RESEARCH ARTICLE

Origin and vertical variation of the bound fatty acids in core sediments of Lake Dianchi in Southwest China

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Abstract Based on the molecular distribution of bound fatty acid (BFA) compound classes in core sediments of Lake Dianchi combined with the compound-specific $\delta^{13}C$ values of the straight-chain BFAs, origin and vertical changes of organic matters in the sediments were investigated. The results indicated a significant change of BFA sources over the past 700 years. Contrast to the low concentrations of the terrestrial BFAs, the abundance of BFAs derived from the plankton/bacteria in the top sections (1944–recent) was more than 80 %. The increasing proportions of the branched and unsaturated BFAs in total fatty acids were closely correlated with the heavy eutrophication and the frequent algal blooms in the decades. Furthermore, the positive shift of $\delta^{13}C$ of C16 and C18 (~2‰) in the upper section might be an indicator of the excess phytoplankton productivity. However, it was found that the plankton/bacteria-derived BFAs were more easily degraded during the early diagenetic process. The special compound carbon isotopic compositions of the long straight-chain BFAs (C24 and C26) in the sediments showed a depletion of heavier $\delta^{13}C$ values (ca. −30‰) in the midsections (1559–1787), reflecting a relatively growing contribution of C3 plants to C4 plants or that C4 plant growth was inhibited in cold and arid climates during the period.

Introduction

Lake Dianchi (DC) (24°40′–25°02′ N, 102°36′–102°47′ E) is a plateau lake located in the southwest of Kunming City, Yunnan Province, China (Fig. 1). It is the sixth largest freshwater lake in China. The average depth of water in the lake is about 5 m, and the maximum depth is 8 m. The surface area of the lake is about 306 km². Historical records showed that the lake watershed had become a densely populated area since the sixteenth century. Due to the excessive population growth and the growing demands for cultivable lands, more and more farmlands were reclaimed around the lake, and the impacts of the cultivation on the lake ecosystem became more and more serious (Xiong et al. 2010). Over the past 30 years, rapid population growth in the basin and economic development had changed the land use in the basin tremendously, and then placed severe pressures on the lake system (Huang et al. 2007). Thus, DC provides a good example for the ecological shifts which were commonly found in many stressed shallow lakes in China (Neumann et al. 2002; Mao et al. 2008).

A recent literature review on pollutants and organic compounds in DC revealed that most studies were performed in surface sediments. In addition to surface sediments, sediment core can provide an excellent means of evaluating and reconstructing historical records. Many sedimentary records have shown that organic matter (OM) and lipids are useful geochemical markers associated with the changes of climate and environment, as well as the impacts of human on

