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A 60-year sedimentary record of natural and anthropogenic impacts on Lake Chenghai, China

Fengyu Zan^{1,2,3}, Shouliang Huo^{2,*}, Beidou Xi^{2,*}, Jingtian Zhang²,
Haiqin Liao², Yue Wang², Kevin M. Yeager⁴

1. School of Environment, Beijing Normal University, Beijing 100875, China. E-mail: zanfengyu@126.com

2. State Key Laboratory of Environmental Criteria and Risk Assessment, Chinese Research Academy of Environmental Science, Beijing 100012, China

3. College of Environmental Science and Engineering, Anhui Normal University, Wuhu 241000, China

4. Department of Marine Science, University of Southern Mississippi, Stennis Space Center, MS 39529, USA

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Abstract

Recent sediments from Lake Chenghai, China, were investigated at high temporal resolution to trace both natural and anthropogenic effects on the lake using total organic carbon (TOC), total nitrogen (TN), total phosphorus (TP), organic phosphorus (P_o), inorganic phosphorus (P_i) and organic carbon and nitrogen stable isotopes ($\delta^{13}\text{C}_{\text{org}}$ and $\delta^{15}\text{N}$) in a ^{137}Cs -dated sediment core. The results indicated that the sedimentary record covers the last 60 years, during which the lake had undergone apparent changes in nutrient sources and productivity in response to nutrient loading. Prior to the late 1980s, the nutrient contents in sediments mainly originated from algae and lake productivity was relatively stable. Since the late 1980s, increasing TOC, TN and TP concentrations together with the change of $\delta^{13}\text{C}_{\text{org}}$ and $\delta^{15}\text{N}$ suggested anthropogenic perturbations in nutrient loading and lake productivity. Endogenous nutrients derived from algae and anthropogenic inputs were two important sources of sedimentary nutrients. The anthropogenic nutrients mainly originated from the discharge of industrial wastewater and artificial cultivation of *Spirulina* after the middle 1980s, and domestic wastewater discharged from Yongsheng County since 1993.

Key words: stable isotope; C/N ratio; organic matter; lake productivity; anthropogenic impacts

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Introduction

Information on both the natural evolution and human impacts on lakes is of crucial importance in understanding the current state and future development of lake systems. Paleolimnological studies have employed stable carbon and nitrogen isotopes ($\delta^{13}\text{C}_{\text{org}}$, $\delta^{15}\text{N}$) with other sedimentary variables including total organic carbon (TOC), total nitrogen (TN) and total phosphorus (TP) concentrations, C/N ratio, and phosphorus fractions, to assess long-term changes in lake trophic status (Brenner et al., 1999; Neumann et al., 2002; Routh et al., 2004, 2007; Das et al., 2008). The combined use of elemental abundances and isotopic ratios in sediments can reveal histories of lake metabolism not afforded by short-term water column monitoring programs (Meyers, 1997).

The C/N ratio, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ are powerful indicators of paleoenvironmental conditions in lacustrine systems (Neumann et al., 2002), providing information on both biological productivity within and terrestrial inputs to lakes (Schelske and Hodell, 1991, 1995; Bourbonniere and Meyers, 1996; Brenner et al., 1999; Herczeg et al., 2001;

Lücke et al., 2003; Routh et al., 2004, 2007; Liu et al., 2010). In general, lakes tend to have high concentrations of TOC, N and P in sediments with increasing primary productivity and inputs of anthropogenic nutrients (Struck et al., 2000; Ruiz-Fernández et al., 2002; Neumann et al., 2002; Das et al., 2008). Moreover, increasing C/P and N/P ratios in sediment profiles are indicative of increasing anthropogenic inputs of nitrogen and phosphorus (Emeis et al., 2000).

Lake Chenghai (26°27'N–26°38'N, 100°38'E–100°41'E) is located in the center of Yongsheng County, Yunnan Province, Southwestern Plateau, China. The lake basin formed in the early Pleistocene by faulting, and the modern lake has a surface area of 77.22 km² with a mean depth of 25.7 m. A subtropical, highland monsoon climate prevails throughout the lake's watershed. The yearly average temperature is approximately 13.5°C, and the yearly rainfall and evaporation are 738.6 mm and 2040.3 mm, respectively (Wang and Dou, 1998). Some other important features of Lake Chenghai and its watershed are listed in Table 1. There has been no discharge from the lake since the late 17th century due to decreased water levels. There is no well-defined inflow channel discharging into Lake Chenghai. Water is supplied to the

* Corresponding author. E-mail: huoshouliang@126.com

Table 1 Features of Lake Chenghai and its watershed (Su and Dou, 1998)

Parameter	Value
Watershed area	228.9 km ²
Lake area	77.22 km ²
Lake volume	19.87 × 10 ⁸ m ³
Maximum depth	35.1 m
Average depth	25.7 m
Length	19.35 km
Maximum breadth	5.4 km
Average breadth	4.0 km
Elevation	1503 m a.s.l.

lake primarily by groundwater, precipitation and runoff. In 1993, the Xianren River (which flows through Yongsheng County) was diverted to discharge into Lake Chenghai to mitigate decreasing water levels. The entire watershed is comprised mostly of agricultural lands with a population of ca. 41,512. Lake water quality has deteriorated over the last twenty years, caused by increasing nutrient loads from the watershed. Nutrient loadings and lake water quality data do not extend back beyond the last twenty years. Information on the onset of anthropogenic eutrophication is critical to developing effective land use and hydrological management practices in the lake's watershed, and can only be traced using the sedimentary record in Lake Chenghai. In this study, stable C and N isotopes, combined with TOC, TN, TP, organic phosphorus (P_o), inorganic phosphorus (P_i), C/N, N/P and C/P ratios, were used to infer historic fluctuations in anthropogenic nutrient inputs and consequent changes in lake productivity.

