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Source characterization of sedimentary organic matter using molecular and stable carbon isotopic composition of *n*-alkanes and fatty acids in sediment core from Lake Dianchi, China

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HIGHLIGHTS

- Long-chain *n*-alkanes and FFAs are mainly derived from terrestrial sources.
- Short-chain *n*-alkanes and fatty acids are mainly derived from bacterial and/or algal sources.
- Long-chain BFAs are mainly derived from algal sources in hypereutrophic lakes.

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ABSTRACT

The distribution and compound-specific carbon isotope ratios of *n*-alkanes and fatty acids in a sediment core (63 cm) collected from Lake Dianchi were examined to investigate organic matter sources in the eutrophic lake. Fatty acids included free and bound fatty acids. The carbon isotope compositions of individual *n*-alkanes and fatty acids from Lake Dianchi sediments were determined using gas chromatography/isotope ratio mass spectrometry (GC–IRMS). The $\delta^{13}C$ values of individual *n*-alkanes (C_{16}–C_{31}) varied between −24.1‰ and −35.6‰, suggesting a dominance of ^{13}C-depleted *n*-alkanes that originated from C_3 plants and lacustrine algae. Fatty acids from the sediment extracts were analyzed for their abundances and carbon isotopic compositions. Molecular and isotopic evidence indicates that most of the short-chain fatty acids from Lake Dianchi sediment extracts are sourced from intense microbial recycling and resynthesis of organic matter. Long-chain free fatty acids are mainly derived from terrestrial sources. However, long-chain bound fatty acids are sourced from a combination of terrestrial organic matter, bacteria and algae, with the contribution from algal sources higher in the hypereutrophic stage.

1. Introduction

Lake Dianchi (24°51′ N, 102°42′ E), in central Yunnan Province, is a shallow, subtropical lake with a volume of 11.69×10^8 m^3 and a surface area of 297.9 km^2. The maximum and average depths are 6.5 and 2.9 m, respectively (Nanjing Institute of Geography and Limnology, 1989). The average annual rainfall is about 1000 mm. During the middle Holocene, the lake was surrounded by flourishing evergreen broad-leaved forest, co-existing or mixing deciduous broad-leaved forest and coniferous forest. However, due to climate changes and/or human activities, the vegetation cover in this area had been greatly reduced in the past 3800 years (Sun et al., 1986). Historical records showed that the lake watershed had become a densely populated area by the 16th century. The excessive population growth resulted in insufficiency of cultivable land and food supplies, so reclamation of farmland around lake can be traced back to 1509 AD (Xiong et al., 2010). The composition of fossil species indicates that Lake Dianchi was mesotrophic before 1958, then eutrophic from 1958 to 1985, and has been hypereutrophic since 1985 (Gong et al., 2009).

Lake sediments can act as reservoirs for natural and anthropogenic organic matter (OM). Sedimentary OM contains a diverse range of lipid compounds derived from organisms living within lakes and their catchments, with differences in lipid composition directly reflecting the different biota (Pearson et al., 2007). The relative contributions from these two general sources of OM to sediments are influenced strongly by algal productivity, land-plant productivity, and transport processes (Meyers, 1997).

Traditionally *n*-alkanes and fatty acids occur almost ubiquitously in lacustrine sediments and their distributions have been widely used to

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identify OM sources. Analyses of individual *n*-alkanes and fatty acids have been shown to be powerful for deciphering their origins in recent sediments. The difference in characteristic chain lengths of lacustrine and terrestrial plants have made the distribution of *n*-alkanes and fatty acids an effective biomarker tool for assessing biogenic sources of OM in terrestrial and lacustrine ecosystems. However, significant emersed or submerged/floating macrophytes and/or riparian–aquatic inputs introduce to the system sources with excursions to larger $\delta^{13}C$ and $\delta^{15}N$ values, making the effective determination of sources by *n*-alkane and fatty acid chain length data alone difficult to accomplish for such complex environments. In comparison with chain length signatures of *n*-alkanes and fatty acids, carbon isotopic signature can be used to better distinguish among sources (Sikes et al., 2009). Organic molecules derived from the same source generally have similar $\delta^{13}C$ values (Monson and Hayes, 1982; Rieley et al., 1991). Although *n*-alkanes and fatty acids can be biodegraded in the sediments, their $\delta^{13}C$ values are minimally affected by degradation, and thus there is no influence on the $\delta^{13}C$ signatures of these compounds (Tanner et al., 2010). Large variations in biomarker compound isotopic compositions are considered to be the result of different biomarkers coming from different sources (Rieley et al., 1991; Freeman et al., 1994; Ishiwatari et al., 1994; Kenig et al., 1994). Common higher plants can be classified into two isotopic categories according to their mode of CO_2 fixation (Smith and Epstein, 1971; O'Leary, 1981). C_3 plants incorporate CO_2 from the atmosphere by ribulose bisphosphate carboxylation (Calvin cycle) and show isotopic values ranging from −24 to −34‰ PDB. In contrast, C_4 plants fix CO_2 by phosphoenol pyruvate carboxylation (Hatch-Slack cycle) and show isotopic values ranging from −6 to −19‰. Algae have intermediate values of −12 to −23‰ (Lichtfouse et al., 1994).

In a previous study of the same core, Xiong et al. (2010) reported that evidence of eutrophication started to be seen in the upper 20 cm depth, and that human activities became a major factor influencing environmental changes at this stage. Vertical profiles of various organic geochemical variables in the upper 20 cm of sediments show evidence that primary productivity of the lake increased progressively and that the lake started to become eutrophic. Especially in the uppermost 10 cm, notable excursions to less negative $\delta^{13}C_{org}$ and $\delta^{15}N_{total}$, and high TOC concentrations have recorded an abrupt change in the lacustrine environment, suggesting that the lake entered a hypereutrophic stage.

As an extension of previous work, this study measured the carbon isotopic composition of *n*-alkanes and fatty acids in a sediment core from Lake Dianchi. Lake Dianchi sediment was selected for this study because its eutrophic characteristics have been well documented by many researchers (Xiong et al., 2010; Gao et al., 2005). This study contributes to a deeper insight into the composition, origin and cycling of aliphatic hydrocarbons and fatty acids, as well as biogeochemical processes, occurring in hypereutrophic Lake Dianchi.

2. Materials and methods

2.1. Sediment samples

Four sediment cores (DC-1, DC-2, DC-3 and DC-4) were collected on May 19th, 2006 from the center of Lake Dianchi using a piston-percussion corer fitted with 58-mm internal diameter perspex tubes, but only DC-3 and DC-4 were used for the analysis in this study. Fig. 1 shows the sampling location. The sediments were sectioned into 1-cm intervals immediately after collection, and then freeze-dried. Sixteen sub-samples from core DC-4 (length = 63 cm) were selected for bulk and molecular organic geochemical analyses. Samples from core DC-3 were used for excess ^{210}Pb and ^{137}Cs dating determinations (following the method described by Xiong et al., 2010).

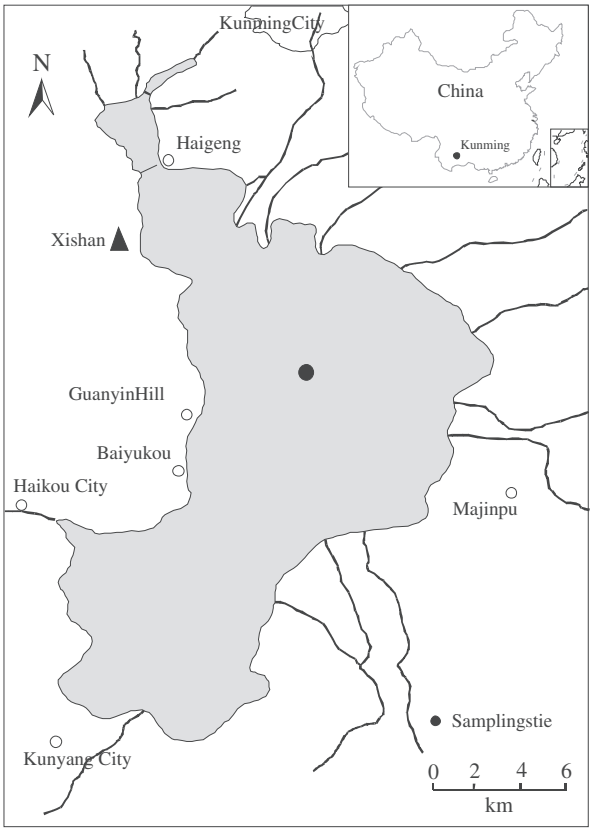

Fig. 1. Map of Lake Dianchi showing the coring site.

2.2. Laboratory methods

Sub-samples for elemental (TOC) and bulk stable isotope composition analyses were acidified with dilute HCl before analysis to remove carbonates. Concentrations of total organic carbon (TOC) were determined on a CHNS Vario E1 III elemental analyzer. Carbon isotope analyses 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. $\delta^{13}C_{org}$ values are reported as per mil relative to Vienna Peedee Belemnite (VPDB) standard. The instrument analytical precision for $\delta^{13}C$ is 0.1‰.

