64 μm), fine silt (4–16 μm) and clay (<4 μm) accounted for about 35%, 40% and 18%, respectively. <4 μm size fraction of the sediments little changed upcore. The profile of medium grain size showed the same general trend with that of 16–64 μm size fraction: the grain size was steady coarser at 52–25 cm and became finer above that depth then remained little changed over the top 12 cm. Rose *et al.*^[14] employed multiple radioactive isotopes to date the sediment cores collected from Meliang Bay. The core dating results showed a mean accumulation rate of 0.30 $\text{g}\cdot\text{cm}^{-2}\cdot\text{a}^{-1}$ (0.41 $\text{cm}\cdot\text{a}^{-1}$) between 1952 and 1986, increasing during 1987–1998 to 0.52 $\text{g}\cdot\text{cm}^{-2}\cdot\text{a}^{-1}$ (0.88 $\text{cm}\cdot\text{a}^{-1}$). Core ML was taken from the same site as their core, with minor sediment disturbance. Thus dates were obtained for core ML by analyzing its grain size^[15] by using the results from Rose *et al.* as reference points (Fig. 2).

3.2 The depth profiles of isotopic compositions and concentrations of TOC and TN, C/N and TP concentration

As shown in Fig. 3, $\delta^{13}\text{C}$ of TOC and $\delta^{15}\text{N}$ of TN in core ML (Fig. 3) ranged from –27‰ to –20‰ and 3‰ to 12‰, respectively. The C/N mass ratio had a narrow range between 8.3 and 10.5. According to the variations in isotopic compositions of organic carbon and nitrogen together with TOC, TN and TP concentrations and C/N ratio, the section could be divided into three segments. At 52–30 cm TOC and TN concentrations and C/N ratio all decreased significantly, reaching the minima, whilst other proxies changed little. At 30–12 cm $\delta^{13}\text{C}$ values of sedimentary OM and C/N ratio both tended to decrease, $\delta^{15}\text{N}$ values showed a slow but fluctuating decline, which coincided with an overall increase in TOC, TN and TP concentrations. Above the depth of 12 cm all proxies

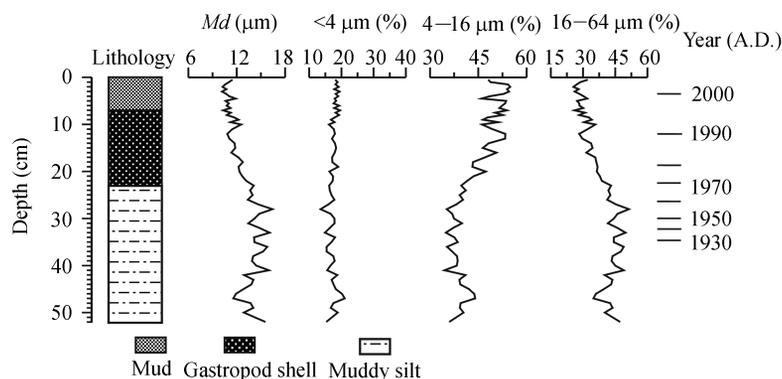


Fig. 2. Strata, grain size profiles for core ML. Data are shown on a sediment depth axis whilst the corresponding chronology is given on the right.

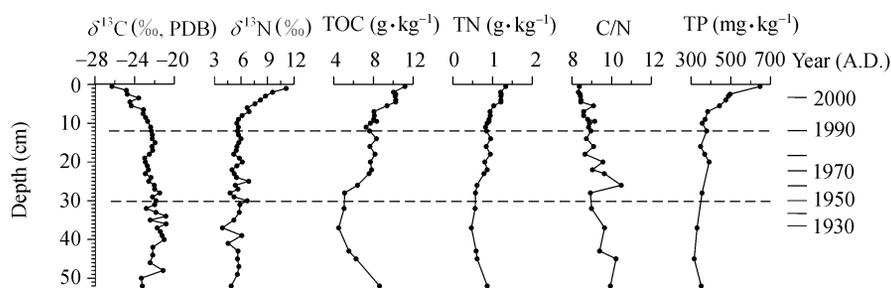


Fig. 3. The depth profiles of isotopic compositions and concentrations of TOC and TN, C/N and TP concentration in core ML.

varied markedly. The $\delta^{13}\text{C}$ values dropped to a minimum as the $\delta^{15}\text{N}$ values increased to a maximum at the top of the core. Over the length of the segment, sediments displayed a $\delta^{13}\text{C}$ range of 4‰ and $\delta^{15}\text{N}$ of 5.5‰. There was a good inverse correlation between $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ ($R = -0.924$). A drastic increase up to the uppermost was observed in the concentration of TOC, TN and TP, whilst there was a consistent trend of declining C/N ratio, reaching its lowest value of 8.3 in surface sediment.

