Historical changes in the phytoplankton community in Fuxian and Dianchi lakes recorded based on alkyl diols and sterol biomarkers

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Abstract

We investigated historical changes in temperature and phytoplankton in Fuxian Lake (FX) and Dianchi Lake (DC), two plateau lakes in Southwest China. We detected sterols and alkyl diols as algal biomarkers (Dinoflagellates, Diatoms, Eustigmatophytes, Cyanobacteria, and Chlorophyta) in the sediment cores by using GC–MS. We characterized sedimentary organic matter (SOM) via C-13 isotope and C/N ratio, and Rock-Eval analysis to obtain total organic carbon (TOC), S2, the hydrogen index (HI), refractory carbon (RC), and nutrient status such as total phosphorus (TP) and total nitrogen (TN) in the sediment cores. The results showed that the sedimentation rates measured by ^{210}Pb dating ranged from 0.02 to 0.30 g cm^{-2} yr^{-1} and 0.07 g cm^{-2} yr^{-1} in FX and DC, respectively. The Bayesian isotope mixing model indicated that organic matter from plankton was the main contributor of organic matter in FX and DC and, its contents was gradually increasing. Primary productivity derived from the S2 and HI parameters showed an increasing trend in FX and DC. Cyanobacteria and Chlorophyta were the two dominant phyla in the two lakes. Algal growth was controlled primarily by temperature and nutrient availability. Principal component analysis (PCA) and multiple linear regression analysis showed that the major factors controlling the historical change in phytoplankton growth were TN and temperature in FX and DC.

Key words: Sterols; alkyl diols; sediment core; phytoplankton communities; Fuxian Lake; Dianchi Lake

1. Introduction

Lake sediment analysis is one of the important tools for the study of past environmental and climate changes. Changes in chemical, biological, and physical characteristics in lake sediments provide insight into past changes in biological communities, surrounding vegetation, and hydrological fluxes, from which we inferred past changes in the local climate. It is a particularly important paleoclimatic tool in many areas although other common paleoclimatic alternatives, including tree rings and ice, are useful. Lake sediments are an important potential source of information for long-term continental paleoclimate reconstruction (Castañeda & Schouten, 2011). Organic biomarkers stored in lake sediments reflect surrounding climatic conditions such as temperature and precipitation in the lake catchment area at the time of deposition (van Bree et al., 2018). As a result, scientists are increasingly using historical changes in the occurrence, distribution, and isotopic composition of these biomarkers as substitutes for the reconstruction of paleoclimate (Berke et al., 2012; Huang et al., 1999; Tierney, et al., 2011).

Lipid biomarkers are organic molecules that serve as indicators of the past presence of certain organisms and, therefore, also indicate the past environmental conditions under which those organisms appeared. For example, long-chain fatty acids ($>C_{24}$) and n-alkanes ($>C_{23}$) are the main components of leaf wax in terrestrial higher plants (Eglinton & Hamilton, 1967), so they are used for biomarkers of vascular plants (Sinninghe Damsté et al., 2012). Similarly, short-chain fatty acids and alkanes ($< C_{21}$) are general phytoplankton biomarkers (Meyers, 1997), while mid-chain (C_{21} - C_{25}) alkanes are biomarkers for aquatic macrophytes (Ficken et al., 2000), and 1, 15 n-alkyl diols are biomarkers for eustigmatophyte algae (Villanueva et al., 2014; Volkman et al., 1992). Sterols such as dinosterol, brassicasterol, and cholesterol are biomarkers of phytoplankton communities in marine and lacustrine environments (Castañeda et al., 2011; Volkman, 2003). Similarly, bulk organic matter (OM) properties, such as TOC, C/N ratio, and carbon and nitrogen isotopic composition, can serve as effective proxies for ascertaining biogeochemical processes and evaluating OM sources in sediments. Multiple indicators (e.g., lipid biomarkers, isotopic composition, and C/N ratio) have assisted in clarifying the OM biogeochemistry in lacustrine systems. Lipid biomarkers have been used to study the OM sources of surface sediments (Zimmerman and Canuel, 2001). In addition, it is also used to study the variation of OM composition with time under human interference. For example, in the Chesapeake Bay, Zimmerman and Canuel (2002) used lipids to document changes in eutrophication. Similar studies have been conducted in other systems, including Puget Sound (Brandenberger et al., 2008), Florida Bay (Xu et al., 2007), and Brazilian Estuary (Carreira et al., 2011). Therefore, the combination of lipid biomarkers with bulk organic matter properties has been useful for investigating the sources, transport, and fates of OM in this investigation.