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). Sulfur was removed by addition of activated copper. The free lipids were further separated into three fractions by silica gel column chromatography using 1 g deactivated silica gel (70–230 mesh). The silica gel was activated at 110 °C for 3 h in Drying Oven, and deactivated using 3% distilled water. The column was eluted with 20 ml hexane, to obtain the aliphatic hydrocarbons (AHs), followed by alkanols and fatty acid fractions, which were successively eluted using 20 ml of 20% ethyl acetate in hexane and 20 ml of methanol, respectively. The extracted 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 decanted. The neutral fractions were extracted with *n*-hexane/ether (9:1 v/v). After acidification to pH = 1 by addition of HCl, acidic fractions were extracted with dichloromethane. AHs and fatty acids were then analyzed by gas chromatography (GC) and gas chromatography–mass spectrometry (GC/MS). Prior to GC and GC/MS analyses, free and bound fatty acids were methylated with saturated HCl-methanol by heating in an oven at 100 °C for 1 h, to yield fatty acid methyl esters (FAMEs).

GC analyses were performed with a Finnigan trace GC instrument equipped with a HP-5 fused silica capillary column (50 m × 0.32 mm × 0.25 μm). Nitrogen was used as carrier gas. The oven temperature was held isothermally for 2 min at 70 °C, then programmed to rise from 70 to 290 °C at 3 °C min^{-1}, and then held isothermally for 30 min at 290 °C. GC/MS analyses were carried out using a Finnigan Plateform II mass spectrometer coupled to a HP 6890 GC and a HP-5 fused silica capillary column (50 m × 0.32 mm × 0.25 μm). Temperature was programmed at 70 °C for 5 min, then at 3 °C min^{-1} to 290 °C, and held for 30 min at 290 °C. Quantification of AHs and fatty acids was achieved by 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 individual *n*-alkanes and fatty acids relative to the standard was assumed to be 1.0.

Carbon isotope analyses of individual compounds were performed on a VG Isoprime instrument (GV Instruments Ltd., UK). Separations were made using a HP-5 capillary column (50 m × 0.32 mm × 0.25 μm, Agilent Technologies, U.S.A.) with helium as the carrier gas, at a flow of 1.5 ml/min. The oven was programmed the same as the GC/MS analyses. The carbon isotope ratios for individual *n*-alkanes were calculated using CO_2 as a reference gas that was automatically introduced into the IRMS at the beginning and end of each analysis, and the data is reported in per mil (‰) relative to the VPDB standard. A standard mixture of *n*-alkanes (C_{14}, C_{16}, C_{18}, C_{20}, C_{22}, C_{25}, C_{28}, C_{30}, and C_{32}, provided by A. Schimmelmann of Indiana University, with a known isotopic composition was used daily to monitor the accuracy of measurements with the GC–IRMS system. Replicate analysis of this mixture showed that the standard deviation for each compound was less than 0.3‰. Reported isotopic data represented the arithmetic means of at least two repeated analyses, and the repeatability was less than 0.5‰.

The isotope composition of fatty acids was measured as methylated derivatives. The formation of fatty acid methyl ester from the fatty acid involved the addition of one methanol carbon with known isotopic composition per fatty acid molecule. The isotopic composition in the methyl group of esterified fatty acids was calculated and the values for fatty acids corrected with the following formula (Abrajano et al., 1994):

$$\delta^{13}C_{FA} = \left[(n+1)\delta^{13}C_{FAME} - \delta^{13}C_{CH3OH}\right]/n$$

where n is the carbon number of the particular fatty acids.

3. Results and discussion

3.1. Total organic carbon (TOC) and bulk $\delta^{13}C_{org}$ values

Vertical profiles of TOC and $\delta^{13}C_{org}$ values are shown in Xiong et al. (2010). Based on these bulk compositions, the core can be categorized into three sections. For the lower section (Section 1: 63–43 cm, 1184–1437 AD), the TOC concentrations range from 0.8 to 1.9%, and gradually increase downward. $\delta^{13}C_{org}$ values are slightly depleted in ^{13}C with depth, varying from −24.8‰ to −25.6‰. The bulk composition of OM remains relatively constant in the middle section (Section 2: 43–20 cm, 1437–1793 AD). TOC concentrations fall between 0.7 and 0.9%, and $\delta^{13}C_{org}$ values are between −24.9‰ and −24.8‰. However, in the upper section (Section 3: 20–0 cm, 1793–2006 AD), TOC concentrations increase markedly from about 1% to more than 4%. In addition, bulk isotope compositions of sediments display considerably positive shifts in $\delta^{13}C_{org}$ over the past 50 years, with $\delta^{13}C_{org}$ values varying from −25.0‰ to −22.2‰.

For the lowest part of the core (63–53 cm, 1184–1314 AD), a relatively high primary productivity is inferred by the relatively high TOC and slight depletion in ^{13}C. Subsequently, gradual decreases are recorded in TOC content, as well as relative enrichment in ^{13}C of OM. Thus, the sediment interval over the depth range of 63–43 cm (1184–1437 AD) basically reflects a period of environmental change. While natural factors were likely important in triggering the environmental change, there was apparently climatic cycle for every 200 years (Chen et al., 2008), the influence of human activities also appears to be quite significant. Sedimentary records in the 43–20 cm (1437–1793 AD) depth interval show no remarkable variation, indicating that the lake was relatively stable, Chen et al. (2008) reported that drought resulted in Lake Dianchi area was apparently becoming small from 1559 to 1787 AD. Lower TOC and less terrestrial inputs imply that Lake Dianchi was probably oligotrophic within this period. Oligotrophic lakes are generally heterotrophic (Verburg, 2007), meaning that more organic matter would be consumed in Lake Dianchi than is produced at this stage. In addition, the Suess effect on organic carbon in Lake Dianchi is likely reduced to a level that it is not necessary to correct for at the heterotrophic stage (O'Reilly et al., 2005).

Early eutrophication occurred in the depth interval of 20–10 cm (1793–1944 AD); at this stage, Lake Dianchi had become an autotrophic lake (meaning that more organic matter would be produced than is respired), as recorded by progressive increases in TOC concentrations. However, there are no obvious variations in $\delta^{13}C_{org}$. A slightly negative shift of $\delta^{13}C_{org}$ values can be explained by the Suess effect; that is, a shift to more negative $\delta^{13}C$ values of atmospheric CO_2 caused by fossil fuel combustion. The shift from preindustrial atmospheric isotopic values approaches −1.7% by 2004 (McCarroll and Loader, 2004), with two-thirds of the shift occurring since 1940 (Francey et al., 1999). Rapid eutrophication in Lake Dianchi since the 1950s is identified based on abrupt variations of TOC and $\delta^{13}C_{org}$ values in the lake sediments (Xiong et al., 2010). The dramatic changes in OM composition at this stage are attributed to enhanced algal productivity caused by an increase in nutrient supply, in turn, due to modern urbanization and industrialization. The positive shift of $\delta^{13}C_{org}$ in the upper section might be due to excess phytoplankton productivity and/or a contribution from land plant-derived OM (Xiong et al., 2010), while the negative shift induced by the Suess effect is still insufficient to counteract the impact of eutrophication on the $\delta^{13}C_{org}$ values. In addition, there was climatic cycle for every 200 years.

3.2. Aliphatic hydrocarbons

The *n*-alkanes content following the sequence of sediment accumulation, ranged from 119.4 μg/g to 417.3 μg g^{-1} (Organic carbon, OC; Fig. 7) within the lower section of the core, remained relatively constant from 43 to 20 cm, then increased gradually from 20 to 0 cm depth, and reached maximal values (>700 μg g^{-1} OC; Fig. 7) in the topmost sediment of the core. A bimodal distribution of *n*-alkanes is displayed in sediments at different depths. A strong peak is dominated by plankton-derived *n*-C_{15}–*n*-C_{20} components, with a maximum at *n*-C_{17} or *n*-C_{18}, and another peak constitutes terrestrial higher plant-derived *n*-C_{21}–*n*-C_{31} components, with a maximum at *n*-C_{25} or *n*-C_{27} (Fig. 2). In addition, a strong odd-over-even predominance was observed in the range of *n*-C_{21}–*n*-C_{31} alkanes throughout the sediment core. As shown in Fig. 2, a trend of plankton-derived C_{15}–C_{20} *n*-alkanes increases from the bottom to the top of this core. In the lower section (63–43 cm), *n*-alkanes were dominated by high carbon number homologues, indicating that a larger proportion of higher plant-derived OM was transported to the lake from the surrounding land over time. The relative content of short-chain *n*-alkanes notably increased above 43 cm in depth, reflecting enhanced distribution of aquatic algae and bacteria in the lake sediments (Xiong et al., 2010). Pristane and phytane are products of geological alteration of phytol and other isoprenoidyl natural products, and are not primary constituents of most terrestrial biota (Didyk et al., 1978; Li et al., 1995; Gao et al., 2007). However, a high concentration of pristane alone can be derived from zooplankton (Blumer et al., 1963). Pristane and phytane were found in all samples. The Pr/Ph ratios were determined in relation to the source of organic matter, depth of burial, and diagenetic transformations. The results