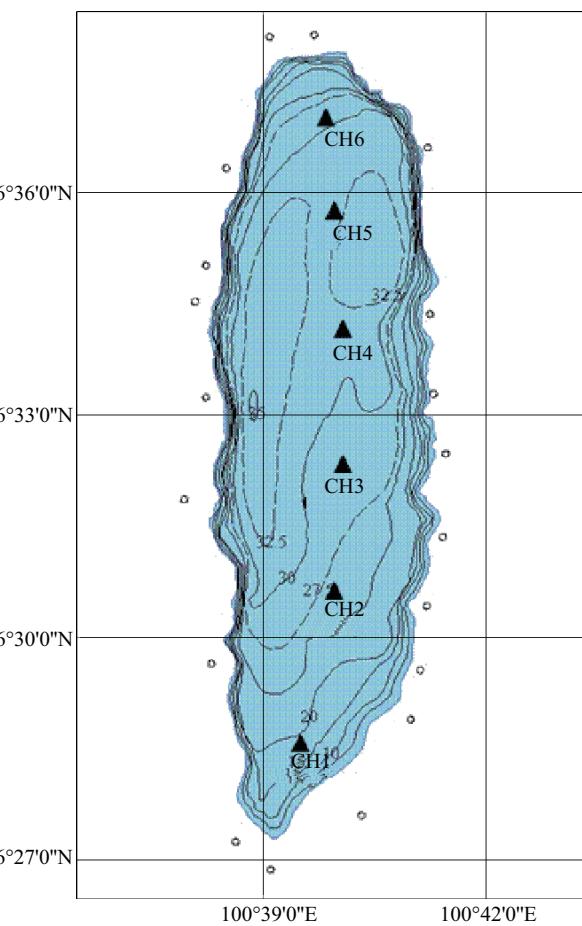
1 Materials and methods

1.1 Water quality

Water quality data (2002–2008) showed that lake water was weakly alkaline with a high hardness and that its total ion concentration was up to 1 g/L, approaching the lower limit ion concentration of salt lakes (Wan et al., 2005). Annual average surface water concentrations of TN, TP and chlorophyll-*a* were 400–600 µg/L, 20–30 µg/L, and 15–25 µg/L, respectively. In addition, abundant sunlight, favorable water temperatures and aquatic chemistry created an environment conducive for the proliferation of blue-green algae. The dominant species of algae included the *Anabaena*, the *Microcystis* and the *Oscillatoria*, indicating that Lake Chenghai was a moderately nutrient-enriched lake (Tao et al., 1999).

1.2 Sediment sampling and preparation

Core and surface sediment samples were collected in November of 2009, and all sampling sites were located well away from lake banks to avoid areas where sediments may have been disturbed by scouring or re-suspension (Fig. 1). Duplicate cores were obtained at Site CH5, at a depth of 32.5 m by a gravity coring sampler mounted to a 150 cm long PMMA tube with an 8 cm inner diameter. Sediment cores were cut at 1 cm intervals and then corresponding layers were mixed thoroughly. Surface

**Fig. 1** Location of sampling points and bathymetry of Lake Chenghai.

sediments were collected by a grab sampler at six sites (CH1, CH2, CH3, CH4, CH5, and CH6). The samples were put into sealed polyethylene tubes and temporarily kept at 4°C. After immediate transfer to the laboratory, samples were stored frozen below -20°C and then freeze-dried under -50°C by FD-1D-50 freeze-dryers. The weight of core sediment samples before and after freeze-drying was recorded to derive dry sediment density and water content data, used to calculate sediment porosity and mass accumulation rates for each core layer (Baskaran and Naidu, 1995). Dried samples were ground with an agate mortar and pestle to homogenize them and sieved to 100 mesh size for analysis.

1.3 Analytical methods

¹³⁷Cs activities were determined using gamma-spectrometry on a Canberra S-100 multi-channel spectrometer mated to a GCW3022 H-P Ge coaxial detector (efficiency 50%). The peak of ¹³⁷Cs used to determine activity was 661.6 KeV. A liquid standard was used and was supplied by the Institute of Atomic Energy, Chinese Academy of Sciences (Catalog No.: 7137, and Source No.: 586-26-2).

Total phosphorus (TP) was measured by combusting samples at 500°C (2 hr), followed by 1 mol/L HCl extraction (16 hr). The P_i concentration was determined by direct extraction with 1 mol/L HCl (16 hr). P_o concentrations were calculated as the difference between TP and P_i.

(Aspila et al., 1976). TN was measured using a Vario El elemental analyzer (Elementar Co., Germany). TOC was analyzed using a TOC analyzer (MultiN/C2100, Analytik Jena AG, Germany) after samples were treated with drops of 1 mol/L HCl to remove inorganic carbon. $\delta^{13}\text{C}_{\text{org}}$ and $\delta^{15}\text{N}$ were measured using an isotope-ratio mass spectrometer (Finnigan Delta^{Plus} XP) having a precision of < 0.1‰ for $\delta^{13}\text{C}$ and < 0.2‰ for $\delta^{15}\text{N}$. For $\delta^{13}\text{C}_{\text{org}}$ analysis, samples were pretreated with 1 mol/L HCl to remove inorganic carbon. Results were expressed in standard per mill (‰) units, relative to international standards-air (for N) or V-PDB (for C). During analysis, machine drift was checked with two inter-laboratory standard materials (glycine and cellulose for $\delta^{13}\text{C}$, glycine and urea for $\delta^{15}\text{N}$) run every three samples.

All samples were analyzed in triplicate and the results were expressed as their average. Experimental data were subjected to a standard analysis of variance technique appropriate for a factorial randomized block design. Whenever appropriate, treatment means were compared at the 5% level of significance using least significant difference.

2 Results

2.1 Dating of sediment core

The vertical profile of ^{137}Cs activity in sediment core CH5 is shown in Fig. 2, together with sediment chronology based on the sediment accumulation rate. The ^{137}Cs activity peak is well-defined at a depth of 34–35 cm, and a sub-peak of ^{137}Cs activity is present at a depth of 39–40 cm. This sub-peak may correspond to the initiation of above-ground nuclear weapons testing in the early 1950s (Robbins and Edgington, 1975). Therefore, it is reasonable to regard the 35 cm layer (mass depth of 19.24 g/cm²) as corresponding to 1964. The average sediment mass accumulation rate was determined to be 0.427 g/(cm²·yr), and the mean sedimentation rate was determined to be 0.795 cm/yr. The sediment chronology was based on the assumption that the sediment accumulation rate was constant.