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Fig. 1 Map of Lake Dianchi
showing coring site
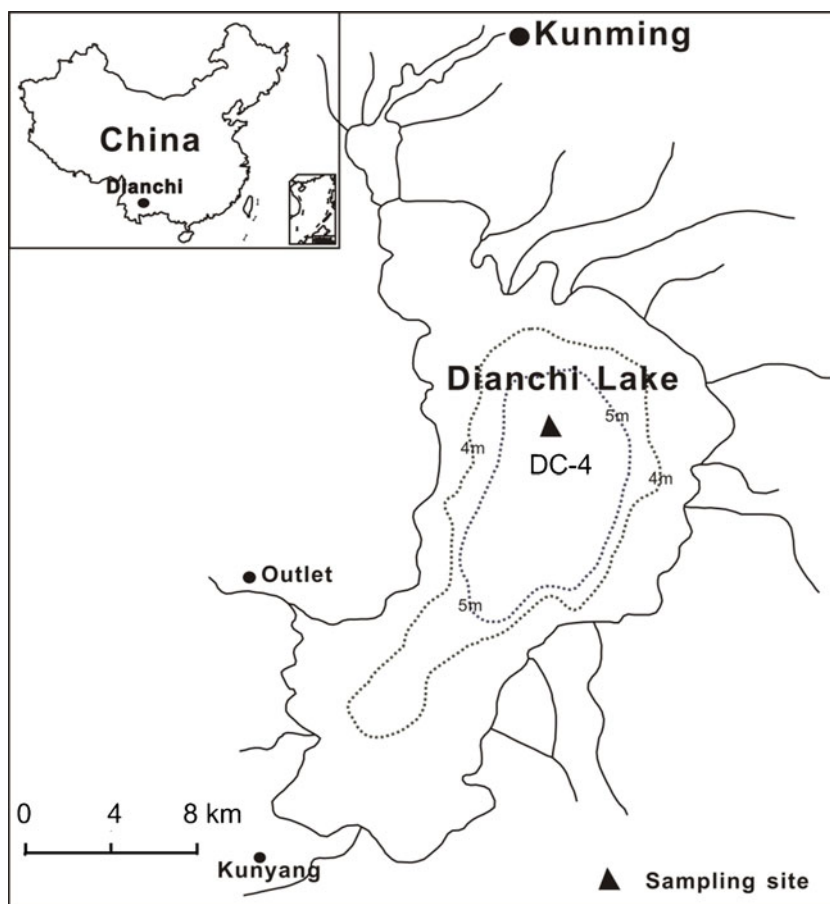
regional ecosystems at different times in the past (Birgel et al. 2004; Lindblom and Järnberg 2004; Xing et al. 2011). Among the various organic constituents which can be analyzed, fatty acids (FAs) were frequently considered because they had been proven to be valid/specific markers for plankton, bacteria, and higher plants (Rodier and Khalil 1982; Hu et al. 2006). Furthermore, in recent years, bound FAs (BFAs) were found to occur by chemically binding to the macromolecular structures of kerogen, asphaltenes, and the mineral matrix in sediments (Barakat and Rullkötter 1995). In a tightly bound state, BFAs are considered to be less susceptible to early diagenetic change than free FAs. Accordingly, they can be a very good indicator to a historical variation of OM (Lajat et al. 1990; Barakat and Rullkötter 1995). Stable carbon isotopic techniques are the most successful techniques for tracing the OM sources in sediments. The combination of distribution and lipid stable isotopic values has proven to be a powerful tool to estimate relative contributions of aquatic versus terrestrial sources and can be used to reveal changes of climate and environment (Tanner et al. 2010; Gómez-Gutiérrez et al. 2011; Tuo et al. 2011).

In this work, the origin of the OM (plankton, bacteria, and higher plants) was investigated based on the bulk parameters (total organic carbon (TOC), total nitrogen (TN), $\delta^{13}C$ values, and $\delta^{15}N$ values) and the distributions of biomarkers such as straight-chain, branched-chain, and unsaturated BFAs, as well as the compound-specific $\delta^{13}C$ values of straight-chain BFAs in the core sediments. The subject is to reconstruct the paleoenvironmental changes and the eutrophication history in DC.

Methods

Sediment samples

Sediment cores (DC-3 and DC-4) were simultaneously collected in one location on May 2006 from the center of the Lake using a piston-percussion corer fitted with 58-mm internal diameter Perspex tube. Its water depth was 6 m. When choosing the sample location, the site with weak dynamic environment which was conducive for the preservation of OM was considered. Figure 1 shows the sampling location. The core sediments were sectioned into 1-cm intervals immediately after collection and then freeze-dried. Sixteen subsamples from core DC-4 (63 cm in length) were selected for bulk and molecular organic geochemical analysis. Samples from core DC-3 were used for excess ^{210}Pb and ^{137}Cs dating determinations.

Elemental and stable isotope analyses

Samples for elemental and bulk stable isotope composition analysis were acidified with dilute HCl to remove carbonates before analysis. Concentrations of TOC and TN were determined on a CHNS Vario E1 III elemental analyzer. Replicate analysis of one sample ($n=3$) gave a precision of ±0.02 wt% for TOC and TN.

Carbon and nitrogen isotope analysis were conducted on a Thermo Finnigan Delta Plus XL mass spectrometer connected with a Flash EA 1112 elemental analyzer via a Finnigan MAT ConFlo III interface. δ^{13}Corg and δ^{15}N are reported as per mill relative to VPDB and air, respectively. The instrument analytical precision was 0.1 % for δ^{13}C and 0.2 % for δ^{15}N.