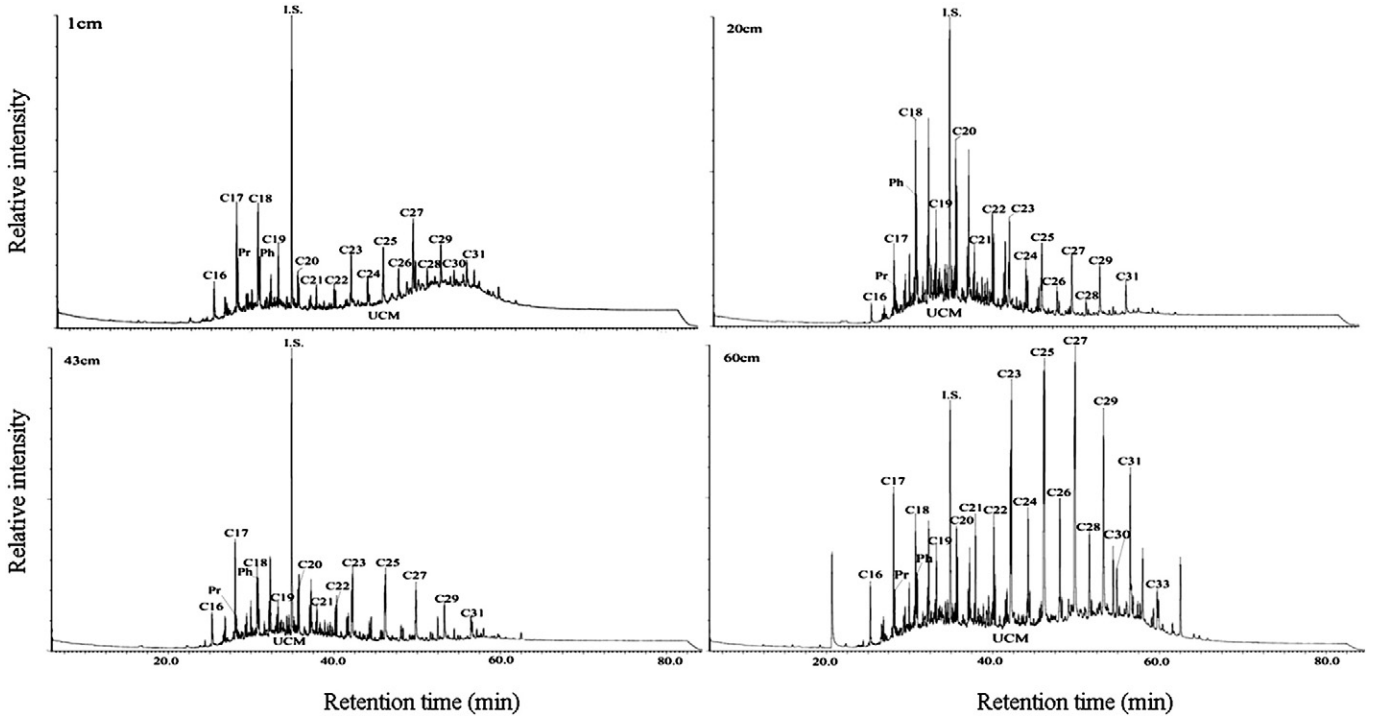

Fig. 2. GC/MS chromatograms (SIM mode) of aliphatic hydrocarbon fraction from the studied sediment core. Numbers indicate *n*-alkane chain length; Pr, pristane; Ph, phytane; and IS, internal standard.

generally tend to increase with an increased terrestrial contribution. A correlation was also found between the ratios of pristane to phytane (Pr/Ph) and the diagenetic history of these ancient sediments; the ratios being generally higher in deeply buried and geochemically altered organic facies (Rashid, 1979). Didyk et al. (1978) reported that Pr/Ph ratios < 1 represented anoxic conditions, while a value greater than 1 reflected oxic conditions. The Pr/Ph ratios are less than 1.1 in the sediment core from Lake Dianchi (Fig. 4L), which suggests that the sedimentary samples were subject to anoxic conditions over the whole sediment core. However, methanogenic microbes can also generate phytane (Brassell et al., 1981; Venkatesan and Kaplan, 1987), and these microbes live in sediments that lack oxygen (and sulfate), which are common in most sub-bottom parts of the lake floor. Therefore, low Pr/Ph ratios in the studied samples could result mainly from microbial activity.

3.2.1. Source identification from aliphatic hydrocarbon proxies

The aliphatic hydrocarbon (AH) composition of many aquatic algae and bacteria is dominated by short-chain *n*-alkanes (C_{15}–C_{20}) (Blumer et al., 1971; Giger et al., 1980; Cranwell et al., 1987), with bacteria normally showing an even predominance of *n*-alkanes, especially C_{18} and C_{20} (Han and Calvin, 1969). Elias et al. (2000) reported that even *n*-alkanes in the C_{14}–C_{22} range originate from diatoms. Submerged and floating aquatic plants commonly maximize *n*-alkanes at mid-chain *n*-alkanes (C_{21}–C_{25}) (Cranwell, 1984; Ficken et al., 2000). The abundance of odd long-chain *n*-alkanes (C_{27}–C_{31}) has been used extensively as an indicator of terrestrial or land-derived OM (Pearson and Eglinton, 2000; Zhao et al., 2003). The even long-chain *n*-alkanes (C_{26} and C_{28}) might be due to a fossil fuel input (Medeiros and Bícego, 2004; Lü and Zhai, 2006). Exceptions, however, have been noted. For example, samples of the emersed macrophyte *Hippuris* also contain mainly C_{27} and C_{29} alkanes (Aichner et al., 2010), whereas some algae (Rhisozolenoid diatoms) also produce long-chain *n*-alkanes (Sinninghe Damsté et al., 1999). Thus, care must be taken when assigning sources to alkanes of particular chain length.

The short-chain *n*-alkane distributions have no significant odd/even carbon number preferences (see $CPI_{15–20}$ values; Fig. 4g) in the sediment core. They may be derived primarily from the membrane lipids of microorganisms and/or by microbial reworking of plant *n*-alkanes (Grimalt et al., 1988; de las Heras et al., 1989). Carbon preference index ($CPI_{25–31}$) distributions are given in Fig. 4h. $CPI_{25–31}$ is an indication of *n*-alkane source. Hydrocarbons derived from land plant material show a predominance of odd-numbered carbon chains with $CPI_{25–31}$ ~5–10, with higher $CPI_{25–31}$ values found in sediment showing a greater contribution from vascular plants (Rieley et al., 1991; Hedges and Prahl, 1993). $CPI_{25–31}$ values close to unity are thought to indicate greater input from microorganisms, recycled OM, and/or petroleum (Bray and Evans, 1961; Kennicutt et al., 1987). The *n*-alkane $CPI_{25–31}$ values in the studied sediment core vary between 2.4 and 5.4. These values strongly suggest that the long-chain *n*-alkanes in these lacustrine sediments were derived mostly from terrestrial sources with some contribution from biogenic and/or petroleum sources.

Terrigenous/aquatic ratios of *n*-alkanes [$TAR_{HC} = (C_{27} + C_{29} + C_{31})/(C_{15} + C_{17} + C_{19})$] in lacustrine sediments can be used to evaluate the relative proportions of terrigenous and aquatic OM inputs (Silliman et al., 1996). Terrigenous OM is commonly enriched in long-chain *n*-alkanes relative to algal and bacterial material (Meyers and Ishiwatari, 1993), such that TAR_{HC} values remain effective in identifying changes in the proportions of terrigenous versus aquatic contributions of hydrocarbons. In addition, TAR_{HC} ratios are sensitive to the contributions of higher plants to sedimentary OM. Therefore, changes of vegetation in the watershed result in an increase of tree and shrub litter inputs to the sedimentary organic matter budget, further causing TAR_{HC} values to rise significantly (Silliman et al., 1996). TAR_{HC} ratios show an overall increasing trend in the lower section of the core (Section 1: 63–43 cm, 1184–1437 AD), indicating that terrestrial input increases with burial depth. TAR_{HC} ratios remain relatively constant in the middle section (Section 2: 43–20 cm, 1437–1793 AD). However, in the upper section (Section 3: 20–0 cm, 1793–2006 AD), the TAR_{HC} ratios progressively increase from 20 to 10 cm, and then decrease markedly from 10 to 0 cm (Fig. 4k). The enhancement of long-chain *n*-alkanes indicates delivery of greater proportions of terrestrial higher plants to the sediments, due to enhanced agricultural activity associated with soil disturbance in the Lake Dianchi watershed. The decrease of TAR_{HC} ratios in the uppermost 10 cm of sediments,