2.2 Surface sediment characteristics

Data on TOC, TN, phosphorus content (TP, P_o and P_i), elemental ratios (C/N, N/P and C/P), and stable isotope ratios ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) of surface sediments from the six sites in Lake Chenghai are shown in Table 2. The bulk geochemical parameters showed only small variation in

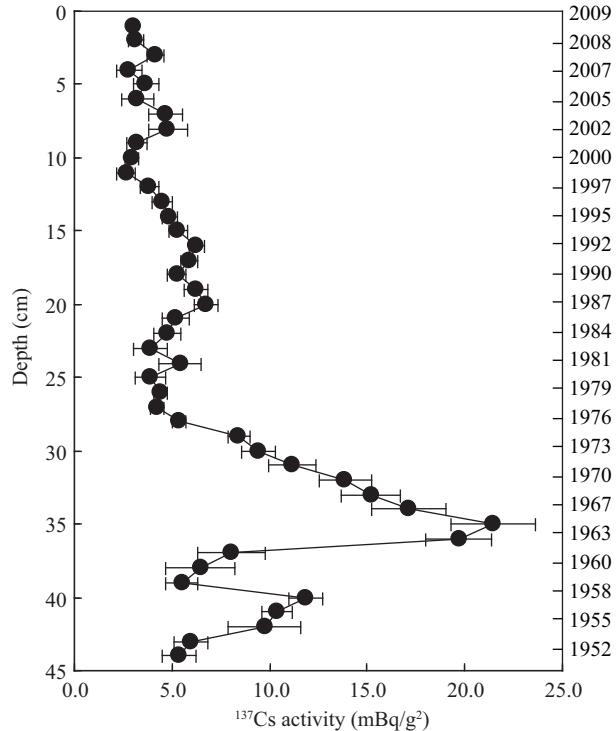


Fig. 2 ^{137}Cs vertical profile in sediment core from station CH5 (Corrected to sampling time).

general among the six sites, as implied by the coefficients of variation (CVs) between 2% and 23%. The six sampling sites were distributed from south to north with an approximately even spacing (Fig. 1). Consequently, these geochemical proxies in sediments indicated little difference from south to north in the lake.

2.3 Core sediments

2.3.1 Profiles of bulk geochemical parameters

The profile variations of bulk geochemical parameters (TOC, TN, TP, P_i, P_o, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) for core CH5 are shown in Fig. 3. The TOC concentration ranged from 8.16 to 54.29 mg/g, TN from 1.27 to 3.82 mg/g, TP from 0.54 to 0.78 mg/g, P_i from 0.51 to 0.36 mg/g, and P_o from 0.04 to 0.36 mg/g.

The TOC concentration was relatively constant (8.63 mg/g) prior to the late 1980s, and then increased smoothly to 54.29 mg/g until the present. Similar to the TOC profiles, the TN concentration was also relatively stable (1.31 mg/g) prior to the late 1980s, followed by a gradual increase to 3.82 mg/g at the present day. Compared to

Table 2 Total organic carbon (TOC), total nitrogen (TN), and total, organic and inorganic phosphorus (TP, P_o and P_i) content, and C and N stable isotope ratios ($\delta^{13}\text{C}$, $\delta^{15}\text{N}$) in surface sediments

Site	TOC (mg/g)	TN (mg/g)	TP (mg/g)	P _i (mg/g)	P _o (mg/g)	Molar C/N	Molar N/P	Molar C/P	$\delta^{13}\text{C}$ (‰)	$\delta^{15}\text{N}$ (‰)
CH1	22.99	1.69	0.62	0.47	0.16	15.87	6.04	95.79	-25.42	3.95
CH2	34.22	2.51	0.63	0.46	0.20	15.91	8.82	140.32	-26.22	4.63
CH3	23.7	1.87	0.6	0.47	0.14	14.79	6.90	102.04	-26.18	4.35
CH4	21.99	1.79	0.61	0.47	0.14	14.33	6.50	93.13	-26.98	4.16
CH5	29.09	2.19	0.6	0.47	0.13	15.50	8.08	125.25	-27.19	4.38
CH6	33.6	2.31	0.68	0.46	0.22	16.97	7.52	127.65	-26.04	4.64
Average	27.60 ± 5.48	2.06 ± 0.32	0.62 ± 0.03	0.47 ± 0.01	0.17 ± 0.04	15.56 ± 0.93	7.31 ± 1.03	114.03 ± 19.57	-26.34 ± 0.65	4.35 ± 0.27
CV (%)	20	16	5	2	23	6	14	17	2	6

CV: coefficient of variation.