3.3 The depth profile of elemental concentrations

Element concentrations in Taihu Lake sediments are presented in Fig. 4. There were two turning points at the depths of 30 cm and 12 cm respectively, which corresponded to the profiles of grain size, isotopic compositions and concentrations of TOC and TN. The concentrations of all elements but Sr, Na and Co were constant below 30 cm and then increased between 30 and 12 cm. The concentrations of heavy metals, particularly Zn, Pb, Cu, Ni and Cr were characterized by a rapid increase above 12 cm. Sediments displayed a fluctuation in the concentration of Ti and Sr at the

same segment. A negative correlation occurred between Fe and Mn on top of the core.

3.4 Stable isotopes of carbon and nitrogen of aquatic plants and ammonium and water chemistry

$\delta^{15}\text{N}$ values of NH_4^+ collected from various sites ranged from 6.2‰ to 33.09‰ as listed in Table 1, which were higher than 12‰ except the values of East Taihu Bay and within the enclosure of Meiliang Bay in July. $\delta^{15}\text{N}$ of NH_4^+ and hydrochemical parameters of East Taihu Bay showed lower values than those of Meiliang Bay. A marked decline of $\delta^{15}\text{N}$ of NH_4^+ was observed inside the enclosure of Meiliang Bay from May to July with a steep monthly difference of more than 10‰, which corresponded with a similar reduction in the concentrations of hydrochemical parameters (except TP) at the same site. The isotopic variation between surface and bottom waters within the enclosure at each month was less than 2‰. There was similar variation between $\delta^{15}\text{N}$ of NH_4^+ and TP outside the enclosure, peaking in June, when TN and Chl-a concentrations reached the lowest level.

The $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values of the main aquatic

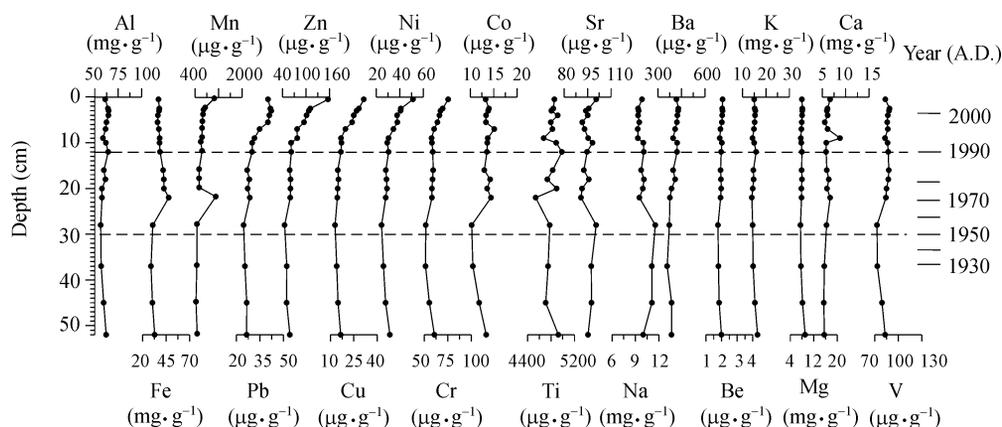


Fig. 4. The distribution with depth of element concentrations for core ML.

plants in Meiliang Bay and East Taihu Bay are listed in Table 2. $\delta^{13}\text{C}$ values of aquatic plants in Meiliang Bay (-27.33‰ – -19.62‰) appeared to be much lower than that in East Taihu Bay (-15.47‰), while $\delta^{15}\text{N}$ values displayed an opposite trend. $\delta^{15}\text{N}$ values of algae samples were in excess of 10‰ , which were enriched in ^{15}N relative to aquatic macrophyte.