The investigated plateau lakes are in Yunnan Province in Southwest China. Fuxian Lake is the largest plateau deep lake in China. The Materials and Methods section further describes their characteristics. Since the 1950s, human activities in the Fuxian Basin have intensified, including agricultural activities and large-scale deforestation from the 1950s to the 1970s, followed by the increasing population and the development of industry and tourism after the 1980s (Gao et al., 2013). These factors resulted in an increased influx of nutrients into the lake, thereby increasing phytoplankton productivity and maintaining total organic carbon and nitrogen levels in the sediment records from 1987 to 2005

(Wang et al., 2011). Dianchi Lake is the largest freshwater lake in the Yunnan-Guizhou Plateau in southwestern China. As the lake is a closed or semi-closed system and the water remains in the lake for a long time, pollutants have an increased possibility of being deposited on the lake bottom (Wu et al., 2017). In recent decades, rapid economic development has intensified the deposition of nitrogen and phosphorus in Dianchi Lake, and the fluxes in this period accounted for more than half of the total accumulation in the last century (Wu et al., 2018). Against the background of intensified human activities and climate warming in recent decades, how have the lake ecosystems of Fuxian Lake and Dianchi Lake responded? What are the controlling factors for the changes in the phytoplankton community? We noted a need for further studying changes in the algal community of lacustrine waters in China and elsewhere by using biomarkers. Multiple biomarker proxies were applied to trace the source of biological productivity. We applied multiple biomarker proxies to trace the source of biological productivity. Hence, this investigation is of great significance for understanding changes in the ecosystems of freshwater lakes under the influences of human activities and climate warming.

We aimed to use lipids as biomarkers to reconstruct lacustrine primary productivity and to investigate the effects of climate change and human activities on the sediment cores in Fuxian and Dianchi in the past century. We analyzed organic matter parameters (TOC, TN, TP, ^{13}C, HI, and S2) and molecular biomarkers (sterols and alkyl diols) in the sediment cores. TOC is a proxy of lacustrine productivity, and TN and TP can elucidate changes in nutrient loading, when increased human activity (e.g., fertilizer use) may have resulted in runoff into the lake. ^{13}C indicates the carbon isotope fractionation of total organic carbon by aquatic organisms and combines with HI and S2, which helps understand primary productivity changes in lakes.

1. **Materials and Methods**

2.1. Study Site and Sampling

Fuxian Lake (24°21'-24°38'N, 102°49'-102°57'E) is located in the central part of Yunnan Province, 60 km from southeastern Kunming City, spanning from Chengjiang County to Jiangchuan County and Huaning County. The lake covers an area of 212 km^2, with a maximum water depth of 157.3 m, an average water depth of 87 m, and water storage of 189×10^8 m^3. It is the second-largest deep-water lake known in China. Fuxian belongs to the Nanpanjiang River system in the Pearl River Basin. At present, Fuxian Lake is an oligotrophic lake with clear and transparent water quality and low suspended particulate material (SPM) content.

Dianchi Lake (24°40'-25°02'N, 102°36'-102°47'E) is in southwestern Kunming. It covers an area of 297 km^2, with a maximum depth of 5.87 m, an average water depth of 2.93 m, and water storage of 11.69×10^8 m^3. Dianchi belongs to the Jinsha River system in the Chang Jiang Basin. With the development of Kunming's economy, Dianchi water quality has deteriorated, and eutrophication is serious in the area close to Kumming city due to the influence of industrial wastewater mainly derived from the chemical, food, medicine, health, textile, printing, and dyeing, papermaking industries, as well as from municipal domestic sewage from Kumming.

We collected one sediment core each from Fuxian Lake (24°36'N, 102°52'E) and from Dianchi Lake (24°47'N, 102°41'E) in July 2019 (Fig. 1). The water depths were 107.6 m and 4.37 m at the sampling sites in FX and DC, respectively. Vertical and temporal variations in salinity, pH, chlorophyll *a*, and temperature in the water column of FX and DC were detected by a CTD-90 M probe (Sea & Sum Technology, Germany) in continuous mode, which enabled obtaining a considerable number of profile records (Fig. S1). We sliced the sediment cores at 2 cm intervals along their respective lengths of 36 cm (FX) and 34 cm (DC). These subsamples were immediately placed into plastic bags, sealed, stored, and transported at low temperatures (0-10°C). We stored the sediment samples at -20°C in the laboratory until freeze-drying and homogenizing them for chemical analysis.