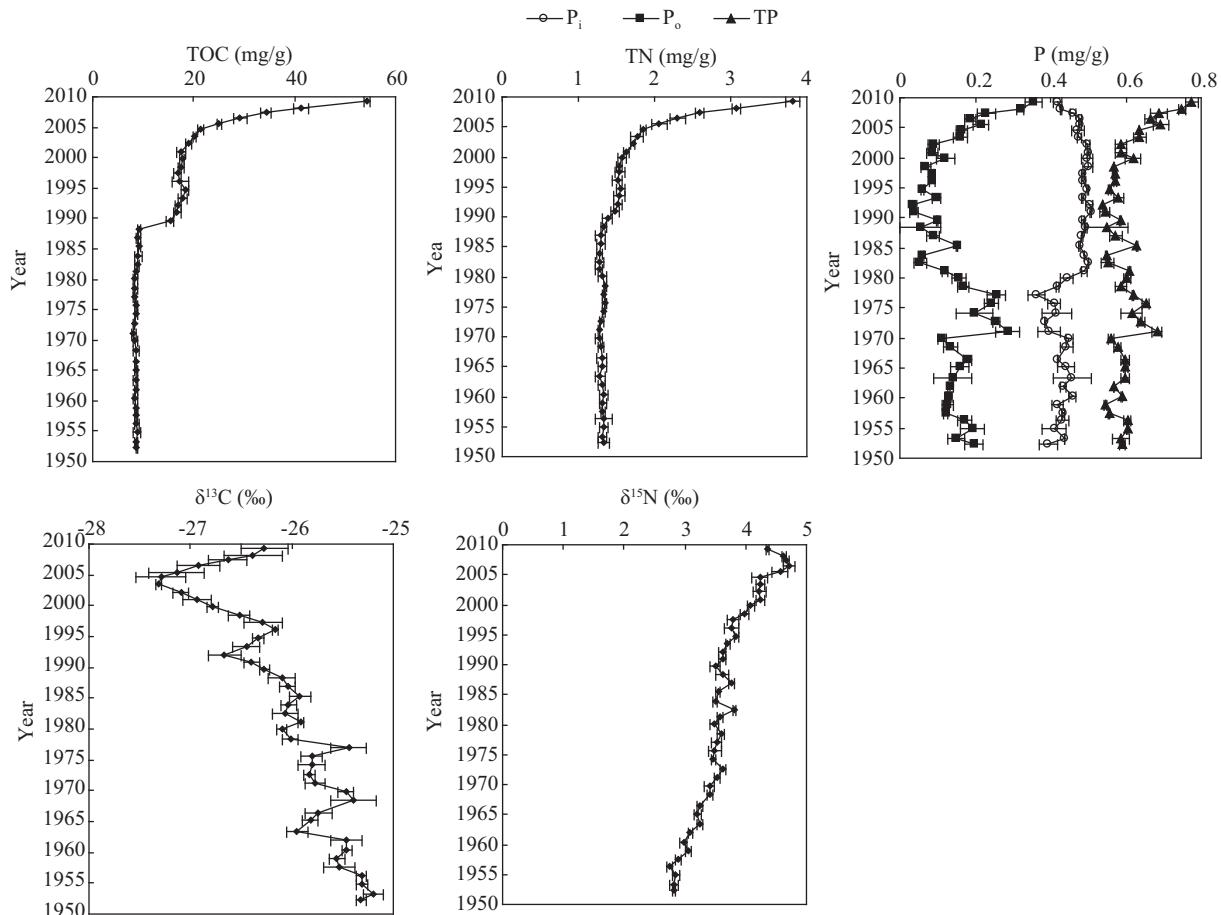


Fig. 3 Profiles of bulk geochemical parameters in sediments from Lake Chenghai.

TN and TOC, the trend of the variation in P (TP, P_i and P_o) concentrations fluctuated and showed little difference. Overall, TOC, TN and TP concentrations in the core showed age profiles progressively increasing in the most recent 20 years.

The $\delta^{13}\text{C}_{\text{org}}$ values ranged from $-27.31\text{\textperthousand}$ to $-25.20\text{\textperthousand}$ and a general trend of depletion of $^{13}\text{C}_{\text{org}}$ over time was observed, despite the existence of some oscillation. Conversely, the $\delta^{15}\text{N}$ values were slowly enriched in the most recent ca. 60 years, ranging from $2.75\text{\textperthousand}$ to $4.71\text{\textperthousand}$.

2.3.2 Profiles of atomic ratios of C/N, N/P, and C/P

The profiles of the atomic ratios of C/N, N/P and C/P for core CH5 range between 7 and 17, 4 and 11, and 31 and 181, respectively (Fig. 4). These ratios were relatively constant from the early 1950s to the late 1980s, and then a gradual increase followed until the present day. The changes of atomic ratios of C/N, N/P and C/P in the sediments indicate that changes in water quality occurred between two periods, the first being before the 1980s, and the second beginning in the late 1980s.

2.3.3 Profiles of nutrient fluxes

Nutrient fluxes for TP, TN and TOC in core sediments were calculated as follows (Cochran et al., 1998):

$$F_x = R_x \rho_x C_x$$

where, F_x ($\text{mg}/(\text{cm}^2 \cdot \text{yr})$) is nutrient flux for the x th depth

interval; R_x (cm/yr) is the ^{137}Cs -derived sedimentation rate for the x th interval; ρ_x (g/cm^3) is the dry bulk density of the x th interval; and C_x (mg/g) is the nutrient concentration for the x th interval.

TOC flux ranged from 3.48 to 23.18 $\text{mg}/(\text{cm}^2 \cdot \text{yr})$, TN from 0.54 to 1.63 $\text{mg}/(\text{cm}^2 \cdot \text{yr})$ and TP from 0.23 to 0.33 $\text{mg}/(\text{cm}^2 \cdot \text{yr})$. The nutrient flux in the core showed profiles progressively increasing from relatively low fluxes before 1988 to higher fluxes since, likely reflecting an increase in nutrient inputs and primary production. The TOC and TN profiles are rather similar (Fig. 5) and increase smoothly from the sediment horizon corresponding to 1988 until the present, while the TP flux starts increasing notably from 1993 (Fig. 5).

3 Discussion

3.1 Nutrient distribution in surface sediments

The factories cultivating *Spirulina* are mainly distributed on the south bank of Lake Chenghai. Large quantities of wastewater are discharged into Lake Chenghai from these factories, which lack any wastewater treatment facilities. As a consequence, the trophic state index in the southern half of the lake was higher than the northern half of the lake according to the monitoring results from Dong et al. (2010). However, the distribution of nutrient concentrations in the surface sediments was not consistent with those in the water column (Dong et al., 2010). This can mainly