Extraction and fractionation of bound fatty acids

The BFA analytical procedure basically followed that described by Barakat and Rullkötter (1995). Sediment samples for molecular composition determination of OM were first Soxhlet extracted for 72 h with dichloromethane/methanol ($9:1 v/v$) to obtain the soluble fraction (free lipids). Residual sediment samples were saponified with 0.5 M KOH in methanol under reflux for 2 h to release bound lipids. The mixtures were centrifuged, and the supernatant was decanted. The neutral fractions were extracted with n-hexane/ether ($9:1 v/v$). Then, the samples were acidified to pH=1 by the addition of HCl. The acidic fraction, in which BFAs were contained, was extracted with dichloromethane. The acidic fraction was analyzed by gas chromatography–mass spectrometry (GC–MS), and prior to GC–MS analyses, the fatty acid fractions were methylated with saturated HCl–methanol by heating in an oven at 100 °C for 1 h to yield fatty acid methyl esters.

GC–MS analyses

GC–MS analyses were carried out using a Finnigan Platform II mass spectrometer coupled to a HP 6890 GC and a HP-5 fused silica capillary column (50 m long×0.32 mm inside diameter×0.25 μm film thickness). Temperature was programmed at 70 °C for 5 min, then increased by 3 °C/min to 290 °C, and held at 290 °C for 30 min. The quantification of BFAs was achieved by the integration of the peak areas in total ion current plot. Deuterated eicosane was used as an internal standard for quantification, and the response factor of the individual FAs relative to the standard was assumed to be 1.0 (Xiong et al. 2010).

Compound-specific δ^{13}C of BFAs

Compound-specific isotopic analyses were made using an Agilent 6890 Series gas chromatograph (GC) interfaced to a Finnigan Delta Plus XL isotope ratio mass spectrometer

through a combustion furnace. The oven-heating program was the same as that for GC analyses. CO_2 gas with pre-calibrated isotopic composition was used as the standard. The isotopic compositions of individual compounds were calculated by the integration of the mass 44, 45, and 46 ion currents (Merrit et al. 1994). Analyses were done in duplicates with standard deviations below 0.5‰.

Determination of ^{137}Cs and excess ^{210}Pb activity

^{137}Cs activity was determined following the methods described by Wan et al. (2005). Briefly, ^{137}Cs activity was assessed by gamma spectrometry on a Canberra S-100 multichannel spectrometer coupled with GCW3022 H-P Ge coaxial detector (efficiency 50 %). The peak of ^{137}Cs used to determine activity was 661.6 KeV. A ^{137}Cs standard was supplied by the Institute of Atomic Energy, Chinese Academy of Sciences (catalog no. 7137 and source no. 586-26-2). The highest ^{137}Cs activity was found at a depth of 8 cm, which can be regarded as 1963, most likely originating from nuclear explosion test in the atmosphere in 1963.

^{210}Po and ^{226}Ra were analyzed according to Wan et al. (1987). Briefly, the ^{210}Po activity in the sediments was analyzed by alpha spectrometry on a Canberra S-100 and multichannel spectrometer with a PIPS Si detector, and ^{226}Ra activity was determined by gamma spectrometry on a Canberra S-100 multichannel spectrometer mated to GCW3022 H-PR Ge well detector. Excess ^{210}Pb activity was obtained by subtracting ^{226}Ra activity from total ^{210}Pb activity, which was derived from ^{210}Po. According to the relatively high correlation between the core depths and unsupported ^{210}Pb activity, the constant sedimentation rates could be calculated using the constant activity model. However, ^{210}Pb has a half-life of 22.3 years; thus, this technology can only trace five to six half-lives (~100 years, at the depth of 14 cm). The sediment ages of 14–63 cm were based on the ^{210}Pb-derived sediment age of the upper section and near-linear increase of cumulative dry mass.

Results and discussion

Sources of OM

Bulk OM

TOC and TN contents in the core sediments ranged from 0.72 to 4.64 % and from 0.09 to 0.52 %, respectively. TOC contents increased abruptly (by approximately three times) across the 20-cm sediment horizon from an average content of 1.2±0.45 % ($n=10$) to 3.8±1.2 % ($n=6$). TN contents varied along with TOC in the upper 20 cm of the sediments,

which indicated a rapid increase in the supply of OM to DC during this period (~1800–2006).