2.2. Temperature Data and Chronological Dating

We obtained the temperature data for Lakes Fuxian and Dianchi from the National Meteorological Information Center. The selected station for FX is the Yuxihongta station and for DC is the Kunming station. Yuxihongta station is 45 km from the sampling site of FX, and Kunming station is 30 km away from the sampling site of DC. We conducted analyses for the activities of ^{210}Pb, ^{226}Ra, and ^{137}Cs at the Institute of Geochemistry, Chinese Academy of Sciences, Guiyang. We calculated the activity of ^{210}Pb from the peak area of 46.5 KeV -ray spectrum, and the activity of ^{226}Ra from the peak area of the ^{214}Pb spectrum (351.9 KeV). ^{214}Pb, with a short half-life, is the decay product of ^{226}Ra (Smith et al., 1997). We calculated the activity of ^{137}Cs from the peak area of the 661.7 KeV-ray spectra. The activity of ^{210}Pb$_{EX}$ is the difference between the specific activity of ^{210}Pb and that of ^{226}Ra. We used the activity of ^{210}Pb$_{EX}$ for the chronological calculation based on a constant rate of supply (CRS) dating model.

1. **Analysis of C, N, and P and Bulk ^{13}C**

We analyzed total organic carbon (TOC) and total nitrogen (TN) with a Vario EL III Elementar analyzer (Germany). Before the analysis, we treated the sediment samples (300-500 mg) with 1 M HCl to remove carbonates and analyzed them in silver boats. We analyzed the samples in duplicate. The mean deviations of the duplicate samples for C and N were $< 0.05\%$. EDTA served as an external standard. We extracted total phosphorus (TP) from sediments with 1 M HCl after ignition at 550°C (2 h) and then determined by ammonium molybdate spectrophotometry (Aspila et al., 1976).

We measured bulk stable carbon isotopic compositions on the acidified sediment samples. We obtained measurements from a ThermoQuest EA coupled online to a Finnigan Mat Delta PlusXLS by a Conflo III system. The values show in formulations as ^{13}C (‰) = [(R_{sample} - R_{std})/Rstd] *1000, where R equals the $^{13}C/^{12}C$ ratio in the sediment sample and the standard compared to the Vienna Pee Dee Belemnite (VPDB) standard. We corrected the ^{13}C value ($^{13}C_{corrected}$) for the Suess effect using the polynomial equation for the correction, modeled by Piet Verburg (2007) as follows:

$^{13}C = 7.7738118 * 10^{-16} * Y^6 - 1.2222044 * 10^{-11} * Y^5 + 7.1612441 * 10^{-8} * Y^4 - 2.1017147 * 10^{-4} * Y^3 + 3.3316112 * 10^{-1} * Y^2 - 273.715025 * Y + 91703.261$

With Y=year. The calculated, time-dependent depletion for a given year resulted by subtracting from the measured ^{13}C for each dated sediment section.

1. **Analysis of Rock-Eval Pyrolysis**

We performed Rock-Eval analyses with a Rock-Eval 6 pyrolyzer (Vinci Technologies). We placed 70 mg of the acidified sediment sample in Incoloy crucibles. The Rock-Eval analytical process consists of two sequential heating steps under different ambient conditions (Behar et al., 2006). This method can determine the quantity and quality of the organic matter in a sample based on the rate of thermal pyrolysis and evolution of various organic compounds. First, we heated bulk sediment in an inert, O_2-free oven (300°C-650°C, 25°C min^{-1}), followed by combustion in an oxidation oven (300°C-850°C, 20°C min^{-1}). Long-chained C-compounds crack and release HC which we recorded as the S2 fraction. Thermal cracking releases the S2 fraction of organic matter between 300°C and 650°C, representing high molecular weight aliphatic hydrocarbons. The ratio of S2 to TOC is HI. The combustion stage burns the remaining OM, yielding the RC (weight percent) peak.

1. **Lipid Extraction and Analysis**

We spiked 4 g of freeze-dried and ground samples with 5.00 µg nonadecanol, Soxhlet-extracted with CH_2Cl_2:CH_3OH (93:7, V: V), and added activated copper turns for 72 h. We ran a blank to check the total extraction procedure, and no noticeable contaminants appeared. Once this time had elapsed, we removed the copper turns, and the excess solvent via rotary evaporation until reaching a final volume of 1 mL in CH_2Cl_2, which we retained at 4°C until further analysis. We isolated the neutral and acid components from the extracts isolated above by saponification with 0.5 N KOH in a 95% methanol/5% water solution. The neutral fraction was overactivated silica gel (120°C, 4 h) that had been pre-extracted by CH_2Cl_2. Before GC-MS analysis, the alkyl diols and sterols were derivatized using 50 µL of bis(trimethylsilyl)-trifluoroacetamide and trimethylchlorosilane (99:1) and 50 µL of pyridine (70°C, 1 h). We performed GC–MS analyses using an Agilent 7890A gas chromatograph linked to an Agilent 5975C mass spectrometer. GC conditions were as follows: We injected samples using a temperature-programmable split-less injector with an 80 °C initial temperature and a linear ramp to 200°C at 25 °C min^{-1}; followed by ramping at 3°C min^{-1} to 250°C; and a final ramp at 1.8°C min^{-1} to 300°C, with a hold time of 2 min. The chromatographic column used was a 30 m J&W Scientific DB-5 with a phase thickness of 0.25 µm and an i.d. of 0.25 mm. The carrier gas was UHP-grade helium, and the GC operated under constant flow at a rate of 1.0 mL min^{-1}. We conducted compound identification by comparison of mass spectra with published spectra and relative retention times.

