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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).

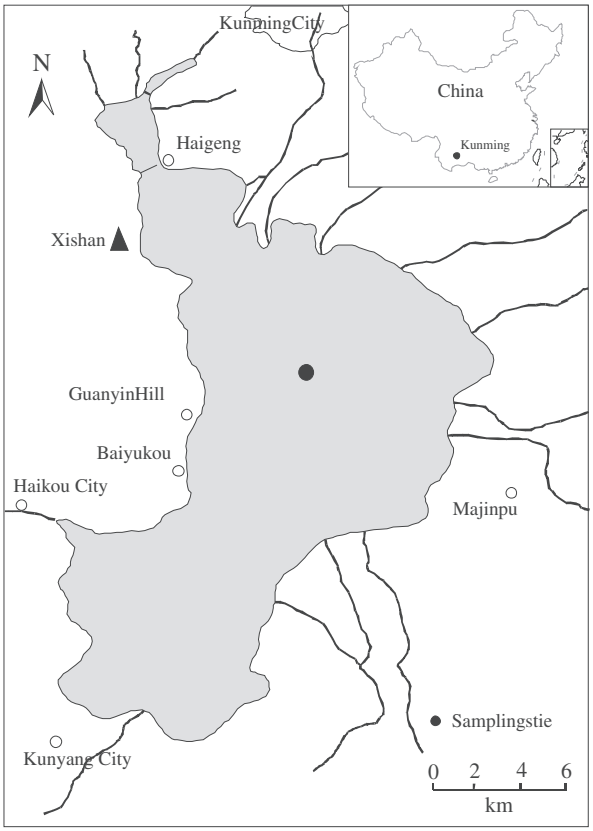

Fig. 1. Map of Lake Dianchi showing the coring site.

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).