TOC/TN, as a useful bulk indicator of the OM sources in paleolimnologic reconstructions, can be used to assess the relative contribution of aquatic and/or terrestrial components. The ratio of TOC/TN usually ranges from 5 to 8 in aquatic plankton and bacteria and from 20 to 100 in terrestrial OM (Meyers and Ishiwatari 1993; Lawrence 1994). Figure 2 shows that the TOC/TN ratios in the sediments of DC range from 9.7 to 12.6, which are between the characteristic values for aquatic and terrestrial OM, indicating a mixed source for the lake's sedimentary OM. Revised TOC/TN ratios are closer to that of the typical aquatic sources than that of the terrestrial sources considering preferential remineralization of N relative to OC over time (Goñi et al. 1998; Hu et al. 2009). Slightly different, the TOC/TN ratios in the section from 43 to 53 cm exhibit an increasing trend. The increasing TOC/TN ratios and the gradually increasing TOC concentrations downward the sediments reflected an

enhanced contribution of the terrestrial OM in the lake sediments during the period.

Straight-chain BFAs

In all samples analyzed, the straight-chain BFAs ranged from C12 to C28. C16 and C18 were the most abundant compounds of BFAs in all samples. Generally speaking, the short-chain homologues ($n \leq C20$) are widely found in multiple sources, including plankton, photosynthesis bacteria, and aquatic plants (Meyers and Ishiwatari 1993; Philip 2003). In the samples from 0- to 20-cm depth, the ratios of short-chain BFAs to long-chain BFAs ($\geq C21$) range from 8 to 10 and gradually decrease with increasing depth (Fig. 2). The long-chain BFAs which showed a strong even predominance were believed to be largely derived from waxes of higher plants (Logan and Eglinton 1994). The relatively slow and gradual enrichment of long straight-chain BFAs compared with short straight-chain BFAs below

Fig. 2 Vertical profiles of TOC, $\delta^{13}C$, TN, $\delta^{15}N$, TOC/TN, L/H, TAR, and C16:1ω7/C18:1ω7 in sediments of Lake Dianchi
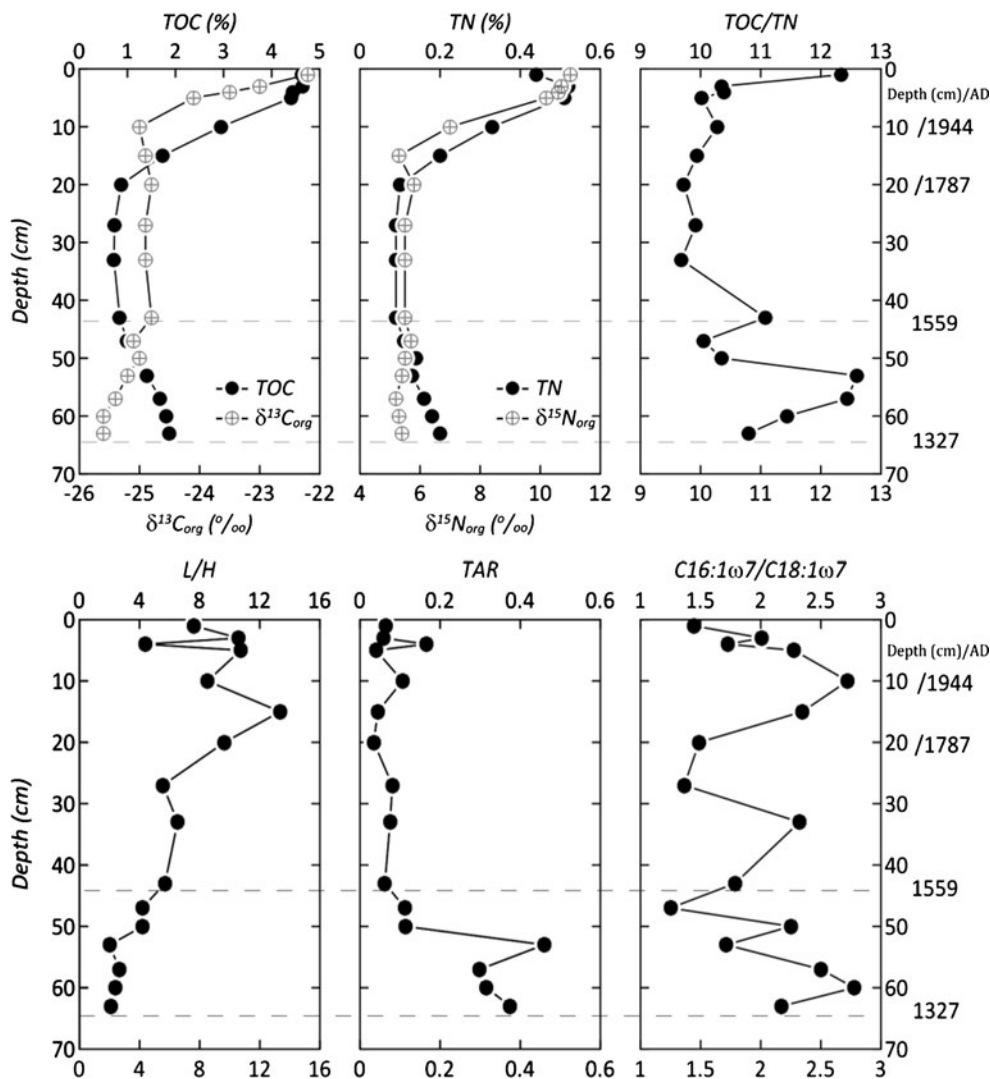
20-cm depth was likely due to the degradation of the short straight-chain BFAs.