1. **Bayesian Mixing Model**

The Bayesian isotope mixing model (MixSIAR, version 3.1.12) was applied in this research (Stock et al., 2018). The ^{13}C and C/N ratios for the sediments and the end members were used as input parameters. The Markov Chain Monte Carlo (MCMC) was set to "normal", and the Gelman-Rubin and Geweke diagnostic tests were used to determine whether the output was reasonable (Stock and Semmens, 2013). We used -23.5±3.5‰, -27.5±4.5‰, -29.8±0.5‰, -15.3±4.2‰, -25.3±2.8‰ as the ^{13}C values of macrophytes, plankton, C3plants, C4plants, and sewage sources, respectively; and 20±10, 6.5±1.5, 18±7.3, 15±4.6, 12.5±0.8 as the C/N values of macrophytes, plankton, C3plants, C4plants, and sewage sources, respectively (Guo et al., 2020; Duan et al., 2022). Among the variables analyzed in this study, none was higher than the lowest estimated factor of 1.05 for the Gelman-Rubin test, thereby suggesting that our output data were reliable.

1. **Results**

3.1 Physicochemical Properties of Water Column

As shown in Figure S1, except for salinity, the other parameters, including pH, chlorophyll a, and temperature, showed an increasing trend from the bottom to the surface in the FX and DC water columns, respectively. The chlorophyll *a* concentrations of FX (< 5.0 µg L^{-1}) were lower than those of DC (< 11 µg L^{-1}) in surface water, and those of FX were below 1.0 µg L^{-1} in deeper water. This means that FX is an oligotrophic lake and DC is a mesotrophic lake.

3.2 Chronological Dating

We analyzed ^{210}Pb and ^{226}Ra contents in the two sediment cores. Figure S2 shows the vertical distribution of $^{210}Pb_{EX}$ in the cores. The activities of $^{210}Pb_{EX}$ in FX and DC are 51.3-658 Bq kg^{-1} and 98.1-312 Bq kg^{-1}, respectively. We estimated ages and sedimentation rates from the ^{210}Pb (half-life 22.23 ± 0.12 years) activities by using the CRS dating model (Ontiveros-Cuadras et al., 2012). The accumulation characteristics of ^{137}Cs in the cores of FX and DC were not obvious, and the recognized time markers were not present, so ^{137}Cs could not serve for dating in FX and DC. The ages of the sedimentary cores from FX and DC ranged from 1926 to 2017 and from 1942 to 2018 (Fig. S3), respectively. The sediment accumulation rates vary from 0.03 to 3.30 cm yr^{-1} and from 0.06 to 3.40 cm yr^{-1} in FX and DC. The sediment mass accumulation rates vary from 0.02 to 0.30 g cm^{-2} yr^{-1} in FX and DC.

3.2 Bulk Parameters and Temperature data

TOC, S2, HI, and RC were determined by Rock-Eval pyrolysis. TOC ranges from 0.45% to 4.10% in FX and from 0.79% to 6.03% in DC. S2 values are in the ranges of 0.33-14.9 mg HC g^{-1} and 0.84-21.9 mg HC g^{-1}, HI values are in the ranges of 73.5-365 mg HC $(gTOC)^{-1}$ and 107-363 mg HC $(gTOC)^{-1}$, and RC values are in the ranges of 0.19-2.41% and 0.36-3.15% in FX and DC, respectively. They showed down core decreasing trends.

Organic carbon isotopes can be used to determine the source of organic matter in sediments. Usually, the composition of carbon isotopes reflects the dynamic process of carbon assimilation in the photosynthesis of different organisms and the carbon isotopes of carbon sources. The value of ^{13}C ranged from -28.6‰ to -24.1‰ with an average of -26.6‰ in FX and ranged from -25.4‰ to -20.5‰ with an average of -23.6‰ in DC. The values showed an increasing trend in DC and a decreasing trend from the bottom layer to the top layer in FX.