4 Discussion

4.1 Environmental significance of geochemical and hydrochemical parameters

(i) TOC, TN and TP concentrations in sediments. TOC together with TN concentrations of lacustrine sediment can be used to infer in-lake primary productivity and reflect both aquatic and terrestrial signals. The high TOC and TN concentrations of these sediments suggest that primary productivity in the water column was high and large volumes of soil OM and plant debris. TP content of sediment is taken as a proxy of nutrient inputs to a lake from the surrounding watershed. A variety and intensity of human activities have greatly increased TOC, TN and TP concentrations in sediment since the beginning of human disturbance^[16]. Enrichment of these elements in surface sediment is directly related to industrial effluent, domestic sewage as well as fertilizer run off from agricultural fields.

(ii) Stable isotope compositions of sediments, biota and dissolved nutrients and water chemistry. Stable carbon and nitrogen isotopic compositions of OM in

lake sediments are proven to be valuable proxies for diagnosing the OM origins, and for describing past primary productivity and the nutrient utilization and cycle of the water column. The isotopic variation of the sedimentary organic carbon is used to trace different OM sources to lakes, especially in lakes dominated by allochthonous organic sources, due to the distinct isotopic signatures of various sources^[17]. In lakes dominated by anthropogenic OM, $\delta^{13}\text{C}$ values of submerged plant are much higher than those of phytoplankton that preferentially utilizes ^{12}C -enriched CO_2 in photosynthesis. Submerged plants usually access two sources of carbon: dissolved CO_2 and HCO_3^- , but the ratio of HCO_3^- to CO_2 is closely associated with water chemistry^[18]. However, when the availability of dissolved CO_2 ($\delta^{13}\text{C} = -7\text{‰}$) is limited and lake algae begin to use dissolved HCO_3^- ($\delta^{13}\text{C} = 1\text{‰}$) as their source of carbon, their isotopic compositions are higher than that of land plants. In other cases, delivery of large amounts of isotopically light soil dissolved inorganic carbon (DIC) to a lake can lead to in-lake production of isotopically light algal OM. Phytoplankton and C_3 land plants usually have overlapping carbon isotopic compositions (-37‰ – -24‰)^[18]. Application of nitrogen isotopic compositions and C/N ratio in sediment and present plants can help to identify the major OM origins to a lake. In general, $\delta^{15}\text{N}$ values of algae become heavier than those of land plants^[19]. The isotopic difference between various sources of nitrogen is roughly preserved in the $\delta^{15}\text{N}$ values of OM from algae (8.5‰) and from C_3 land

Table 1 $\delta^{15}\text{N}$ of NH_4^+ and hydrochemical parameters of Meiliang Bay and East Taihu Bay

Sampling location	Item	May		Jun		Jul		Aug		Sep
		Surface water	Bottom water	Surface water						
Inside the enclosure in Meiliang Bay	$\delta^{15}\text{N-NH}_4^+$ (‰)	31.31	33.09	18.86	20.51	6.79	6.2	a)	a)	a)
	TN ($\text{mg}\cdot\text{L}^{-1}$)		7.52		4.75		4.65		5.37	2.78
	TP ($\text{mg}\cdot\text{L}^{-1}$)		0.02		0.29		0.09		0.28	0.21
	Chl-a ($\mu\text{g}\cdot\text{L}^{-1}$)		47.03		43.50		23.66		48.03	52.21
Outside the enclosure in Meiliang Bay	$\delta^{15}\text{N-NH}_4^+$ (‰)	19.91	25.71	30.33	30.31	24.84	12.67	a)	a)	a)
	TN ($\text{mg}\cdot\text{L}^{-1}$)		10.71		6.44		13.80		4.53	2.72
	TP ($\text{mg}\cdot\text{L}^{-1}$)		0.09		0.32		0.12		0.18	0.22
	Chl-a ($\mu\text{g}\cdot\text{L}^{-1}$)		25.23		8.21		39.42		27.33	17.09
Platform at TLLER in Meiliang Bay	$\delta^{15}\text{N-NH}_4^+$ (‰)			25.09						20.56
	TN ($\text{mg}\cdot\text{L}^{-1}$)			4.95						1.73
	TP ($\text{mg}\cdot\text{L}^{-1}$)			0.10						0.08
East Taihu Bay	Chl-a ($\mu\text{g}\cdot\text{L}^{-1}$)			30.5						22.7
	$\delta^{15}\text{N-NH}_4^+$ (‰)			9.9				8.58	11.44	
	TN ($\text{mg}\cdot\text{L}^{-1}$)			1.06				2.75		
	TP ($\text{mg}\cdot\text{L}^{-1}$)			0.05				0.05		
	Chl-a ($\mu\text{g}\cdot\text{L}^{-1}$)			1.9				5.76		

a) indicates value below the detection limit ($< 0.2 \text{ mg N/L}$).