One of the commonly used proxies to evaluate the relative importance of terrigenous and planktonic/bacterial sources was derived from a study on Lake Erie by Bourbonniere and Meyers (1996) who omitted the midchain biomarkers (C19–C22) to avoid the effects from aquatic higher plants (submerged and floating aquatic higher plants) and defined the terrigenous:planktonic/bacterial ratio (TAR) of the FAs as TAR=(C24+C26+C28)/(C14+C16+18).

Figure 2 shows that the values of TAR in the top 20 cm of the core are about 0.1 and maintained stable during the middle section. The terrestrial-derived BFAs showed an abrupt rebound at the lower section of the core (43–67 cm), with values between 0.4 and 0.6. Thus, although the compositional changes of BFAs in the core sediments were probably influenced by the degradation process, the organic biomarker profiles of the straight-chain BFAs also reflected a progressively increasing production of the terrestrial-derived OM in the lower sections (43–67 cm) in this study (Fig. 2).

Branched and unsaturated BFAs

In this study, some branched and unsaturated BFAs which can be assigned to dominant sources were detected. For example, the monounsaturated fatty acid 16:1ω7 and the polyunsaturated acids with even carbons (C18, C20, and C22) are considered as the most important sources from plankton (Meyers and Ishiwatari 1993). The odd-branched chain acids, especially the iso (i) and anteiso (a) acids i15:0, i17:0, a15:0, and a17:0, are the most abundant single component in bacteria (Wakeham and Beier 1991; Countway et al. 2007).

In general, 18:1ω7 is the dominant monounsaturated fatty acid in sediment. It may reflect the bacterial contribution to the total BFA pool. Differently, in planktonic materials, the content of 18:1ω7 is typically lower than that of its monounsaturated counterparts 16:1ω7 and 18:1ω9 (Kaneda 1991; Camacho-Ibar et al. 2003). Thus, compared to 16:1ω7 and 18:1ω9, the occurrence of the monounsaturated acid 18:1ω7 is in a relatively high proportion, which suggests the importance of bacterial sources of FAs in sediments. In this study, the 16:1ω7/18:1ω7 ratios in the sediment core are >1, and most values are between 1.5 and 2.5. A dominance of 16:1ω7 suggested that unsaturated BFAs had received a larger contribution from planktonic materials.

Totally, the changes of the relative abundance of terrestrial high plant, planktonic, and bacterial sources throughout the core (defined as the sum of the concentrations of the BFAs above assigned to each source. Long-chain BFAs 24:0, 26:0, and 28:0 are typically associated with terrestrial high plants. 16:1ω7, 18:1ω9, and 18:2ω6 in the sediments are typically associated with planktonic material, and bacterial origin is the sum of iso-15:0, anteiso-15:0, iso-17:0, and

anteiso-17:0) are shown in Fig. 3. This figure shows that the relative abundance of the plankton-derived BFAs (∑Plank) with the top 20 cm is 40–50 % and decreases to less than 30 % in the lower section. A similar trend is observed in ∑Bact. In contrast, at the top of the core, the concentrations of the terrestrial BFAs (∑Terre) show a lower abundance than ∑Plank do. However, the proportion of ∑Terre continues to increase in the lower 43 cm, and the highest values are found at the bottom of the core.