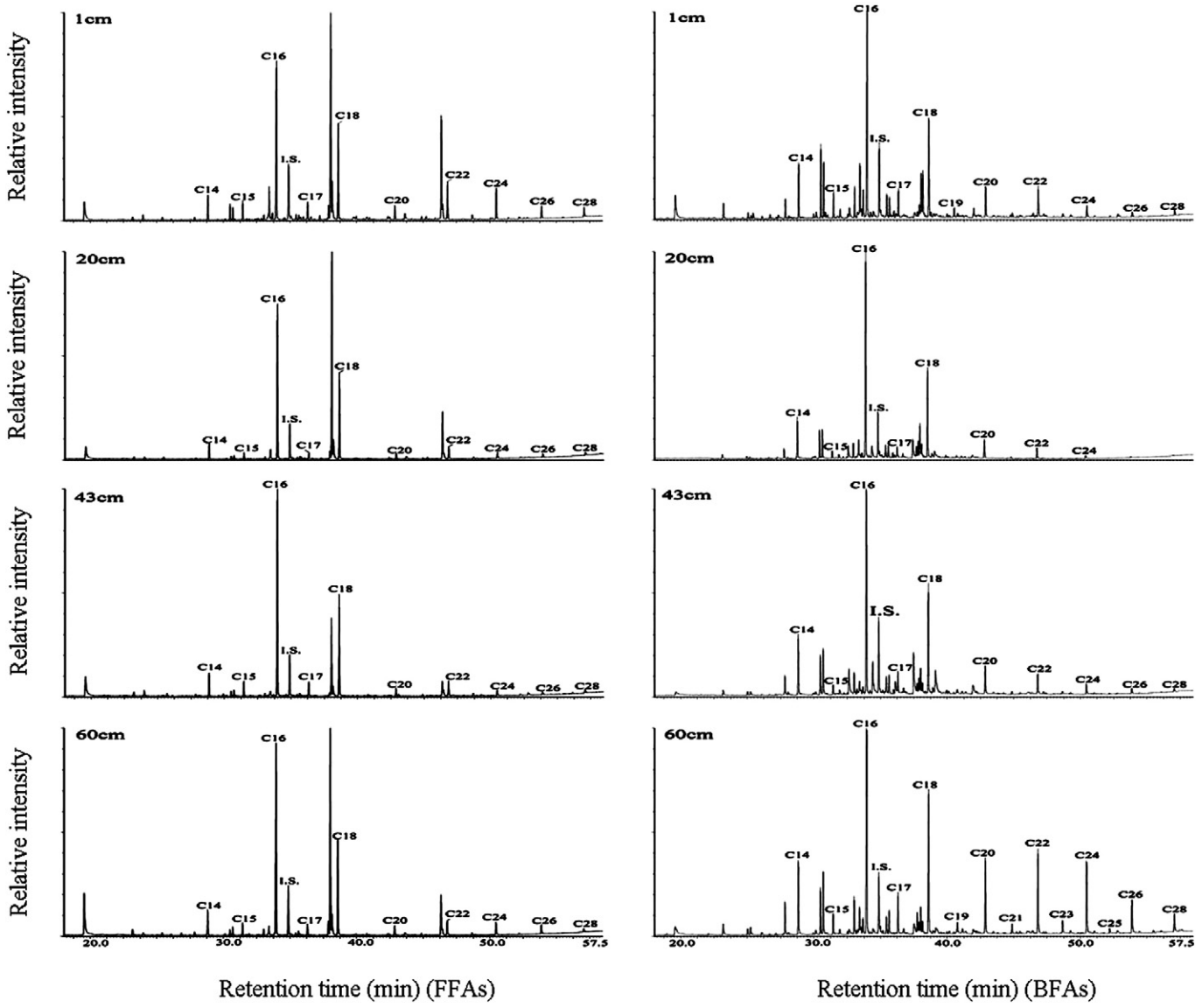

Fig. 3. GC/MS chromatograms (SIM mode) of fatty acid fraction from the studied sediment core. Numbers indicate fatty acid chain length; and IS, internal standard.

with increasing TOC contents and $\delta^{13}C_{org}$ values, can be explained by increases in algal and bacterial inputs over higher plant inputs for the past 50 years. The dramatic changes in organic matter composition at this stage are attributed to enhanced algal productivity caused by an increase in nutrient supply, due to modern urbanization and industrialization (Xiong et al., 2010). Lake Dianchi is adjacent to Kunming City, the capital of Yunnan Province; therefore large quantities of industrial wastewater and municipal sewage have been discharged into the lake. In Dianchi Catchment, phosphate rock and phosphatic chemical enterprises exist in the southern area, and industrial estates, farmlands, and habitation surround the remaining lakeshore. Consequently, the catchment runoff drains a significant amount of nitrogen and phosphorus nutrients into the Lake Dianchi (Gao et al., 2005). In Lake Dianchi, TN and TP increased from 1988 to 2000, ranging from 1.02 to 11.89 mg/l and 0.109 to 1.06 mg/l, respectively (Tuo, 2002; Meng, 1999). Increasing TN and TP concentrations have caused a rapid outburst of cyanobacteria bloom in Lake Dianchi (Nanjing Institute of Geography and Limnology, 1989).

The *n*-alkane average chain length (ACL) is the weight-averaged number of carbon atoms of the higher plant C_{25}–C_{31} *n*-alkanes. The abundance of individual *n*-alkanes from higher plant sources generally increases with increasing carbon number in lake sediments. The present study shows that ACL_{25-31} values are markedly low in the lowest (63–53 cm, 1184–1314 AD) and uppermost parts of the core (10–0 cm, 1944–2006 AD) (Fig. 4i). On the contrary, ACL_{25-31} values are generally high from 53 to 10 cm. There are two main reasons for the change in ACL_{25-31} values. First, environmental changes and/or anthropogenic activities result in terrestrial OM fraction changes in the sediment core. Second, in the hypereutrophic stage (10–0 cm, 1944–2006 AD), aquatic macrophyte (submerged and floating-leafed) blooms may contribute to lower ACL_{25-31} values.

In general, ACL_{25-31} values have been used widely in the study of long-chain *n*-alkanes in sediments. However, for our study, ACL_{25-31} values could not effectively distinguish terrestrial and aquatic plant types. We calculated *n*-alkane ACL values for C_{17} to C_{31}, which ranged from 23.0 to 25.1 (Fig. 4j). ACL_{17-31} results indicate a 2.1 unit difference between the two sources, which appears to be a dependable boundary between terrestrial and aquatic sources. In addition, ACL_{17-31} values show a consistent trend with TAR_{HC} ratios in the sediment core. We suggest that *n*-alkane ACL_{17-31} values can serve as a method for identifying terrigenous and aquatic source inputs in sediments.

All the samples analyzed in the present study contained an unresolved complex mixture (UCM) as shown in the chromatogram of typical samples (Fig. 2). UCM, composed of cyclic and branched alkanes,

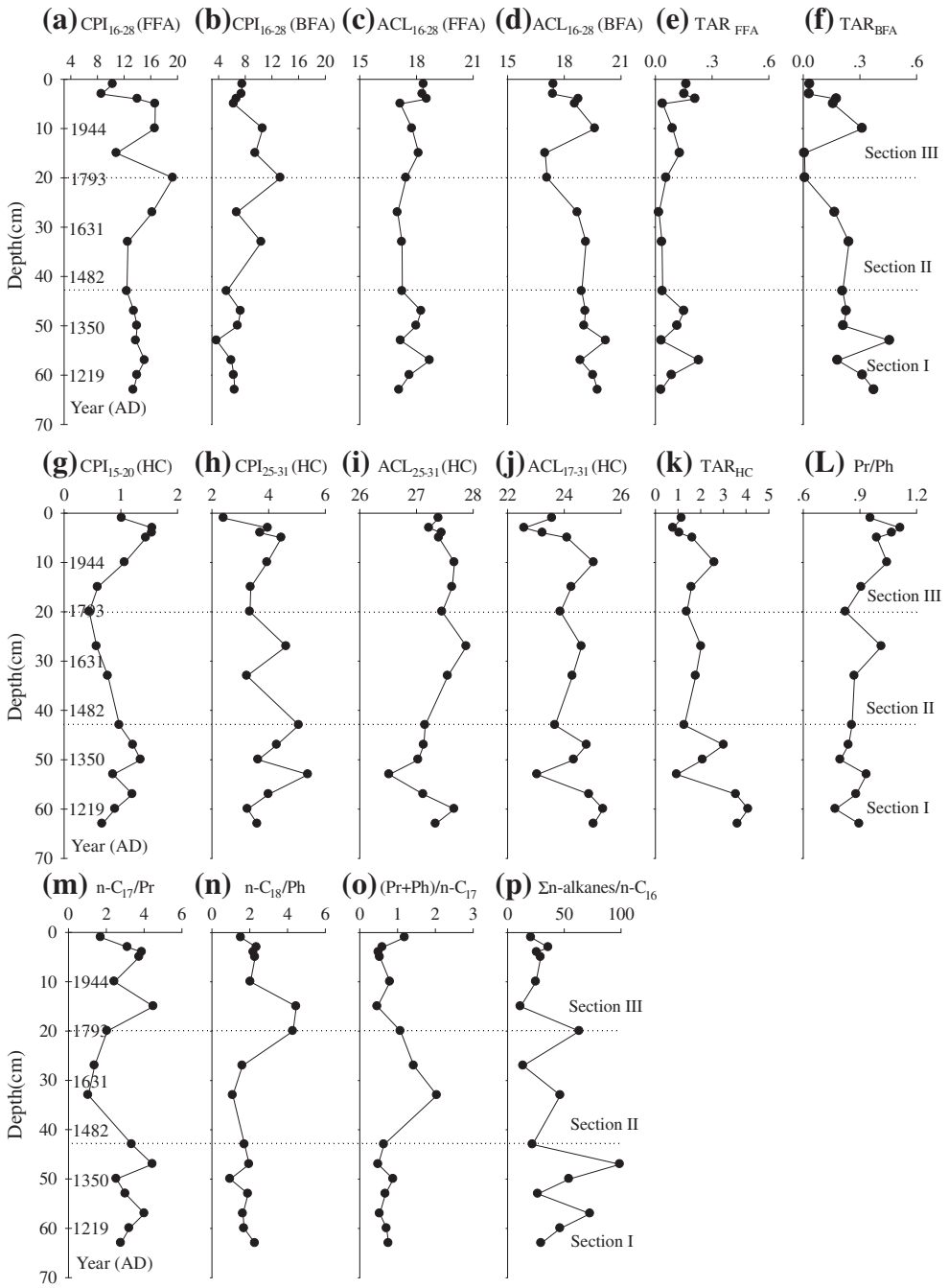

Fig. 4. Variations of CPI, ACL, TAR and Pr/Ph ratios for aliphatic hydrocarbons (HC) and fatty acids in the studied sediment core.

is known to resist microbial degradation more effectively than *n*-alkanes and thus has a greater tendency to remain in the environment after *n*-alkanes have degraded (Lytle et al., 1979). UCM alone may not be sufficient in confirming the presence of petroleum products (Keizer et al., 1978). In order to further differentiate the probable sources of organic matter in the sediment core, $\sum$ *n*-alkane/*n*-C_{16}, *n*-C_{17}/Pr and *n*-C_{18}/Ph, and (Pr + Ph)/*n*-C_{17} ratios were used. The $\sum$ *n*-alkanes/*n*-C_{16} ratio is usually <15.0 for petroleum contaminated samples (Gao et al., 2007). The ratio varied from 11.6 to 99.2 in the sediment samples (Fig. 4p). The ratio is generally lower for Section 3 (20–0 cm, 1793–2006 AD). This again implies that Section 3 was more seriously contaminated from petroleum hydrocarbons than Sections 1 and 2.