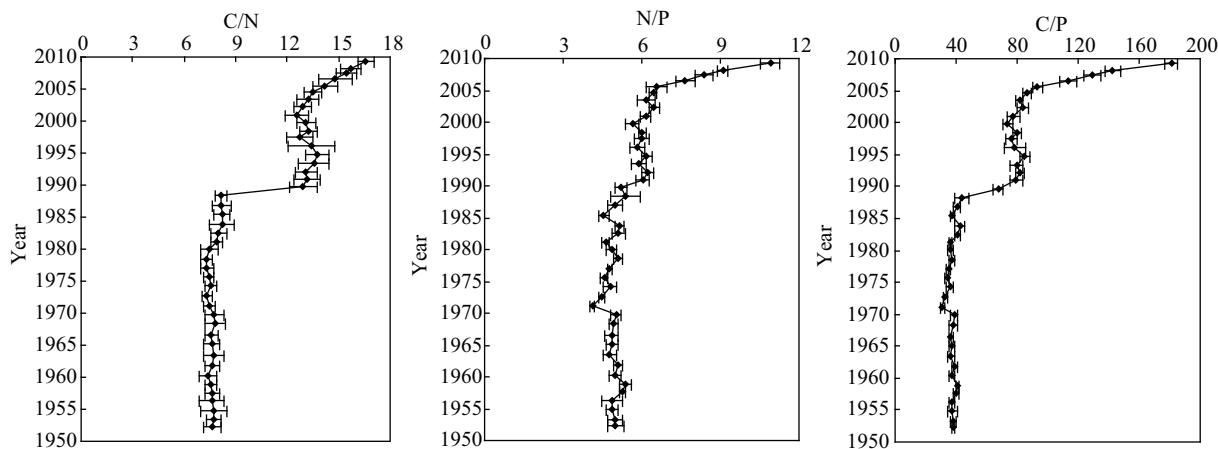


Fig. 4 Profiles of C/N, N/P and C/P ratios in sediments from Lake Chenghai.

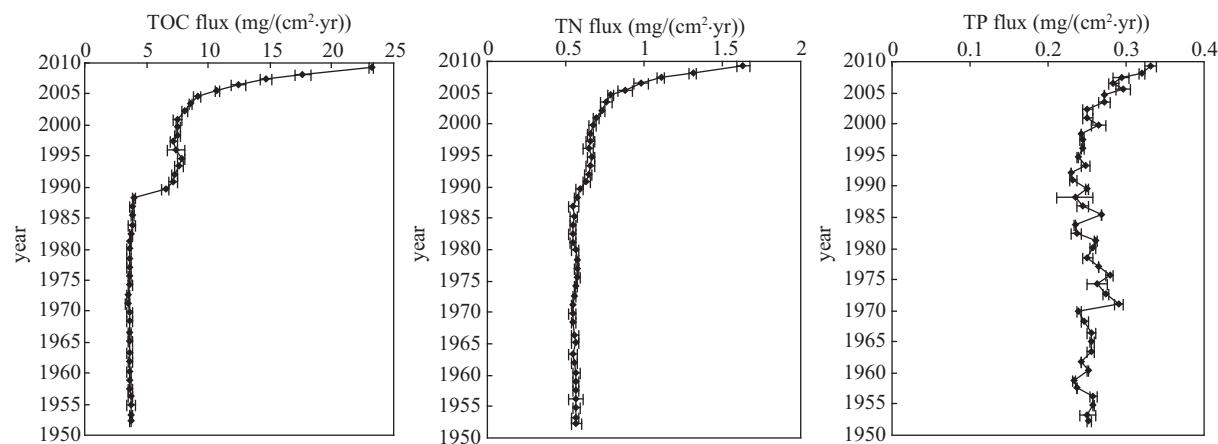


Fig. 5 Profile of nutrient fluxes in sediments from Lake Chenghai.

be attributed to strong lake currents resulting from complex bathymetry and special hydrodynamic conditions, resulting in a well-mixed water column (Dong et al., 2010). It is implied that there is a relatively homogeneous distribution of particle nutrients in the lake sediment in general.

3.2 Temporal trends for historical nutrient sources

The sediment records changes in historical nutrient sources to the lake. The vertical variation, particularly for elemental C, N and P as well as $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$, indicate that the input history of nutrients to Lake Chenghai contrasted over two periods, the first being before the 1980s and the second beginning in the late 1980s. The physical and chemical characteristics of the sediment record changes in response to changing watershed activities. Temporal shifts in nutrient accumulation in Lake Chenghai are probably attributable to a suite of human-induced watershed modifications.

C/N molar ratios, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values have been widely used to distinguish between algal and land plant origins of sedimentary organic matter (Meyers, 1994; O'Leary, 1988; Meyers and Lallier-Vergés, 1999). Algae typically have C/N ratios of 4–10, whereas vascular land plants have C/N ratios of 20 and greater (Meyers, 1994). C/N ratios below or slightly above 10 would be indicative of sedimentary organic matter from phytoplanktonic sources (Ruiz-Fernández et al., 2002). $\delta^{13}\text{C}$ has been used to distin-

guish between algal and land plant sources of sedimentary organic matter due to an average $\delta^{13}\text{C}$ for higher, terrestrial plants of $-27\text{\textperthousand}$ which is distinct from that of phytoplankton, ranging from $-17\text{\textperthousand}$ to $-24\text{\textperthousand}$ with an average of $-21\text{\textperthousand}$ (Das et al., 2008). $\delta^{15}\text{N}$ is an excellent indicator of N derived from human wastes (Ruiz-Fernández et al., 2002). It can be easily distinguished from typical planktonic $\delta^{15}\text{N}$ values, which range from 4\textperthousand to $10\text{\textperthousand}$ with an average of 6\textperthousand and terrestrial organic matter, that ranges from $-10\text{\textperthousand}$ to $10\text{\textperthousand}$ averaging 2\textperthousand (Ruiz-Fernández et al., 2002). $\delta^{15}\text{N}$ values for commercial fertilizers have been determined to vary from $-2\text{\textperthousand}$ to 4\textperthousand soil organic nitrogen nitrate from 3\textperthousand to 8\textperthousand and human and animal waste nitrate from $10\text{\textperthousand}$ to $20\text{\textperthousand}$ (Aravena et al., 1993; Ruiz-Fernández et al., 2002).