TP concentrations varied from 1.03 to 1.32 g kg^{-1} and from 1.43-2.78 g kg^{-1} in FX and DC, respectively. The TN contents were in the ranges of 0.40-4.30 g kg^{-1} and 1.11-7.28 g kg^{-1} in FX and DC, respectively.

We obtained meteorological data from nearby base stations in the investigated regions in Yunnan. As shown in Figure 3, since 1975, the five-year average temperature (T_5) has risen by 2 °C in Yuxihongta (near Fuxian Lake) and Kunming (near Dianchi Lake) (Figure 2), but it also showed a significant historical low value in approximately 2005 in Yuxihongta. Thus, the data support overall warming over the past 70 years.

3.3 Molecular Biomarkers

Six sterols, cholesterol (C_{27} ^{5}), brassicasterol (C_{28} $^{5,\ 22}$), 24-methylcholesta-5-en-3 -ol (C_{28} ^{5}), 24-ethylcholesta-5-en-3 -ol (C_{29} ^{5}), 24-ethylcholesta-22-en-3 -ol (C_{29} ^{22}), and dinosterol, and two alkyl diols, 1,15-C_{30}-diol and 1,15-C_{32}-diol, were analyzed by GC–MS in FX and DC. Their mass chromatography plots are presented in Figure S4. The concentrations of total sterols and alkyl diols ranged from 2.25 µg g^{-1} to 59.1 µg g^{-1} and from 2.20 µg g^{-1} to 76.4 µg g^{-1}, with maximum concentrations at 0-2 cm and 8-10 cm in FX and DC, respectively. In FX, brassicasterol and dinosterol concentrations were in the range of 0.35-7.82 µg g^{-1} and 0.12-9.14 µg g^{-1}, with average concentrations of 1.43 µg g^{-}1 and 1.03 µg g^{-1}, respectively. The average concentration of n-alkyl diols in FX (24.7 µg g^{-1}) was higher than that in DC (6.36 µg g^{-1}) in the top layer of 0-4 cm.

1. **Discussion**

4.1 OM Input and Variation in the Sediment Cores

The TOC contents reflect lake algal, bacterial, and phytoplankton productivity and the land plant input (Gon alves, 2002; Harris et al., 2004; Street et al., 2012). The Rock-Eval analysis is a traditional petroleum geochemical analysis technique, and it has proven to be suitable for the characterization of algal organic matter (AOM) in bulk sediments. S2 represents higher molecular weight algae-derived aliphatic hydrocarbons. It has been applied in the pyrolysis of algal macromolecular organic matter because this material degrades less easily than other organic components in early diagenesis (Chen et al., 2020; Duan et al., 2015). Moreover, photosynthesis could fractionate the isotopic values of CO_2. Algae prefer lighter CO_2 when high biological productivity and dissolved CO_2 are insufficient. Plankton consumes more bicarbonate ions in water because the carbon isotopic composition of bicarbonate is 7-10‰ heavier than that of dissolved CO_2 (Chen et al., 2020), which leads to enrichment of ^{13}C in these organisms.

Due to the isotope fractionation of aquatic photosynthesis, aquatic plants have a lighter ^{13}C (Falkowski and Raven, 1997). Increased or decreased productivity is observed based on the enrichment or depletion of ^{13}C in OM from sediments. However, for over a decade, we have known the correct change in ^{13}C atmospheric CO_2 owing to human activities (such as fossil combustion) in OM from lacustrine sediments (Verburg 2007). Thus, during the period of frequent human activities, ^{13}C should include a correction for the Suess effect used as a proxy of aquatic productivity in FX and DC. Primary producers (such as C3 plants, C4 plants, and phytoplankton) usually have distinctive carbon isotope compositions. The average ^{13}C of terrestrial OM is over -27‰, and the average ^{13}C of aquatic OM is below -20‰ (Zhang et al., 2014).