Bulk and compound-specific δ^{13}C and their implication for paleoenvironment change

Bulk δ^{13}C values have been widely used to distinguish aquatic and terrestrial OM. In the core samples, OM was isotopically the heaviest at the surface (δ^{13}C around −22‰) but then became rapidly enriched in the lighter isotope within 10 cm of the surface. Most samples had values of δ^{13}C around −24‰ in the middle section (43–20 cm; Fig. 2). Following the approach of Volkman et al (2000), an estimate of the relative proportions of aquatic and terrestrial OM was made using a linear-mixing ratio of aquatic and terrestrial components, and the end member δ^{13}C values of −19‰ (representing aquatic OM) and −26‰ (representing terrestrial material). Accordingly, the aquatic fraction clearly predominates in the surface sample (>60 %) and strongly decreases within the upper 20 cm. From 20 to 43 cm, the proportion of terrestrial OM remains virtually constant at about 50 %. Further down, the estimated terrestrial contribution is >55 % in the lower section. Actually, similar as the results from compositional variation of BFAs in the lower section (43–67 cm), the downward gradual
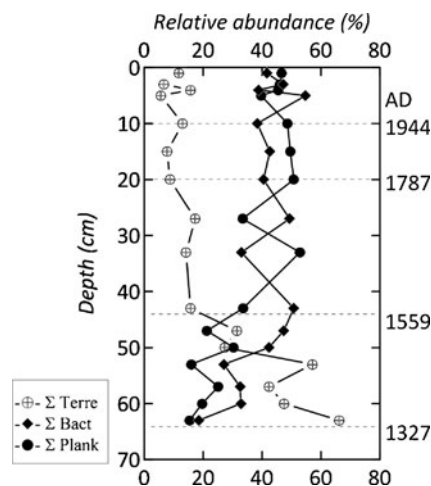

Fig. 3 Relative abundance of the different BFA sources in core DC-4. Long-chain BFAs 24:0, 26:0, and 28:0 are typically associated with terrestrial high plant ∑Terre. 16:1ω7, 18:1ω9, and 18:2ω6 in the sediments are typically associated with planktonic material ∑Plank, and bacterial origin ∑Bact is the sum of iso-15:0, anteiso-15:0, iso-17:0, and anteiso-17:0
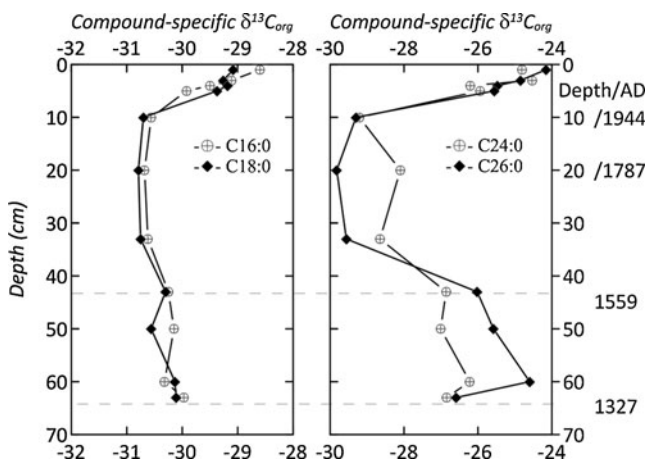
Fig. 4 Down-core variation of special compound stable carbon isotopes (C16:0, C18:0, C24:0, and C26:0) in the Lake Dianchi sediment core DC-4

depletion of heavier carbon isotope can also be explained by these two reasons: (1) a generally high input of the terrestrial OM and/or (2) the preferred degradation of the heavier $\delta^{13}C$ easily mineralizable planktonic and bacterial OM fraction, leaving behind the more refractory terrestrial components than the aquatic components (Freese et al. 2008).