According to the criteria previously mentioned, it can be inferred that organic matter in Lake Chenghai mainly originated from algal sources prior to 1988, due to C/N ratio values of 7–8, and terrestrial sources after 1988 based on C/N ratio values of ca. 13–17 (Figs. 4 and 6). Sediment $\delta^{13}\text{C}_{\text{org}}$ values ranged from $-27.31\text{\textperthousand}$ to $-25.20\text{\textperthousand}$ in Lake Chenghai, indicating that the organic matter mainly originated from algae or C₃ land plants (Figs. 3 and 6). In the 36 years prior to 1988, Lake Chenghai sediments had relatively low $\delta^{15}\text{N}$ values, averaging ca. 3\textperthousand , indicating that N₂-fixing cyanobacteria were dominant in the lake (Fogel and Cifuentes, 1993; Meyers and Lallier-Vergés,

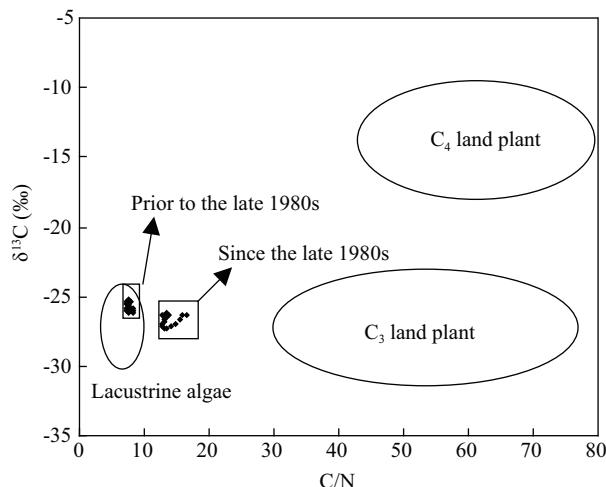


Fig. 6 Representative elemental and carbon isotopic compositions of organic matter from lacustrine algae, C₃ land plants, and C₄ land plants (Meyers, 1994; Meyers and Lallier-Vergés, 1999).

1999; Talbot and Lærdal, 2000). A slight 1‰ rise of δ¹⁵N values indicates an increase of non-N₂ fixing algae during this period. Moreover, the increase of δ¹⁵N values also can be explained as a result of contamination from sewage or agriculture wastes.

Non-point source pollutants from runoff may also be contributing to nutrient loads in the lake. According to Li et al. (2006), the entire watershed has high soil erosion rates and modulus reaching 61.05% and 784,000 tons/yr, respectively. However, the soil adjacent to the lake basin is generally barren and only contains 1% organic matter (Li et al., 2006). Since land uses in the watershed have not varied considerably over the previous twenty years (1985–2005) (Table 3), the elevation of TOC, TN and C/N ratios likely was not due to land use change and non-point source pollution input (Enters et al., 2006).

Anthropogenic point source pollution was likely responsible for these changes over the previous 20 years. The increase of C/P and N/P ratios in sediments are indicative of increased anthropogenic input of nitrate and phosphate (Emeis et al., 2000). The less variable C/P and N/P ratios in sediments from 1952 to 1988 suggest that anthropogenic influences did not increase nutrient loads to

Lake Chenghai during this period (Fig. 4). The increasing C/P and N/P ratios in sediments suggest progressively increasing anthropogenic inputs of nitrate and phosphate to the lake after 1988. In the middle 1980s, Lake Chenghai was found to be fit for the growth of a kind of blue algae –*Spirulina*, which is used as a dietary supplement and in health foods. From then on, development to support the cultivation of *Spirulina* occurred. Significant amounts of untreated cultivation wastewater containing organic matter and nutrients are discharged into the lake, which constitutes a main source of organic matter.

The water level of Lake Chenghai has gradually decreased since 1690, when it became a closed lake. The average rate of water level decrease was 0.137 m/yr during the 275 year period from 1690 to 1965, and 0.212 m/yr during the 18-year period from 1966 to 1984. In 1983, the establishment of a pumping station with an annual pump discharge of 9,000,000 m³ for farm irrigation aggravated the water loss problem, resulting in a faster water level reduction rate of 0.285 m/yr between 1985 and 1988. And in 1988, the water level even decreased 0.5 m. In 1993, the Xianren River was diverted to discharge into Lake Chenghai to mitigate water losses. The untreated domestic wastewater from the Xianren River then became another source of organic matter to the lake. However, the urban population was less than 10,000 in the Xianren River basin before 1997 and the quantity of untreated domestic wastewater was very small; subsequently, a large number of people immigrated and settled, the urban population increased to about 20,000 in 2000 and then rapidly increased to approximately 50,000 in 2009 in the Xianren River watershed.

Minimal changes observed down core in TOC, TN, C/N ratios and stable isotope compositions before 1988, uniformly point towards minimal diagenetic alteration, and therefore, to a fair preservation and storage of anthropogenic organic matter. Moreover, the isotopic and elemental compositions of C, N and P found in these sediments after 1988 were quite similar to those found in sediments enriched by wastewater-derived organic matter elsewhere (Ruiz-Fernández et al., 2002), indicating that a pollution source to Lake Chenghai is untreated wastewater.

Table 3 Land use in the basin of Lake Chenghai (1985–2005)

First-level	Category	1985		1995		2000		2005	
		Secondary	Area (km ²)	Proportion (%)	Area (km ²)	Proportion (%)	Area (km ²)	Proportion (%)	Area (km ²)
Farmland	Paddy	8.84	2.86	8.82	2.85	8.80	2.84	8.78	2.84
	Dry land	17.50	5.66	17.01	5.50	17.07	5.52	17.01	5.50
Woodland	Forest	82.19	26.57	82.19	26.57	80.13	25.90	80.31	25.96
	Shrubbery	49.82	16.11	50.13	16.21	50.09	16.19	50.10	16.20
Grassland	Open forest land	15.00	4.85	15.03	4.86	15.03	4.86	14.96	4.84
	High-coverage grassland	23.46	7.58	23.48	7.59	23.63	7.64	23.58	7.62
	Middle-coverage grassland	18.44	5.96	18.58	6.01	20.46	6.61	20.46	6.61
Water	Low-coverage grassland	1.07	0.35	1.07	0.35	1.07	0.35	1.07	0.35
	Graff	9.86	3.19	9.86	3.19	9.86	3.19	9.86	3.19
	Lake	77.20	24.96	77.20	24.96	77.20	24.96	77.20	24.96
	Pond	0.34	0.11	0.33	0.11	0.33	0.11	0.33	0.11
Industrial warehouse space, residential land, urban and rural land	Bottomland	0.21	0.07	0.21	0.07	0.21	0.07	0.21	0.07
	Urban land	0.45	0.15	0.46	0.15	0.46	0.15	0.47	0.15
	Rural residential land	3.36	1.09	3.37	1.09	3.39	1.10	3.39	1.10
	Other land	1.61	0.52	1.61	0.52	1.61	0.52	1.62	0.52