The ^{13}C values showed a downward decreasing trend in FX (Fig. 3), while the corrected ^{13}C values showed no obvious changes and were steady at -20‰, which indicated that the aquatic productivity was stable and primarily derived from algae. Due to the isotope fractionation of aquatic photosynthesis, aquatic plants have a lighter ^{13}C (Falkowski and Raven, 1997). FX has an open surface area with a large volume and a small catchment, and its storage time is up to 167 years (Wang and Dou1998). It receives water from more than 20 small rivers, indicating that the lake water body has a strong buffering effect on the input of external sources, and the concentration of dissolved oxygen in deep water is less than 3 mg L^{-1} (Yao et al., 2017). FX is located in the subtropical humid monsoon climate zone. Except for the vertical distribution of water temperature in January and February, there is a stable vertical stratification in the other months, in which the water temperature is relatively stable, and the vertical mixing effect is weak. This result suggested that the carbon source of algal organic matter was mainly derived from dissolved carbon dioxide in the lake water in the past 100 years. However, the ^{13}C ranged from -25.4‰ to -21.3‰ and showed an obvious upward increasing trend since 2000 in DC (Fig. 3), and the corrected ^{13}C showed the same trend, indicating that the carbon isotope composition was becoming heavier. The ^{13}C in DC sediments was more enriched than that in FX, which may result from anaerobic sediments with high rates of methanogenesis and a lack of terrestrial carbon inputs in shallow water bodies. The removal of CH_4 (^{13}C light) by intensive methanogenesis leads to the accumulation of ^{13}C-heavy OM in sediments (Gu et al., 2004).

The Bayesian mixing model was used to evaluate the relative contribution of different organic matter sources in FX and DC (Fig. 4). The results showed that 39.3-68.2% of organic matter in sediment mainly came from plankton. Fig. 4(c) and Fig. 4(c) (d) showed that the variation of contribution rates of organic matter from different sources with depth is not obvious, which indicated that the source composition of sedimentary organic matter in FX and DC is stable. To understand the historical changes of the organic matter from plankton, the calculated contribution percentage of the organic matter from plankton in each layer was multiplied by the corresponding organic carbon content, as shown in Figure 4(b). The results showed that the contents of planktonic organic matter in the sediments of FX and DC increased significantly since 1980. This indicated that organic matter from plankton was the main contributor of organic matter in FX and DC and, its contents were gradually increasing.

HI and S2 are considered indicators of the primary productivity of algae. HI is the ratio of S2 to TOC, and its vertical profiles could provide a better understanding of historical changes in AOM in sedimentary organic matter (Stein et al., 2006; Duan et al., 2015). RC, which represents a thermally resistant organic material, originates from terrestrial organic matter (e.g., lignin, cellulose) and, hence, reflects terrestrial inputs (Lafargue et al., 1998). When HI is over 100 mg HC (gTOC)$^{-1}$, 2006; Duan et al., 2017). We used S2/RC ratios as an indicator of sediment diagenesis (Outridge et al., 2007) which showed an increasing trend in FX and DC (Fig. S5), suggesting excellent preservation of the S2 fractions in both lake sediments Moreover, HI has been widely used as an indicator of primary productivity in recent years (Stein et al., 2006; Duan et al., 2015; Duan et al., 2017). As shown in Figure 3, the HI values of FX and DC increased significantly and were over 100 mg HC (gTOC)$^{-1}$. This result suggested that the AOM fractions in FX and DC played a dominant role in SOM.

4.2 Biomarkers in the sediment cores of Fuxian and Dianchi

The concentrations of -sitosterol (C_{29} ^{5}), brassicasterol (C_{28} $^{5, 22}$), cholesterol (C_{27} ^{5}), and dinosterol compare with those in other studies from surface sediments with similar water depths (Ladd et al., 2018; Schwab et al., 2015) (Table 1). In the 0-2 cm layer, the cholesterol, -sitosterol, and brassicasterol concentrations were 7.46, 9.34, and 2.38 g g^{-1} dw in FX, which were similar to those in Lucerne Lake (the maximum water depth was 120 m) in Switzerland, and the cholesterol, -sitosterol and brassicasterol concentrations were 25.7, 13.9 and 3.80 g g^{-1} dw in DC, which were similar to those in Greifen Lake (the maximum water depth was 7 m) in Switzerland. In the 2-4 cm layer, the cholesterol, -sitosterol, and dinosterol concentrations were 115, 121, and 82.0 g g^{-1} TOC in FX and 253, 216, and 25.2 g g^{-1} TOC in DC, respectively. Its concentrations were close to those of crater lakes in Cameroon. This result suggested that water depth may be correlated with sterol concentrations in surface sediments. There was a thermocline in the FX water column (Fig. S1), which caused a slowdown in the material transport in the deep water column, while there was no obvious thermal stratification in the DC water column (Fig. S1).