The *n*-C_{17}/Pr, *n*-C_{18}/Ph and (Pr + Ph)/*n*-C_{17} ratios are useful to identify the presence of freshly derived or degraded petroleum hydrocarbons in sediments (Gao et al., 2007). Low (<1.0) *n*-C_{17}/Pr, *n*-C_{18}/Ph ratios imply the presence of degraded petroleum hydrocarbons while higher ratios (>1.0) suggest the presence of less degraded or relatively fresh hydrocarbons (Harji et al., 2008). The *n*-C_{17}/Pr and *n*-C_{18}/Ph ratio varied from 1.1 to 4.5, and 1.0 to 4.5 in the sediment core (Fig. 4m and n). Similarly, >1 and <1.0 (Pr + Ph)/*n*-C_{17} ratio indicates the presence of degraded and fresh petroleum hydrocarbons, respectively (UNEP, 1995). This ratio varied from 0.5 to 2.0 in these samples (Fig. 4o). For most of the sedimentary samples from Sections 3 and 1, the ratios were <1, indicating the presence of freshly derived petroleum hydrocarbons at these sections.

3.2.2. Evidence for source from carbon isotopic compositions of n-alkanes

The compound-specific $\delta^{13}C$ data show that odd-numbered *n*-alkanes (C_{17}–C_{31}) in the studied Lake Dianchi core range from −23.5‰

to −35.6‰, whereas the even-numbered *n*-alkanes (C_{16}–C_{30}) range from −22.4‰ to −32.4‰ (Table 1). Given that bulk organic $\delta^{13}C$ values integrate multiple influences, compositional analysis and compound-specific isotope analysis of *n*-alkanes have been increasingly used to distinguish different origins of these OM components. For example, C_{16}–C_{20} *n*-alkanes are commonly considered as autochthonous biomarkers (Cranwell et al., 1987; Neunlist et al., 2002). The $\delta^{13}C$ values of short-chain *n*-alkanes (C_{16}–C_{20}) in this study were in the range of −24.1‰ to −30.7‰, while the long-chain *n*-alkanes (C_{27}–C_{31}) exhibited values between −26.4‰ and −35.6‰ throughout the profile (Table 1), indicating at least two distinct sources. If the differences of $\delta^{13}C$ values are not evident between short-chain and long-chain *n*-alkanes, then there is a strong petrogenic input to the sediments (Sikes et al., 2009). The $\delta^{13}C$ values of individual *n*-alkanes (C_{16}–C_{31}) varied between −24.1‰ and −35.6‰ in the sediment core from Lake Dianchi, suggesting a dominance of ^{12}C-enriched *n*-alkanes that originated from C_3 plants and lacustrine algae.

Long-chain *n*-alkanes mainly derive from terrestrial higher plants. The $\delta^{13}C$ values for long-chain *n*-alkanes in the sediment core from Lake Dianchi are in the range of −26.4‰ to −35.6‰, indicating that C_3 plants are the major sources. The variation of $\delta^{13}C$ of higher plant *n*-alkanes (C_{27}, C_{29}, and C_{31}) could also be divided into three sections. The slightly lighter $\delta^{13}C$ values of higher plant *n*-alkanes in Section 1 (20–0 cm, 1793–2006 AD) and III (63–43 cm, 1184–1437 AD) are probably due to gradual expansion of C_3 plants in the source area, and similar conclusion can be gotten from ($C_{27} + C_{29} + C_{31}$) changing trend (Fig. 7a). Similar results also are confirmed from shifts in ACL_{25-31} values with depth. $\delta^{13}C$ values for C_{27}, C_{29}, and C_{31} are relatively constant in Section 2 (43–20 cm, 1437–1793 AD), indicating that the lake assumed a relatively stable state during this period. Lower TOC and less terrestrial input reflect that the lake was oligotrophic during this interval (Xiong et al., 2010). Variations of $\delta^{13}C$ values in the long-chain *n*-alkanes depend on multiple factors such as physiological responses, vegetation utilizing different photosynthetic pathways, the $\delta^{13}C_{CO_2}$ value, and changes in plant types (Farquhar et al., 1982; Meyers, 2003). Water-use efficiency (WUE) is one of the more important physiological factors that affect carbon isotope composition. Studies have reported significant negative correlations between the $\delta^{13}C$ value of plant tissues and precipitation or effective precipitation (Stevenson et al., 2005). The mean annual precipitation varied from 797 to 1007 mm in the Dianchi catchment (Liu et al., 2006), so the influence on the $\delta^{13}C$ values of plant tissues from precipitation was relatively small. In addition to sensitivity to the WUE, $\delta^{13}C$ records of long-chain alkanes have been used to estimate the relative abundances of C_3 and C_4 plants at some sites (Huang et al., 2006). C_3-dominated forest remained relatively stable in the area of Lake Dianchi during the past 3800 years (Sun et al., 1986; Xiao et al., 2011). The negligible contributions from WUE and C_4 plants allow us to exclude the effects of precipitation and different photosynthetic pathways (i.e., C_4 vs. C_3). Another factor to consider is that the $\delta^{13}C_{CO_2}$ value of atmospheric CO_2 has been declining during the past 200 years as a consequence of the Suess effect. Terrestrial plants utilize the ^{13}C-depleted, fossil fuel-derived CO_2, which leads to the lower $\delta^{13}C$ values of long-chain *n*-alkanes in lake sediments (Verburg, 2007). The Suess effect is the main cause of the more negative $\delta^{13}C$ values for long-chain *n*-alkanes in the Lake Dianchi core.

Short-chain *n*-alkanes ($<C_{21}$) may originate from bacteria (Nishimura and Baker, 1986), algae, and/or phytoplankton (Youngblood and Blumer, 1973). Aliphatic hydrocarbons of bacterial and planktonic origins are dominated by even (*n*-C_{16}, *n*-C_{18}, and *n*-C_{20}) (Han and Calvin, 1969; Nishimura and Baker, 1986) and odd (*n*-C_{15}, *n*-C_{17}, and *n*-C_{19}) (Youngblood and Blumer, 1973) carbon *n*-alkanes, respectively. Similar trends in $\delta^{13}C$ values have been found for C_{16}, C_{18}, and C_{20} *n*-alkanes in the sediment core from Lake Dianchi (Fig. 5), indicating they have similar bacterial sources. There were apparently different trends between ($C_{16} + C_{18} + C_{20}$) and ($C_{17} + C_{19}$) contents (Fig. 7a). The $\delta^{13}C$ values of the C_{17} and C_{19} *n*-alkane biomarker, which are commonly considered representative of algae (Blumer et al., 1971; Filley et al., 2001), are in the range of −24.1‰ to −30.4‰ in Section 3 (20–0 cm, eutrophic stage). There are different trends indicated with respect to bulk $\delta^{13}C_{org}$ values and $\delta^{13}C$ values for C_{17} *n*-alkanes, whereas the trend of $\delta^{13}C$ values for C_{19} *n*-alkane is consistent with the bulk $\delta^{13}C_{org}$ value at the eutrophic stage (20–0 cm) (Fig. 5). The difference between the $\delta^{13}C$ values of C_{17} and C_{19} *n*-alkanes is possibly due to different sources; a bacterial source is possibly the main source for C_{17} *n*-alkane in the Lake Dianchi core, and similar trends have been found between C_{17} and C_{20} *n*-alkanes. In limnic systems, $\delta^{13}C$ values of short-chain compounds are often linked with rates of primary production, because algae use dissolved inorganic carbon (DIC) to produce organic matter. In oligotrophic lakes, competition for available carbon is low; therefore, algae tend to discriminate against the heavier isotope, resulting in more negative $\delta^{13}C$ values (Hollander and Mckenzie, 1991). However, in eutrophic lakes, with enhanced productivity, CO_2 in the water becomes depleted, and phytoplankton are forced to consume ^{13}C, resulting in less negative $\delta^{13}C$ values in the algae (Sun et al., 2013). Bulk $\delta^{13}C_{org}$ values record the classic excursion to heavier values that accompanied eutrophication in Lake Dianchi (Xiong et al., 2010).

The range of isotope values for the middle-chain alkanes (C_{21}–C_{25}) in Lake Dianchi sediment is between the values for long-chain alkanes (C_{27}–C_{31}) and short-chain alkanes (C_{16}–C_{20}). The middle-chain alkanes come from emersed and submerged macrophytes, which can utilize both atmospheric carbon and the carbon pool in the water (Cranwell, 1984; Ficken et al., 2000). In this study, we found similar trends for the $\delta^{13}C$ values of the C_{21}, C_{23}, and C_{25} *n*-alkanes, probably caused by similar submerged and floating aquatic plant sources, and the ($C_{21} + C_{23} + C_{25}$) contents were generally higher in Sections 3 and 1 than Section 2, the change trend was similar with ($C_{27} + C_{29} + C_{31}$) (Fig. 7a). At the hypereutrophic stage (10–0 cm, 1944–2006 AD), such organisms probably have lived in relatively CO_2-limited environments, possibly because of the consumption by carbonate mineral precipitation

Table 1
$\delta^{13}C$ values of *n*-alkanes in the studied sediment core.