3.3 Change of lake productivity

Geochemical proxies (TOC, N, P, $\delta^{13}\text{C}_{\text{org}}$ and $\delta^{15}\text{N}$) can be used to reconstruct lacustrine palaeoproductivity and trophic conditions (Schelske and Hodell, 1991, 1995; Routh et al., 2004, 2007; Bourbonniere and Meyers, 1996; Herczeg et al., 2001; Lücke et al., 2003). The records of these proxies in sediments of Lake Chenghai revealed some variations in lacustrine productivity over two different periods.

Before 1988, Lake Chenghai had a relatively steady productivity level, as inferred from stable TOC and C/N (Fig. 3). The C/N ratio values of 7–8 indicate that the sedimentary organic matter of Lake Chenghai originated from algae, as discussed above. Furthermore, low C/P (40) and N/P (5) ratios indicate P enrichment. Data from the middle 1980s also indicated a low N/P ratio in water (N/P: 9.2) (Shan and Wang, 1989). The $\delta^{15}\text{N}$ values of organic matter originating from N_2 and non- N_2 fixing algae are ($0 \pm 2\%$) and 7% to 10% respectively (Fogel and Cifuentes, 1993; Talbot and Laerdal, 2000). Therefore N deficiency may cause abundant N_2 fixing algae growth in Lake Chenghai, resulting in low $\delta^{15}\text{N}$ (3‰ in sedimentary organic matter). Lake Chenghai likely had high primary productivity in the 40 years prior to the late 1980s, which is in accordance with the study of Wang and Qiang (1987), in which blue algae blooms occurred every year in the lake. This high productivity is in congruence with the lake's history, particularly its closing since 1690, high evaporation capacity, and gradual decrease in water level, resulting in a long hydraulic retention time and a high nutrient accumulation rate.

The data presented herein indicate that Lake Chenghai experienced high and relatively stable productivity during the period 1952–1988. Since the late 1980s, increasing TOC, N and P concentrations indicate a marked change in both lake productivity and nutrient loads. Since then, algal blooms have occurred not only in late spring and early summer, but also in winter (Dong et al., 2010). From 1985 to 2005, $\delta^{15}\text{N}$ values increased 1, showing a higher rate of increase than during the period 1952–1988. This was likely due to wastewater inputs, with a high $\delta^{15}\text{N}$ value (Aravena et al., 1993) and increasing primary productivity (Neumann et al., 2002). The oscillation of $\delta^{13}\text{C}_{\text{org}}$ during this period was likely linked to the $\delta^{13}\text{C}_{\text{org}}$ change of DIC available for algae and the input of organic matter from wastewater. The N and C stable isotopes were loosely coupled to lake trophic status owing to the effect of external input on Lake Chenghai, compared to other trophic state indicators.

4 Conclusions

The vertical distributions of TOC, TN, P, $\delta^{13}\text{C}_{\text{org}}$ and $\delta^{15}\text{N}$ in lake sediments record natural changes and anthropogenic influence on Lake Chenghai during the 57 years (1952–2009). The lake has undergone major changes in productivity and trophic state in response to nutrient loading from its watershed over this period. During the

period 1952–1988, the lake had not been significantly impacted by human activities and had relatively stable productivity as indicated by constant TOC and TN concentrations and TOC/TN ratios in the sediment profile. During this period, algae-derived organic matter dominated the sedimentary organic matter pool. From 1988 to 2009, significant changes in the geochemical proxies occurred, reflecting a progressive impact of anthropogenic influence on the lake. The lake nutrient loads and productivity were greatly enhanced during this period. The endogenous organic matter from algae was supplemented by allochthonous organic matter inputs, resulting in a larger sedimentary organic matter pool. The allochthonous organic matter was mainly derived from the discharge of industrial wastewater from the cultivation of *Spirulina* around the lake since the middle 1980s, and domestic wastewater from Yongsheng County via the Xianren River since 1993.

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References

- Aravena R M, Evans M L, Cherry J A, 1993. Stable isotopes of oxygen and nitrogen in source identification of nitrate from septic systems. *Ground Water*, 31(2): 180–186.
- Aspila K I, Agemian H, Chau A S Y, 1976. A semi-automated method for the determination of inorganic, organic and total phosphate in sediments. *Analyst*, 101(1200): 187–197.
- Baskaran M, Naidu A S, 1995. ^{210}Pb -derived chronology and the fluxes of ^{210}Pb and ^{137}Cs isotopes into continental shelf sediments, East Chukchi Sea, Alaskan Arctic. *Geochimica et Cosmochimica Acta*, 59(21): 4435–4448.
- Bourbonniere R A, Meyers P A, 1996. Sedimentary geolipid records of historical changes in the watersheds and productivities of lakes Ontario and Erie. *Limnology and Oceanography*, 41(2): 352–359.
- Brenner M, Whitmore T J, Curtis J H, Hodell D A, Schelske C L, 1999. Stable isotope ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) signatures of sedimented organic matter as indicators of historic lake trophic state. *Journal of Paleolimnology*, 22(2): 205–221.
- Cochran J K, Hirschberg D J, Wang J, Dere C, 1998. Atmospheric deposition of metals to coastal waters (Long Island Sound, New York U.S.A.): Evidence from saltmarsh deposits. *Estuarine, Coastal and Shelf Science*, 46(4): 503–522.
- Das S K, Routh J Roychoudhury A N, Klump J V, 2008. Elemental (C, N, H and P) and stable isotope ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) signatures in sediments from Zeekoevlei, South Africa: A record of human intervention in the lake. *Journal of Paleolimnology*, 39(3): 349–360.
- Dong Y X, Jin Y, Hu J Q, Guan Z G, He X X, 2010. Characteristics and origin and countermeasures of water bloom of Chenghai Lake in the winter. *Environmental Science Survey*, 29(3): 28–31.
- Emeis K C, Struck U, Leipe T, Pollehne F, Kunzendorf H, Christiansen C, 2000. Changes in the C, N, P burial rates in