We detected eight biomarkers for the different algae species in the two sediment cores. First, 24-methylcholesta-5-en-3 -ol (C_{28} ^{5}), 24-ethylcholesta-5-en-3 -

ol ($C_{29}{}^{5}$), and 24-ethylcholesta-22-en-3 -ol ($C_{29}{}^{22}$) were relatively abundant in FX and DC, and they had been used as biomarkers for Chlorophyta represented by biomarker contents (Volkman, 2003). Moreover, a previous investigation did not find biomarkers of eustigmatophytes in the aquatic phytoplankton community in FX. However, 1,15-C_{30}-diol and 1,15-C_{32}-diol showed relatively high concentrations in FX, and they have been used as biomarkers of Eustigmatophytes denoted by biomarker MARs or contents in both marine and lacustrine sedimentary environments (Castañeda & Schouten, 2011; Castañeda et al., 2011; van Bree et al., 2018; Volkman et al., 1992). Furthermore, Cyanobacteria, Diatoms, and Dinoflagellates were present in the phytoplankton community in FX. Cholesterol ($C_{27}{}^{5}$) and 24-ethylcholesta-5-en-3 -ol ($C_{29}{}^{5}$) served as biomarkers of cyanobacteria, and 24-ethylcholesta-5-en-3 -ol ($C_{29}{}^{5}$) was present in both cyanobacteria and chlorophyta (Volkman, 2003). As Chlorophyta prevailed in FX and DC, $C_{29}{}^{5}$ also appeared from Chlorophyta in those sediment cores. Similarly, we identified brassicasterol and dinosterol in the two cores and these have been widely used as biomarkers of diatoms and dinoflagellates, respectively (van Bree et al., 2018).

Figure 5 shows the historical changes in MARs for the eight biomarkers in FX and DC. In FX, the deposition profile for the eight biomarkers can be divided into two stages. Wang et al. (2018) found that the changes in sediment accumulation rates corresponded to the effects of diverse types and impacts of human activities during the period 1910 to 1980, and human activities were the main driving factor influencing current changes in the lake sedimentary environment. He et al. (2019) reported that no significant trend occurred in the annual water level fluctuation of Fuxian Lake and Dianchi Lake. The results showed that the eight algae-originated biomarker MARs increased rapidly after the 1990s, which implied that the biomass of phytoplankton increased simultaneously. This result suggested that the sedimentary environment changed significantly in FX in the 1990s. In DC, the deposition profiles for the eight biomarkers are slightly different. The average MAR was 0.43 µg cm^{-2} yr^{-1} before 1990, and it reached 11.1 µg cm^{-2} yr^{-1} from 1990 to 2010. However, the MARs showed a decreasing trend from 2010 to the present. This result suggested that the sedimentary environment in DC changed obviously in 1980 and 2010. After 2000, the impacts of water contaminants were effectively controlled in FX and DC. Hence, controlling measures led to decreasing algal productivity in the two lakes.

4.3 Relationship between Bulk Parameters and Proxies of Primary Productivity

Considering the common post degradation of organic matter in lacustrine systems, the MAR values of multiple parameters are depicted in Figure 3 and Figure 5. MARs for TOC, TN, TP, S2, and biomarkers (sterols and alkyl diols) showed similar patterns in FX and DC. First, TOC, S2, and HI were used as proxies of marine and lacustrine productivity and represented organic matter originating from aquatic plants, phytoplankton, zooplankton, microorganisms, and terrestrial higher plants that were buried and preserved during the deposition processes (Schoepfer et al., 2015). We calculated S2 from the pyrolysis hydrocarbon contents at 300-650°C and represented highly aliphatic macromolecular compounds whose carbon atoms form chains (as in the alkanes), not aromatic rings produced by aquatic phytoplankton (Sanei et al., 2012). High aliphatic macromolecular compounds derived from algal cell walls persist (Sanei et al., 2005) because they show good thermal stability and are preserved in the process of deposition and burial; thus, they can be used as an indicator of AOM. Other environmental factors have played a key role in affecting the growth of phytoplankton. Temperature is one of the major factors controlling algal growth and can indirectly or directly control algal growth (Li et al., 2021). Changes in this species can cause the migration and transformation of nutrients in the aquatic environment, thus changing the composition and concentration level of nutrients used by algal growth. As its change can also cause the algae itself to adjust enzyme activity, it directly affects the growth of algae (Zhang et al., 2020). Nitrogen and phosphorus are essential nutrients for the growth of algae. Among lacustrine ecosystem algal blooms (Yu et al., 2017), nitrogen-restricted blooms occur when the N content is low and exceeds a critical value; phosphorus-restricted blooms occur when the P content is low and exceeds a critical value. We will discuss the above factors in the following sections.