Table 2 $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of the main aquatic plants in Meiliang Bay and East Taihu Bay (‰)

	Inside the enclosure in Meiliang Bay		Outside the enclosure in Meiliang Bay	Platform at TLLER in Meiliang Bay	East Taihu Bay
	<i>Trapa bispinosa</i>	Cyanobacteria accumulations	Cyanobacteria accumulations	Cyanobacteria accumulations	<i>Vallisneria spiralis</i>
$\delta^{15}\text{N}$	6.59	16.79	13.16	14.16	6.34
$\delta^{13}\text{C}$	-27.33	-22.14	-19.62	-21.11	-15.47

plants (0.5‰)^[20]. Thus the clear isotopic distinction between aquatic plants collected from Meiliang Bay and East Taihu Bay suggested that the preponderant types of plants in these two lake areas were different (Table 2). OM from lake algae has C/N ratios that commonly present between 4 and 10, whereas vascular land plants create OM that usually has C/N ratios of 20 or greater. The proportions of sedimentary OM that originate from these two general sources can consequently be distinguished by their characteristic C/N ratios^[21,22].

Changes in phytoplankton productivity and species composition can strongly influence the $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values of sediment. A change or opposite change in the dominant phytoplankton group from N-fixing cyanobacteria ($\delta^{15}\text{N}$ close to 0‰) to non N-fixing cyanobacteria can be inferred from shifts in nitrogen isotopic composition of sediment. N-fixing blue-green algae directly fix atmospheric N_2 to produce OM with a $\delta^{15}\text{N}$ value near 0‰ when dissolved inorganic nitrogen (DIN) concentrations are consistently low^[23].

Phytoplankton preferentially takes up $^{12}\text{CO}_2$ and $^{14}\text{NO}_3^-$ to produce ^{12}C - and ^{14}N -enriched OM. However, this mechanism of selective uptake is restricted during periods of high abundance of phytoplankton and the availability of dissolved CO_2 and NO_3^- becomes diminished, such that phytoplankton has high isotopic values relative to land plants^[3,24,25]. In a closed system, Raleigh fractionation dictates that ^{13}C and ^{15}N fractionation decrease with increasing $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values of newly produced OM as HCO_3^- and NO_3^- is progressively depleted^[26-29].

When only a minor portion of available nitrogen is consumed, the nitrogen isotopic composition of the dissolved inorganic nitrogen (DIN) is never significantly altered. This is because P, and not N, commonly limits primary productivity in lakes. Under these conditions, $\delta^{15}\text{N}$ values of OM produced by phytoplankton become relatively constant. Yet surface nitrate concentrations and sedimentary nitrogen isotopic compositions can be used as a proxy to reconstruct nutrient utilization in lakes with large changes in nu-

trient inputs and primary productivity^[1]. Due to a general decrease in nutrient concentrations and isotopic fractionation in highly productive lakes^[26–29], DIC and DIN are utilized unselectively by phytoplankton, resulting in its positive carbon and nitrogen isotope excursions^[30,31]. Stable carbon and nitrogen isotopic values of phytoplankton-derived OM rise in response to elevated primary productivity and thus a positive relationship occurs among sedimentary $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values^[32].

This interpretation, however, is not consistent with other situations where a negative relationship between them is observed. High inputs of external nutrients from domestic sewage, industry and agricultural runoff to a lake will alter the $\delta^{15}\text{N}$ values of DIN in the water column and cause a subsequent change in sedimentary $\delta^{15}\text{N}$ values^[1]. Nitrogen fertilizer has a large range of $\delta^{15}\text{N}$ values, which is much lower than those of human and animal waste. Increased use of fertilizer would result in a decrease in $\delta^{15}\text{N}$ of composition in the sediment^[33]. NH_4^+ and NO_3^- derived from human and animal waste are enriched in ^{15}N ($\delta^{15}\text{N} > 10\%$), as industrial runoff and human sewage show high $\delta^{15}\text{N}$ values ranging from 10% to 25%^[34]. In addition, water column denitrification in an anoxic condition will enrich the residual NO_3^- in ^{15}N ^[4]. Thus $\delta^{15}\text{N}$ of NH_4^+ can help to identify the contributions of nitrogen fertilizer and human and animal waste in sediments^[35].