- some Baltic Sea sediments over the last 150 years-relevance to P regeneration rates and the phosphorus cycle. *Marine Geology*, 167(1-2): 43–59.
- Enters D, Lücke A, Zolitschka B, 2006. Effects of land-use change on deposition and composition of organic matter in Frickenhauser See, northern Bavaria, Germany. *Science of the Total Environment*, 369(1-3): 178–187.
- Fogel M L, Cifuentes L A, 1993. Isotope fractionation during primary production. In: Organic Geochemistry Principles and Applications (Engel M H, Macko S A, eds.). Plenum, New York. 73–94.
- Herczeg A L, Smith A K, Dighton J C, 2001. A 120 year record of changes in nitrogen and carbon cycling in Lake Alexandrina, South Australia: C:N, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ in sediments. *Applied Geochemistry*, 16(1): 73–84.
- Li G X, Fang X J, Meng G T, Zhang Z H, Rui A M, Guo T Q, 2006. Soil condition analysis and application technology of forestation at sides of Chenghai Lake. *Journal of West China Forestry Science*, 35(2): 113–116.
- Liu E F, Shen J, Zhang E H, Wu Y H, Yang L Y, 2010. A geochemical record of recent anthropogenic nutrient loading and enhanced productivity in Lake Nansihu, China. *Journal of Paleolimnology*, 44(1): 15–24.
- Lücke A, Schleser G H, Zolitschka B, Negendank J F W, 2003. A lateglacial and Holocene organic carbon isotope record of lacustrine palaeoproductivity and climatic change derived from varved lake sediments of Lake Holzmaar, Germany. *Quaternary Science Reviews*, 22(5-7): 569–580.
- Meyers P A, 1994. Preservation of elemental and isotopic source identification of sedimentary organic matter. *Chemical Geology*, 114(3-4): 289–302.
- Meyers P A, 1997. Organic geochemical proxies of paleoceanographic, paleolimnologic, and paleoclimatic processes. *Organic Geochemistry*, 27(5-6): 213–250.
- Meyers P A, Lallier-Vergés E, 1999. Lacustrine sedimentary organic matter records of late Quaternary paleoclimates. *Journal of Paleolimnology*, 21(3): 345–372.
- Neumann T, Stögbauer A, Walpersdorf E, Stüben D, Kunzendorf H, 2002. Stable isotopes in recent sediments of Lake Arendsee, NE Germany: Response to eutrophication and remediation measures. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 178(1-2): 75–90.
- O’Leary M H, 1988. Carbon isotopes in photosynthesis. *Bio-science*, 38(5): 328–336.
- Robbins J A, Edgington D N, 1975. Determination of recent sedimentation rates in Lake Michigan using Pb-210 and Cs-137. *Geochimica et Cosmochimica Acta*, 39(3): 285–304.
- Routh J, Meyers P A, Gustafsson Ö, Baskaran M, Hallberg R, Schöldström A, 2004. Sedimentary geochemical record of human-induced environmental changes in the Lake Brunnsviken watershed, Sweden. *Limnology and Oceanography*, 49(5): 1560–1569.
- Routh J, Meyers P A, Hjorth T, Baskaran M, Hallberg R, 2007. Sedimentary geochemical record of recent environmental changes around Lake Middle Marviken, Sweden. *Journal of Paleolimnology*, 37(4): 529–545.
- Ruiz-Fernández A C, Hillaire-Marcel C, Ghaleb B, Soto-Jiménez M, Páez-Osuna F, 2002. Recent sedimentary history of anthropogenic impacts on the Culiacan River Estuary, northwestern Mexico: Geochemical evidence from organic matter and nutrients. *Environmental Pollution*, 118(3): 365–377.
- Schelske C L, Hodell D A, 1991. Recent changes in productivity and climate of Lake Ontario detected by isotopic analysis of sediments. *Limnology and Oceanography*, 36(5): 961–975.
- Schelske C L, Hodell D A, 1995. Using carbon isotopes of bulk sedimentary organic matter to reconstruct the history of nutrient loading and eutrophication in Lake Erie. *Limnology and Oceanography*, 40(5): 918–929.
- Shan Z G, Wang H X, 1989. The environment and protection of Chenghai. *Journal of Yunnan Normal University (Natural Sciences Edition)*, 9(2): 79–81.
- Struck U, Emeis K C, Vog M, Christamsen C, Kunzendorf H, 2000. Records of southern and central Baltic Sea eutrophication in $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of sedimentary organic matter. *Marine Geology*, 164(3-4): 157–171.
- Talbot M R, Lærdal T, 2000. The late Pleistocene-Holocene palaeolimnology of Lake Victoria, East Africa, based upon elemental and isotopic analyses of sedimentary organic matter. *Journal of Paleolimnology*, 23(2): 141–164.
- Tao W D, Xia F, Jing C Y, 1999. On environmental issues of Lake Chenghai and its management strategy. *Resources and Environment in the Yangtze Basin*, 8(2): 210–214.
- Wan G J, Chen J A, Wu F C, Xu S Q, Bai Z G, Wan E Y et al., 2005. Coupling between $^{210}\text{Pb}_{\text{ex}}$ and organic matter in sediments of a nutrient-enriched lake: An example from Lake Chenghai, China. *Chemical Geology*, 224(4): 223–236.
- Wang R N, Qian C Y, 1987. The blue-green algae in Chenghai Lake. *Journal of Yunnan University (Natural Science)*, 9(1): 87–88.
- Wang S M, Dou H S, 1998. Records of Chinese Lakes. Beijing Science Press, Beijing. 377–378.

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