Depth (cm)	C_{16}	C_{17}	C_{18}	C_{19}	C_{20}	C_{21}	C_{22}	C_{23}	C_{24}	C_{25}	C_{26}	C_{27}	C_{28}	C_{29}	C_{30}	C_{31}
1	−29.3	−26.6	−26.9	−25.4	−28.4	−29.2	−30.4	−29.6	−31.0	−26.7	−31.3	−30.0	−30.5	−31.8	−30.5	−32.9
3	−25.7	−25.1	−26.1	−24.1	−26.3	−27.6	−29.4	−29.6	−32.3	−32.6	−31.8	−35.6	−32.4	−32.1	−29.9	−33.2
4	−28.6	−28.8	−26.7	−24.8	−27.5	−28.2	−29.5	−29.5	−29.0	−32.5	−32.3	−29.1	−30.4	−31.4	−31.5	−32.5
5	−26.6	−28.3	−27.4	−25.6	−28.5	−28.9	−29.7	−30.5	−29.3	−31.4	−31.7	−29.3	−30.4	−31.1	−31.0	−32.0
10	−25.5	−27.6	−27.5	−27.6	−28.3	−29.0	−30.6	−32.1	−30.9	−34.8	−30.3	−30.4	−30.7	−31.5	−30.7	−31.0
20	−28.3	−27.5	−27.5	−30.4	−26.2	−30.7	−29.5	−31.7	−30.2	−30.2	−29.9	−29.1	−29.5	−31.3	−29.6	−30.3
33	−27.5	−26.4	−27.5	−30.3	−27.0	−31.6	−31.0	−31.9	−31.4	−32.5	−31.0	−28.7	−30.3	−31.6	−30.7	−30.2
43	−28.7	−28.2	−29.1	−29.6	−27.9	−30.3	−28.9	−29.5	−31.2	−31.8	−29.4	−29.6	−29.4	−30.7	−29.2	−29.8
50	−27.8	−29.0	−30.7	−29.0	−28.5	−29.6	−28.6	−28.2	−28.4	−30.9	−29.8	−27.2	−29.2	−29.6	−29.5	−29.4
60	−26.9	−29.8	−28.7	−29.0	−28.9	−28.5	−27.4	−26.0	−26.8	−29.9	−30.5	−26.4	−29.0	−29.0	−29.5	−29.3

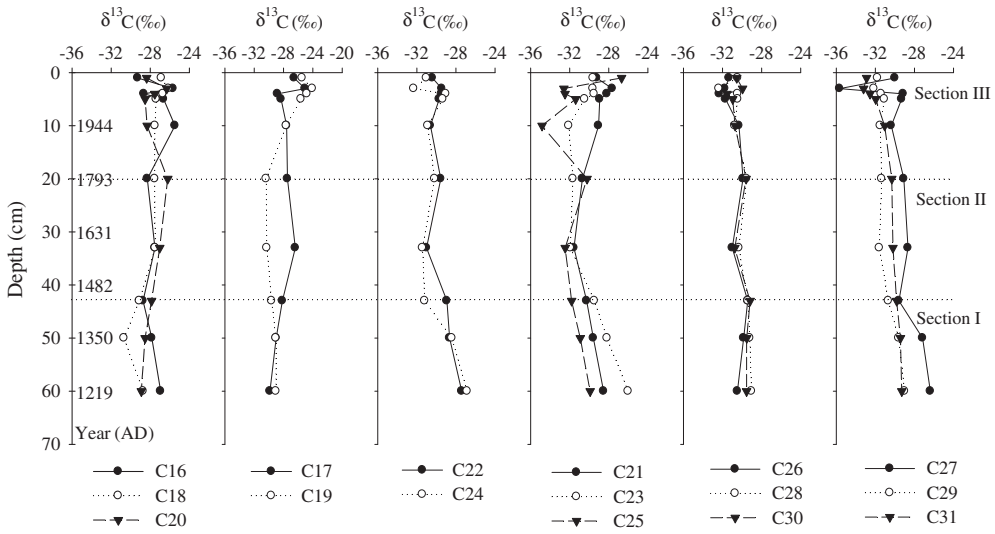

Fig. 5. Vertical profiles of carbon isotopic compositions of individual *n*-alkanes in the studied sediment core.

at high pH or during high levels of productivity and reduced DIC supply by in-flowing freshwater. The algae and submerged and floating aquatic plants may have used more dissolved HCO_3^- ($\delta^{13}C = 1‰$) as their source of carbon, resulting in heavier $\delta^{13}C$ values for short-chain and middle-chain *n*-alkanes, and the influence from the Suess effect can be neglected at the hypereutrophic stage.

According to Silva et al. (2008), the difference in the isotopic composition of odd to even *n*-alkanes in the sediment core from Lake Dianchi reveals different origins. Elias (1997) reported that C_{22} *n*-alkane was possibly derived from an input of algal detritus and further bacterial biodegradation. Sediment samples from a deltaic environment in Spain also had this unusual *n*-C_{22} predominance, and it was attributed to microbial degradation of algal detritus (Albaigés et al., 1984). In the present study, the trends of $\delta^{13}C$ values are similar between C_{22} and C_{24} *n*-alkanes, and they are apparently different with respect to bulk $\delta^{13}C_{org}$ values in the hypereutrophic stage, indicating that algae are not the main source for C_{22} and C_{24} *n*-alkanes, and the ($C_{22} + C_{24}$) contents did not apparently change with depth (Fig. 7a). On the basis of measured $\delta^{13}C$ values (−26.8‰ to −32.3‰), we suggest that C_{22} and C_{24} *n*-alkanes are mainly derived from microbial degradation of algal detritus and/or C_3 plants. The higher molecular weight components (>C_{24}) with no or low odd-to-even carbon number preferences indicate a contribution of geologically more mature hydrocarbons (Elias, 1997). The lack of carbon number preference of the *n*-alkanes was regarded as a result of the particular environmental conditions prevailing in that area and possibly due to bacteria (Grimalt et al., 1985). The *n*-alkane $CPI_{25–31}$ values in the studied sediment core vary between 2.4 and 5.4. The trends of $\delta^{13}C$ values are similar for even-numbered C_{26}, C_{28}, and C_{30} *n*-alkanes, with a range of −29.0‰ to −32.4‰, indicating these long-chain even-numbered *n*-alkanes are derived from similar sources, and the ($C_{26} + C_{28} + C_{30}$) contents did not apparently change with depth (Fig. 7a). These values strongly support the view that long-chain even-numbered *n*-alkanes in lacustrine sediments are mostly derived from terrestrial sources. Bondada et al. (1996) investigated epicuticular leaf waxes of cotton (*Gossypium hirsutum*) and found a majority of even-numbered *n*-alkanes ranging from *n*-C_{24} to *n*-C_{32}.

3.3. Fatty acid biomarkers

Free and bound fatty acids were detected as fatty acid methyl esters. The concentration of total free fatty acids (FFAs) was relatively constant (from 639.0 to 2262.9 μg g^{-1} OC) below a sediment depth of 20 cm, but increased abruptly to up to 6541.3 μg g^{-1} OC in the more recently deposited sediments (Fig. 7b). Total bound fatty acids (BFAs) showed a distribution profile similar to the *n*-alkanes (Fig. 7b). There was an obvious difference between FFA and BFA concentrations in the upper section of the core. The unsaturated fatty acids (UFAs) in free lipids had a similar vertical profile to that of bound UFAs (Fig. 7b), except for one sample in the uppermost sediments, indicating that the difference between FFA and BFA concentrations was mainly derived from saturated fatty acids (SFAs) and/or saturated branched fatty acids (BRFAs) (Xiong et al., 2010). High amounts of BRFAs have been reported to be present in anaerobic bacteria (Edlund et al., 1985; Rajendran et al., 1997), sulfate-reducing bacteria (Taylor and Parkes, 1983, 1985; Edlund et al., 1985), and gram-positive bacteria (Kaneda, 1977). The BRFA contents are apparently higher in BFAs than in FFAs (Fig. 7b), possibly owing to diverse anaerobic bacteria sources. The FFA and BFA in this study were dominated by either the *n*-$C_{16:0}$ or *n*-$C_{18:0}$ component, and had a strong even-over-odd predominance in the range of $C_{12:0}$–$C_{28:0}$ homologues (Fig. 3). Longer chain fatty acids ($C_{22:0}$–$C_{28:0}$) derived from higher plant waxes (Rieley et al., 1991) were relatively low in abundance in the sediment core from Lake Dianchi.

3.3.1. Source identification from fatty acid proxies

The $CPI_{16–28}$ values for BFAs ranged from 3.7 to 13.3 and from 8.6 to 19.3 for FFAs (Fig. 4a and b), which are higher than the $CPI_{25–31}$ values (2.4 to 5.4) for *n*-alkanes. The greater microbial alteration of *n*-alkanes implied by the smaller *n*-alkane CPI values agrees with the larger fatty acid CPI values that signify greater microbial production of secondary acids (Zhou et al., 2010).

Long-chain fatty acids, such as *n*-$C_{24:0}$, *n*-$C_{26:0}$, and *n*-$C_{28:0}$ are major components of the waxy coatings on land-plant leaves, flowers, and pollen (Rieley et al., 1991). Shorter-chain *n*-$C_{14:0}$, *n*-$C_{16:0}$, and *n*-$C_{18:0}$ are produced by all plants, but are the dominant lipid components of algae and bacteria (Cranwell et al., 1987). We used these source identifiers to calculate ratios of terrigenous-to-aquatic fatty acids: $TAR_{FA} = (n\text{-}C_{24:0} + n\text{-}C_{26:0} + n\text{-}C_{28:0})/(n\text{-}C_{14:0} + n\text{-}C_{16:0} + n\text{-}C_{18:0})$. Higher TAR_{FA} values can indicate increased terrigenous sources of lipid matter relative to aquatic sources, but they also may signify degradation of aquatic fatty acids relative to land-derived components (Tenzer et al., 1999). Selective degradation and other diagenetic effects commonly overprint fatty acid source signatures. Short-chain acids often are preferentially degraded by microbes during early diagenesis (Ho and Meyers, 1994). Such preferential degradation will elevate TAR_{FA} values, whereas microbial synthesis of secondary fatty acids from primary organic matter produces shorter-chain components (Kawamura et al., 1987), which can depress TAR_{FA} values. All TAR_{FA} values for the BFAs

Table 2
$\delta^{13}C$ values of *n*-fatty acids in the studied sediment core.