Chlorophyll is necessary for photosynthesis in plants and the intensity of photosynthesis affects primary productivity. Chl-a may serve as a key indicator of primary productivity in lakes. We use Chl-a as proxy for algae productivity in Meiliang Bay because of its absence of vascular plants. As shown in Table 1, $\delta^{15}\text{N}$ values of NH_4^+ from May to September in Meiliang Bay except the value in July inside of the enclosure, were in excess of 12%, suggesting that the lake was profoundly influenced by industrial and human sewage. Inside the enclosure, $\delta^{15}\text{N}$ values of NH_4^+ over time showed similar trends to TN and Chl-a concentrations and failed to be consistent with TP concentrations, indicating that it was controlled mainly by algae productivity, not external nutrient loading.

Out-side the enclosure, the increase of $\delta^{15}\text{N}$ of NH_4^+ in accordance with TP concentrations reflected large external nutrient inputs. The $\delta^{15}\text{N}$ composition of NH_4^+ of surface water outside the enclosure was 12.07‰ higher than that of bottom water in July. This might indicate that degradation of sedimentary OM decreased the $\delta^{15}\text{N}$ composition of NH_4^+ of bottom water and consequently increased $\delta^{15}\text{N}$ values of residual OM^[30]. More positive nitrogen isotopic excursion might occur during denitrification under anoxic condition in surface sediments, as a consequence of oxygen depletion resulting from OM decomposition^[4]. Based on observed changes of bacteria biomass in surface sediments from Lake Taihu during various seasons, Liu Shuangjiang¹⁾ found that denitrifying bacteria were the dominant species during summer and autumn (during algae blooms). Both $\delta^{15}\text{N}$ of NH_4^+ and hydrochemical parameter values in East Taihu Bay were lower than those in Meiliang Bay, suggesting that the isotopic geochemistry at sediment-water interface of these two lake areas were entirely distinct from one another due to their different ecosystem types.

(iii) Element concentrations. Element distributions in lake sediments are profoundly influenced by sediment chemical composition, sediment grain-size, runoff inputs, and human activities. Alkaline earth metals such as Sr are rapidly corroded by water, whereas other metals are actively absorbed and complexed with OM, humus, colloid, and suspended matter in the water column, and then deposited at sediment. The affinities are so strong that most elements in sediment are hardly released into the water in a natural water system. The finer the grain size, the larger the specific surface area and the stronger the affinities, thus most metals are accumulated and enriched in fine sediments^[36]. The profile of heavy metals shows the same general trend with that of Al during natural deposition in a lake, whereas the variation in the concentration of some heavy metals is mainly controlled by changes in their sources^[37]. The increasing inflow of industrial and municipal sewage to a lake results in a particularly strong accumulation of anthropogenic heavy metals in sediments due to urbanization and industrialisation^[38]. In addition, it is concluded that

1) Liu Shuangjiang, Unpublished observations.

anthropogenic heavy metals like Pb buried in the sediments are derived from automobile tail gas and industrial waste gas^[39]. Therefore, vertical distribution of heavy metals in sediments can provide a record of pollution history for the overlying water column, which is significant to the study of water pollution caused by human activities^[40].

4.2 Eutrophication history of Meiliang Bay as recorded in sediment core ML

The sediment samples from core ML had $\delta^{13}\text{C}$ values of organic carbon between -27‰ and -20‰ and $\delta^{15}\text{N}$ values between 3‰ and 12‰ , similar to those of aquatic plant samples (from -27.33‰ to -19.62‰ for C and from 6.59‰ to 16.79‰ for N), and their C/N ratios were very low and displayed a narrow range between 8.3 and 10.5 (Fig. 2; Table 2), which suggested that the organic material is composed largely of aquatic plant material. Integrating multiple proxies from core ML had been shown to reconstruct the history of eutrophication in Meiliang Bay as follows.

(1) 52–30 cm (prior to 1950): Neither elemental nor isotopic records displayed significant change, together with coarser grain-size, minor clay minerals, suggesting a stable deposition in the lake. The falling TOC content and C/N ratio were associated with the coarser grain size and also indicated lower aquatic primary productivity.

(2) 30–12 cm (1950s–1990s): Rising TP and heavy metals content in contrast to little change in clay and Al contents reflected the progressive nutrient and element input due to human activities in the catchment. The sediments recorded a gradual change to lower $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$, while TOC and TN concentrations rose and C/N ratio fell over the same period. It suggested that the autochthonous OM was relatively enriched in ^{12}C and ^{14}N , as a consequence of the presence of abundant phytoplankton, enhanced aquatic primary productivity and the beginning of eutrophication.