Distributions of straight-chain BFAs in the core sediments showed abundances maximizing at C16 and C18. C16 and C18 are typical biomarkers for plankton or photosynthetic bacteria. In this study, C16 and C18 compound-specific carbon isotope values were in good agreement with each other and co-varied with bulk values ($R^2=0.76$, $n=16$). Our results indicated that plankton had significantly affected the bulk carbon isotopic values in the sediments in the past decades. The positive shift of $\delta^{13}C$ (bulk, C16, and C18) in the upper section might be due to the excess phytoplankton productivity. The phytoplankton preferentially removed dissolved $^{12}CO_2$ from water and left the remaining dissolved inorganic carbon depleted in ^{12}C (Hollander and MacKenzie 1991; Hodell and Schelske 1998). With the increase of lake productivity, the availability of $^{12}CO_2$ gradually diminished,

and a progressively increased fraction of the $^{13}CO_2$ was incorporated into OM. However, when productivity continues to increase to a certain extent, the availability of dissolved atmospheric CO_2 ($\delta^{13}C=-7‰$) was limited, and lake algae had to use dissolved HCO_3^- ($\delta^{13}C=1‰$) as their carbon source, resulting in a rapid change in their isotopic compositions.

Actually, one of the primary causes of eutrophication is an excessive concentration of plant nutrients originating from agriculture and/or industrial sewage. The $\delta^{15}N$ value of dissolved NO^{3-} used by algae is typically 7–10‰, which is greater than that of the atmosphere-derived N_2 used by the land nitrogen-fixing plants. The isotopic difference between the two sources of nitrogen is roughly preserved in the $\delta^{15}N$ values of OM from algae (8.5‰) (Peterson and Howarth 1987). In addition, $\delta^{15}N$ values can also be employed in investigating the sources and mechanisms of pollution, for example, typical $\delta^{15}N$ values ranging from −2 to 4‰ are for commercial fertilizers, 3–8‰ are for soil organic nitrogen nitrate, and 10–20‰ are for human and animal waste nitrate (Aravena et al. 1993). From the 10-cm depth, the $\delta^{15}N$ values increased rapidly upwards and reached 13.9‰ at the top of the core (Fig. 2), which indicated the rapid increase of anthropogenic nitrogen contribution in the last 50 years.

For long-chain BFAs, different photosynthetic plant types (C3 and C4) show different levels of ^{13}C depletion. This carbon isotopic heterogeneity between plant types is also observed within specific-compound classes, including straight-chain BFAs. Therefore, the compound-specific carbon isotopic analysis of BFAs C24 and C26 allows an estimation of the relative contributions from C3 and C4 plants. Rieley et al. (1993) found that the isotopic signature of C3 plants has a $\delta^{13}C$ value from −30 to −40‰, which is distinctly different from that of the C4 plants (ca. from −17 to −24‰). Cerling et al. (1993) reported that C3 vegetation predominates during the wet and cold periods, while C4 plants are more proliferated during the arid and warm periods. Figure 4 shows that C24 and C26 compound-specific

Fig. 5 Concentration variations of total straight-chain BFAs, branched and unsaturated BFAs with depth in the DC-4 core
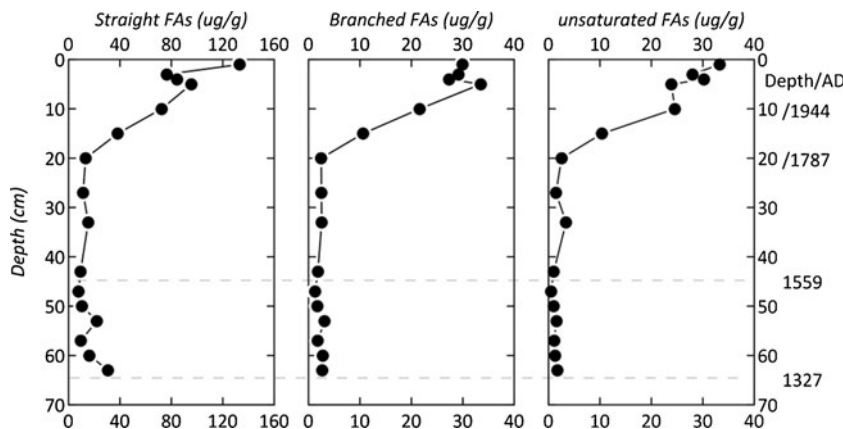
carbon isotope values co-vary. The lower section (63–43 cm) $\delta^{13}C$ values ranged from −24.5 to −26.5‰. $\delta^{13}C$ values were depleted in ^{13}C in the middle section (43–20 cm, ~−29.5‰). In the upper section, $\delta^{13}C$ values increased markedly from −29.5 to −24‰. Based on ^{210}Pb, ^{14}C chronology, and the measurements of mass susceptibility, $\delta^{13}C$, $\delta^{18}O$ isotope, grain size, mineral component, calcium carbonate, and organic substances, the climate variation during the past 700 years in the area of DC had a distinct period of 200 years with two high water levels and a low one (Chen et al. 2008). The climate in this area alternated with warm–dry periods and cold–wet periods (Chen et al. 2008). During the period of 1327–1559, the lake corresponded to high-water temperatures and high-lake levels. The lake was characterized with low-lake levels and cold and arid climates during the period of 1559–1787. From 1787 to the recent years, the temperature increased gradually with the increase of lake area. These three time periods correspond to 63–43, 43–20, and 20–0 cm in this study, respectively. Thus, it was suggested that cold temperature had a dominant control on the increasing growth of C3 relative to C4 plants in the middle section. Alternatively, Bird et al. (1994, 1998) found that transport of soil and high plant detritus (mainly C4 plants) during the wet season was from areas far away from the lake, but during the dry season, OM in the lake was dominated by inputs of C3 plants from the close lakeside.