Depth (cm)	$C_{16:0}F$	$C_{16:0}B$	$C_{18:0}F$	$C_{18:0}B$	$C_{20:0}F$	$C_{20:0}B$	$C_{22:0}F$	$C_{22:0}B$	$C_{24:0}F$	$C_{24:0}B$	$C_{26:0}F$	$C_{26:0}B$	$C_{28:0}F$	$C_{28:0}B$
1	−29.6	−28.6	−29.9	−29.1	−32.6	−27.5	−33.0	−26.9	−29.7	−24.8	−29.3	−24.2	−33.1	−29.5
3	−29.8	−29.1	−29.1	−29.3	−32.2	−27.5	−32.1	−26.7	−29.6	−24.5	−30.8	−24.9	−35.7	−29.7
4	−30.1	−29.5	−28.3	−29.2	−31.1	−27.7	−31.3	−27.5	−29.5	−26.2	−28.6	−25.5	−33.5	−30.2
5	−30.7	−29.9	−28.3	−29.4	−30.3	−28.5	−31.7	−27.3	−29.9	−25.9	−30.5	−25.6	−33.4	−30.0
10	−30.2	−30.6	−28.8	−30.7	−33.2	−28.5	−32.3	−28.7	−32.8	−29.2	−33.3	−29.3	−35.2	−31.4
20	−29.6	−30.7	−30.3	−30.8	−32.7	−30.0	−35.0	−31.4	−33.1	−28.1	−33.4	−29.8	−36.5	−30.8
33	−29.1	−30.6	−28.9	−30.8	−32.3	−29.2	−36.2	−30.0	−34.2	−28.7	−33.1	−29.6	−37.2	−31.1
43	−28.8	−30.3	−28.9	−30.3	−32.2	−29.8	−35.9	−31.2	−33.9	−26.9	−30.8	−26.0	−35.8	−28.8
50	−30.0	−30.2	−30.8	−30.6	−32.9	−30.2	−34.5	−31.7	−29.8	−27.0	−29.2	−25.6	−32.5	−28.6
60	−29.9	−30.3	−30.6	−30.1	−32.3	−29.2	−32.7	−29.2	−28.2	−26.2	−28.1	−24.6	−31.6	−28.9

F: free fatty acid; B: bound fatty acid.

and FFAs in this study are low (Fig. 4e and f), which either indicates that algal contributions have been predominant in fatty acids or that microbial reworking of sedimentary OM has overprinted the original source characteristics of the fatty acid components. Both land-plant and algal fatty acids would need to have been heavily reworked to yield the low TAR_{FA} values found in these sediments.

In Lake Baikal sediments, Ishiwatari et al. (2006) used ACL to evaluate the distribution of *n*-$C_{24:0}$ to *n*-$C_{30:0}$ fatty acids. They suggested that a predominance of terrestrial higher plants, such as angiosperms, moss, sedge, and lichen, may cause higher ACL values, whereas aquatic macrophytes (submerged and floating) may contribute to lower ACL values. The acid ACL calculation equation is as follows:

$$\text{Fatty acid ACL} = \left(\sum C_i \times i\right) / \sum C_i$$

where C_i is the concentration of a fatty acid containing *i* carbon atoms ($i = 24$–30).

Wang and Liu (2012) used the equation to calculate ACL values of *n*-acids with various carbon number ranges, including C_{16}–C_{32} and C_{18}–C_{32} through C_{28}–C_{32}. Results showed that the potential for determining the input source by way of *n*-acid ACL values was entirely dependent on the calculation. The fatty acid ACL proxy showed enough of a distinction to estimate a reliable boundary between terrestrial and aquatic inputs when the short-chain group of *n*-acids (C_{16}–C_{19}) was added to the calculation. The mean $ACL_{16–32}$ values are 23.3 for terrestrial sources and 18.6 for aquatic sources (Wang and Liu, 2012). $ACL_{16–28}$ values range from 17.0 to 18.7 for FFAs, and from 17.0 to 20.2 for BFAs (Fig. 4c and d). The FFAs and BFAs show 1.7 and 3.2 unit differences between them. Furthermore, $ACL_{16–28}$ values are generally higher in BFAs than in FFAs, possibly owing to higher degradation rate constants for long-chain FFAs than for long-chain BFAs (Sun et al., 2000).

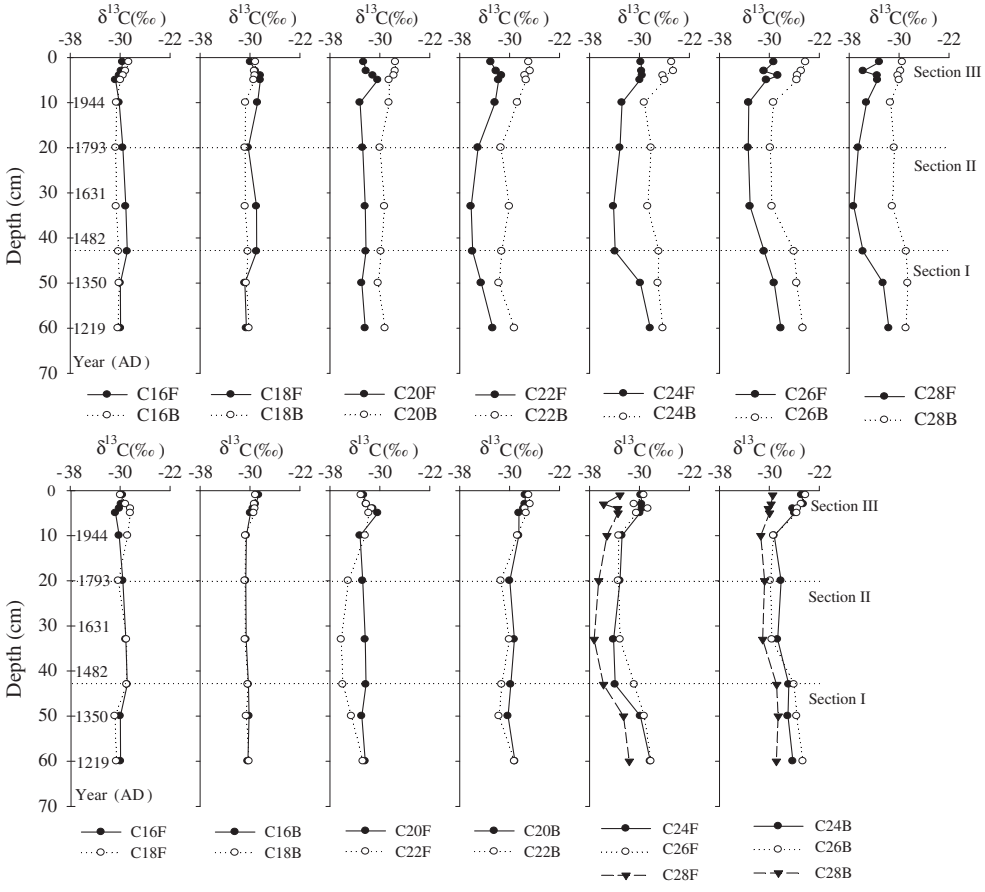

Fig. 6. Vertical profiles of carbon isotopic compositions of individual fatty acids in the studied sediment core (F: free fatty acid; B: bound fatty acid).

3.3.2. Evidence of source from carbon isotopic compositions of fatty acids

The short-chain fatty acids ($C_{16:0}$ and $C_{18:0}$) have similar $\delta^{13}C$ values, ranging from −30.8‰ to −28.3‰ (Table 2), with an average of −29.8‰. In particular, $\delta^{13}C$ values of bound $C_{16:0}$ are entirely consistent with those of bound $C_{18:0}$ (Fig. 6), indicating the same biological sources. The ($C_{16:0}$ + $C_{18:0}$) contents are generally higher in Section 3 (20–0 cm, 1793–2006 AD) (Fig. 7b), indicating aquatic fatty acids are major sources for sedimentary OM in eutrophic Lake Dianchi. Reworking of primary OM by anaerobic and aerobic bacteria will significantly alter the isotopic composition of short-chain fatty acids preserved in the sedimentary record and water column particulates; anaerobically produced fatty acids are depleted in ^{13}C by up to 12‰ relative to the carbon source, whereas those from aerobic growth were slightly enriched in ^{13}C (+1.5‰) (Teece et al., 1999). As an example, Teece et al. (1999) reported that anaerobic bacterial processes can result in phytoplankton (average $\delta^{13}C$ value of −22‰) having short-chain fatty acid-derived $\delta^{13}C$ values of −30‰ to −32‰. Detection of these ^{13}C-depleted fatty acids in sediments could be used to infer bacterial reworking of terrestrial OM, particularly C_3 plant-derived material. Similar results from algal degradation studies indicate changes in the $\delta^{13}C$ of fatty acids over time (Harvey and Macko, 1997). The experiments of Rhead et al. (1971) pointed to rapid degradation and resynthesis of fatty acids by bacteria in sediments. The result was replacement of algal acids by bacterial acids during the early stage of burial. In this study, because the sediment core was under anoxic conditions, rapid degradation of algal fatty acids under anoxic conditions will be caused only by microbial processes, and higher bacterial abundance occurs in anoxic systems (Ding and Sun, 2005). We suggest that these isotopic changes for $C_{16:0}$ and $C_{18:0}$ were mainly a combination of new anaerobic bacterial biomass and remaining algal fatty acids.