(3) 12–0 cm (1990s to the present): An abrupt increase in Zn, Cu, Ni, Cr accompanied by stable grain-size indicated the excessive input of industrial sewage. Pb concentration increased, peaking at 4 cm, and then remained at high levels, which was the evidence for the contribution of both air and soil pollution.

The rapid increase in TOC, TN and TP was related to the increased nutrient loading and elevated primary productivity. The ammonium nitrogen of Meiliang Bay had $\delta^{15}\text{N}$ values of 6.2‰ – 33.25‰ as shown in Table 1, which was close to the range of industrial and domestic sewage and more heavier than that of fertilizer. The inverse relationship between $\delta^{15}\text{N}$ and C/N ratio suggested that the autochthonous OM was enriched in ^{15}N . Utilization of ^{15}N -enriched DIN by phytoplankton are probably one reason for the rising $\delta^{15}\text{N}$ trend, which indicated similar $\delta^{15}\text{N}$ values of sediment compared to algae were attributed to industrial effluents and domestic sewage (Table 2). Moreover, the uptake of $^{12}\text{CO}_2$ by the flourishing algae resulted in excursions to less negative $\delta^{13}\text{C}$ values in autochthonous OM, but not yet reaching hypereutrophic status characterized by excursions to more positive $\delta^{13}\text{C}$ values^[5]. The negative correlation between Fe and Mn may occur under chemical reducing conditions at the sediment-water interface. When dead algae sank in vast numbers and preserved into the sediment, their decomposition depleted the oxygen levels and led to anoxia at the sediment-water interface^[41]. Under these conditions, decomposition and denitrification probably had an impact on the increase in $\delta^{15}\text{N}$ of sediment OM. Shifts in carbon and nitrogen isotopic values in the section were thought to be a response to the increasing eutrophication in the lake.

The environmental change as recorded in $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values of sedimentary OM in Meiliang Bay during the past five decades showed synchronous response to hydroenvironmental monitoring data over a period of decades^[10]. According to these investigation data, water quality in Lake Taihu changed from class I–II in the early 1960s to class II–III in the early 1980s. Class III was mostly common in the lake until the late 1980s, whilst class IV and V characteristics were indicated in some parts. In the mid-1990s the water there was ranked as class IV. At present 83.5 percent of the lake is eutrophic, only East Taihu Bay and the central part of the lake is mesotrophic.

5 Conclusions

Stable isotopic signatures ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) from present plants in Lake Taihu provided information on

OM source dominated by aquatic plants and revealed the distinction of plant species composition and trophic status among different lake areas accompanied by shifts in $\delta^{15}\text{N}$ of NH_4^+ . Variations in $\delta^{15}\text{N}$ of ammonium and water chemistry from Meiliang Bay through time indicated that external nutrient input had significant impact on the lake environment. In particular, the enhanced discharge of ^{15}N -enriched industrial runoff and domestic sewage to the lake altered nitrogen isotopic composition of DIN in the water column. Thus an increase in abundance of algae during summer caused a negative excursion in $\delta^{13}\text{C}$ values and a positive excursion in $\delta^{15}\text{N}$ values of OM. Furthermore, a large amount of organic detritus sank down rapidly, and then led to anoxia in the surface sediments. The more positive excursion in $\delta^{15}\text{N}$ in sediments was a function of both the organic decomposition and denitrification within the sediment, which resulted in the inverse correlation between $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ in sediments and the similarity of N-isotopic composition between surface sediments and algae. Shifts in nitrogen isotopic composition in sediments suggested that the cycling process was still progressing. The profiles of carbon and nitrogen isotopic compositions of OM were in relative synchrony with other geochemical record and hydrochemical data in Meiliang Bay and thus successfully traced the history of eutrophication at the lake during the past five decades, which was subdivided into three sections: the less productive, oligo-mesotrophic lake with better water quality prior to 1950; the more productive, degraded lake resulting from increased nutrient and pollutant concentrations as a result of the expansion of human populations and activities (a transfer of agricultural practices such as aquatic animal culture to industry and city development) between the 1950s and 1990s, which represented the beginning of an eutrophication process; the more eutrophic lake with massive algae blooms since 1990, which was attributed to the discharge of a huge amount of industrial and domestic sewage under rapid industrialization and urbanization.

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