Impact of diagenetic change

Total BFA concentrations decreased from 197.5 μg/g at the top to 17.7 μg/g at 20-cm depth in the sediment core, which was equivalent to a reduction of 11 %/cm. Total straight-chain BFA concentrations decreased from 133.0 μg/g at the surface to 12.7 μg/g at 20 cm in the sediment core, which was equal to 91 % reduction. The reductions of the branched and unsaturated BFAs within the top 20 cm of the sediment were 92 and 93 %, respectively. The straight-chain BFAs showed similar rapid degradation as the branched and unsaturated BFAs did (Fig. 5). This suggested that the significant change of molecular concentrations was involved in the early diagenetic transformations. In addition, the most abundant BFAs of the 30-identified BFAs were C16:0 (18–36 % of total BFAs), C18:0 (9–15 %), antiso-C15:0 (6–10 %), and C16:1ω7 (6–10 %) in the upper 20-cm sediments. With further increase in depth, long-chain BFAs were distinctly enriched compared to the other BFAs. In the deep sediment (>47 cm), C16:0, C18:0, C24:0, and C22:0 were the dominant species in the total BFA pool. The observed enrichment of long-chain BFAs with increasing sediment depth is an evidence for the selective preservation during early diagenesis (Stefanova and Disnar 2000).

Conclusion

This study showed that the relative abundance of the plankton-derived BFAs with the top 20 cm (~1800–2006) was closely correlated with the heavy eutrophication and the frequent algal blooms during this period. In addition, the isotope data (including $\delta^{13}C$, $\delta^{15}N$, and compound-specific $\delta^{13}C$ values of straight-chain C16 and C18 BFAs) supported this result. It was found that the positive shift of $\delta^{13}C$ (bulk, C16, and C18) in the upper section might be due to the excess phytoplankton productivity.

The proportion of the higher plant-derived BFAs continued to increase in the lower 43 cm, and the highest values were found at the bottom of the core. The relatively slow and gradual enrichment of long straight-chain BFAs compared with short straight-chain BFAs was likely due to the more degradation of the short straight-chain BFAs or increase input of terrestrial OM. The special compound carbon isotopic compositions of the long straight-chain BFAs (C24 and C26) in the sediments recorded a depletion of heavier $\delta^{13}C$ values (ca. −30‰) in the mid sections (20–43 cm, 1559–1787), reflecting a relatively growing contribution of C3 to C4 plants or that C4 plant growth was inhibited in cold and arid climates during the period.

Total BFA concentrations were decreased by 11 %/cm within the top 20 cm. The reductions of the branched and unsaturated BFA within the top 20 cm of the sediment were 92 and 93 %, respectively. The straight-chain BFAs showed similar degradation rate as the branched and unsaturated BFA did. This suggested that strong bacterial activities seemed to have a significant effect on the degradation of the plankton- and terrestrial-derived BFAs during the early diagenetic process in DC.

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