This interpretation of the $C_{20:0}$–$C_{30:0}$ fatty acid sources based on their carbon isotopic compositions is supported by previous observations of fatty acid distributions obtained by other investigations, which signified that long-chain fatty acids in modern sediments can originate from higher-land plants (Cranwell, 1974; Matsuda and Koyama, 1977; Duan et al., 1995). The present results show that although they are present in low concentration, long-chain fatty acids (C_{20}–C_{28} even carbon numbers) in the FFAs have lighter stable carbon isotopic values than those in the BFAs (Fig. 6). Previous studies have suggested that distributions of free lipids are typical of terrestrial organic matter, whereas bound lipids are dominated by autochthonous sources, and are better preserved than free lipids during microbial degradation (Cranwell, 1978, 1981). In this study, $\delta^{13}C$ values of >C_{20} (−28.1‰ to −37.2‰) for FFAs in the sediment core are closer to the isotopic composition of terrestrial C_3 plants (Meyers, 1997; Naraoka and Ishiwatari, 2000). However, $\delta^{13}C$ values of long-chain fatty acids for BFAs are in the range of −24.2‰ to −31.7‰ (Table 2), and the $\delta^{13}C$ values apparently become heavier above 10 cm, indicating more algal components in the BFAs of these

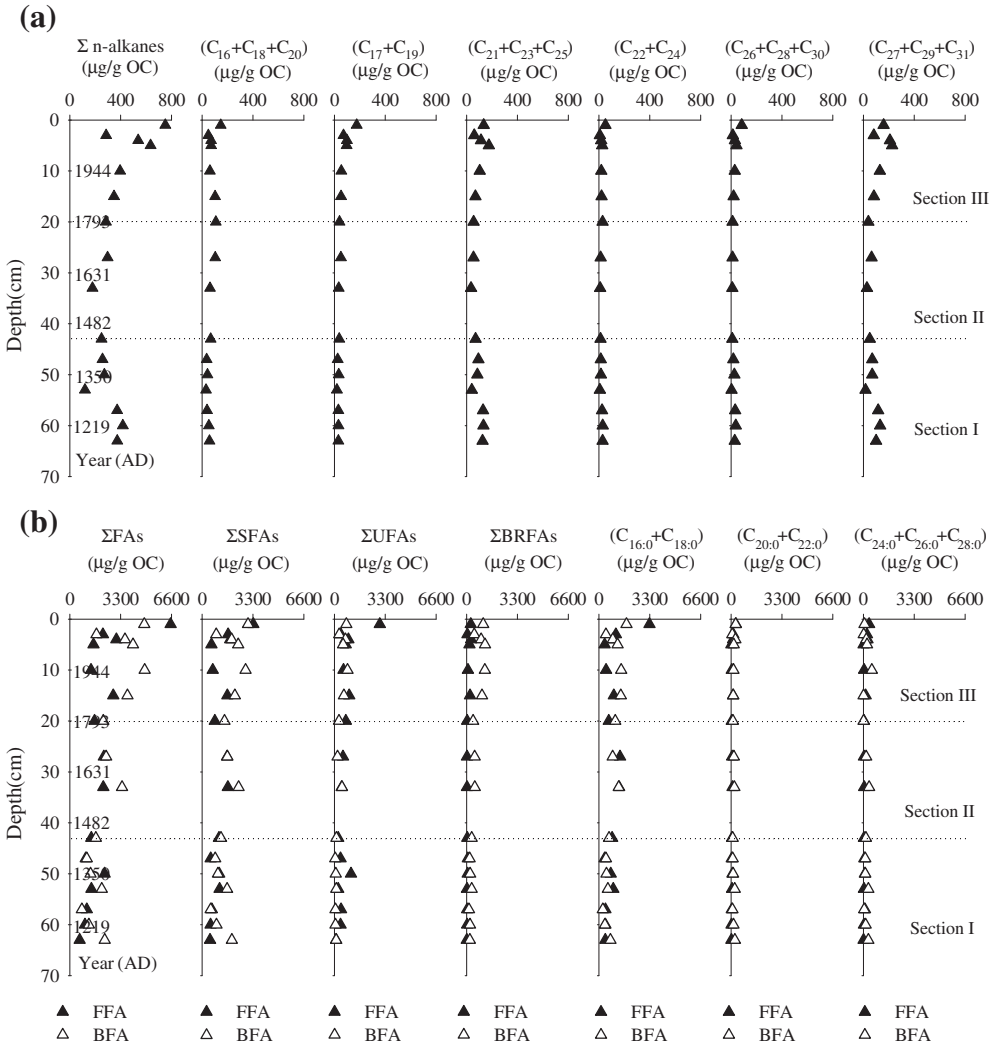

Fig. 7. Vertical profiles of (a) *n*-alkane and (b) fatty acid parameters in the studied sediment core (FAs: fatty acids; SFAs: saturated fatty acids; UFAs: unsaturated fatty acids; BRFAs: branched fatty acids; FFA: free fatty acid; BFA: bound fatty acid).

uppermost sediments. Recent studies have shown that long-chain fatty acids not only are derived from terrestrial sources, but they may also arise from bacterial and algal sources (Naraoka and Ishiwatari, 1999, 2000). Some bacteria have the ability to synthesize fatty acids with chain lengths of up to C_{30}, yet $C_{26:0}$, $C_{28:0}$, and $C_{30:0}$ derived from bacterial sources have $\delta^{13}C$ values significantly more depleted than the possible range of terrestrial fatty acids (Gong and Hollander, 1997). At the hypereutrophic stage (10–0 cm, 1944–2006 AD) in the studied core, $\delta^{13}C$ values of $C_{24:0}$, $C_{26:0}$, and $C_{28:0}$ are apparently positively shifted, which is contrary to the trend for long-chain *n*-alkanes, indicating they are derived from different sources, and the ($C_{24:0}$ + $C_{26:0}$ + $C_{28:0}$) contents are not obviously increase at hypereutrophic stage (Fig. 7). Long-chain alkanes in Lake Dianchi sediment core are exclusively derived from terrestrial organic matter. Usually, a long-chain *n*-alkane with a particular number of carbons is considered to be biosynthesised from the fatty acids with one more carbon, both the *n*-alkanes and *n*-fatty acids should have similar stable carbon isotopic fingerprints (Ratnayake et al., 2005). If the isotopic values differ significantly, the fatty acids may originate from multiple sources. In addition, the negative shift of $\delta^{13}C$ values Suess effect is not observed in long-chain fatty acids, that is apparently different with long-chain *n*-alkanes in the sediment core, indicating higher proportions of long-chain fatty acids are derived from algal sources versus C_3 plant sources. Furthermore, the changes are more apparent for BFAs than for FFAs; algal sources may be the main sources for the $C_{24:0}$ and $C_{26:0}$ BFAs in the hypereutrophic stage (10–0 cm, 1944–2006 AD), with $\delta^{13}C$ ranges of −24.2‰ to −26.2‰ (Table 2).

4. Conclusions

A sediment core from Lake Dianchi was investigated to evaluate the origin of its *n*-alkanes, FFAs, and BFAs. Results show that:

1. Long-chain *n*-alkanes (>C_{24}) are mainly derived from higher land plants. Significantly ^{13}C-depleted values indicate a major origin as terrestrial C_3 plants.
2. Short-chain even-numbered *n*-alkanes are mainly derived from bacterial sources, whereas an algal source may explain the C_{17} and C_{19} *n*-alkanes. In addition, C_{22} and C_{24} *n*-alkanes are mainly derived from microbial degradation of algal detritus.
3. Molecular and isotopic evidence indicates that mid-chain *n*-alkanes (C_{21}, C_{23}, and C_{25}) in the sediment core are sourced from submerged/floating macrophytes, and their isotopic shifts within the core are consistent with that of bulk $\delta^{13}C_{org}$ values of the hypereutrophic stage.
4. $\delta^{13}C$ values for short-chain fatty acids are the composite signal of organic matter from primary production and bacterially derived components, indicating that short-chain fatty acids are mainly derived from bacterial and/or remaining algal detritus.
5. Long-chain FFAs are mainly derived from C_3 plants. However, long-chain BFAs probably derive from mixed sources of terrestrial organic matter, bacteria, and algae, with the contribution from algal sources being higher in the hypereutrophic stage.

Our data suggest that long-chain *n*-alkanes and FFAs are mostly of terrestrial origin, while long-chain BFAs, short-chain *n*-alkanes and fatty acids are mainly contributed by algae and bacteria in the hypereutrophic Lake Dianchi. Since evident changes in organic matter origin were observed in the whole sediment core, we conclude that eutrophication has had a profound impact on lipid composition and origin in Lake Dianchi sediment core.

Conflict of interest statement

We declare that we have no financial and personal relationships with other people or organizations that can inappropriately influence our work. There is no professional or other personal interest of any nature or kind in any product, service and/or company that could be construed as influencing the position presented in, or the review of, the manuscript entitled, “Source characterization of sedimentary organic matter using molecular and stable carbon isotopic composition of *n*-alkanes and fatty acids in sediment core from Lake Dianchi, China”.

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