Pearson's correlation analysis was useful in quantitatively assessing the relationship between bulk parameters and lipid biomarkers using SPSS 26.0 (IBM SPSS software). The significant level was set to p<0.05. Pearson's correlation coefficient is a nonparametric rank statistic proposed as a measure of the strength of the association between two variables and is widely used for this purpose (Duan et al., 2015). In this study, we conducted correlation analyses to demonstrate the relationships among bulk parameters, including TOC, TN, TP, S2, HI, and T_5, and biomarkers (sterols and alkyl diols) in FX and DC. The correlation coefficients appear in Table 2. The MAR of different sterols and alkyl diols from the corresponding sources is indicative of algal community changes. . As discussed above, $C_{28}\ ^{5}$, $C_{29}\ ^{22}$, and $C_{29}\ ^{5}$ are biomarkers of Chlorophyta, $C_{27}\ ^{5}$ is a biomarker of cyanobacteria, 1,15-C_{30}-diol and 1,15-C_{32}-diol are biomarkers of eustigmatophytes, brassicasterol is a biomarker of diatoms, and Dinosterol is a biomarker of dinoflagellates. Pearson s correlation coefficients showed significant positive correlations between TOC, HI, and S2 (p < 0.01, r > 0.96) (Table 2), suggesting that the algal components represented by S2 were an important contribution to the sedimentary organic matter in the sediment cores. S2 represents organic matter pyrolysis products, including sterols and alkyl diols derived from AOM. This means that AOM was an important component of SOM. Early diagenesis of organic matter after deposition should be considered to correctly understand the proxies of productivity (S2 and HI). We observed that the degradation of nonhydrolytic nonprotein alkyl carbons was significantly related to oxygen exposure time in marine sediments (Gélinas et al., 2001). Their observations suggested that the S2 fraction would degrade by only 5% over 1000 years. Hence, the degradation of natural organic matter in the sediment cores was not significant after the deposition. Furthermore, Outridge et al. (2007)

used the patterns of S2/RC ratios in a sediment core to analyze the effect of diagenesis on S2. In this study, the S2/RC profiles exhibited increasing trends from the bottom layer to the top layer in FX and DC (Fig. S5), which was consistent with the change trends of biomarker MARs.

As shown in Table 2, positive correlations among HI, $T_{5,}$ and algal biomarkers were significant in DC. Moreover, the HI values and algal biomarkers showed the same trend, and they showed a high positive correlation. Thus, the HI values and algal biomarkers are suitable for reconstructing historical productivity in plateau lakes.

TN showed significant positive correlations with the MAR of Chlorophyta ($p < 0.01$, $r > 0.87$). The historical change in TN MAR is shown in Figure 3. In FX, the changing trend of total TN MAR appeared to occur in two stages, showing a slowly increasing trend before 2000 and a rapidly increasing trend after 2000. The increasing trend of TN MAR was like that of TOC MAR, indicating that the major driving factors may be the same. In DC, the statistical analysis demonstrated that algal biomarkers had positive correlations with T_5. This result indicated that the increase in temperature promoted the growth of algae and elevated algae biomass production. The five algal biomarkers showed significant positive correlations, which implied that increasing biomass production of different algae species may have a common driving factor in FX and DC. Since 1990, nutrients have increased in FX (Gao et al., 2013), and the water quality in the northern and coastal areas has deteriorated. This is related to the discharge of domestic sewage and the pollution of phosphate rock and the phosphorus chemical industry in Chengjiang County, the northern coastal region of Fuxian Lake (Su et al., 2014). As a result, the algae biomass in the water body increased significantly during this period. In DC, the MAR of N and P gradually increased from the lower layer to the upper layer and then stabilized at higher levels from 1990 to 2010 (Fig. 3). This result indicated that frequent human activities and rapid socioeconomic development caused rapid inputs of nutrients in lake water. In addition, the temperature showed an increase (Fig. 2), which promoted the growth of mesophilic algae. Therefore, we recommend the combined use of these proxies, which assists in better understanding the historical algal community changes in plateau lakes.

Principal component analysis (PCA) aimed at using the ideas of dimension reduction, the index is converted into a few more comprehensive indicators, and it is a mathematical transformation method, given by a group of related variables linear transformation into another set of uncorrelated variables, these new variables according to the variance. We performed PCA to identify the major affecting factors in FX and DC. Figure 6 shows the factor loadings of PCA for T_5, TN, TP, OM parameters, and algal biomarkers in FX and DC. We extracted and rotated two components, which accounted for more than 87% of the variance in the dataset. Tables S1 and S2 show the rotated component matrix and component score coefficient matrix in FX and DC. In FX, TN gathered with TOC, S2, HI, and algal biomarkers, while T_5, C/N, and TP were farther from algal biomarkers and the related OM parameters. In DC, TN and T_5 gathered with TOC, S2, HI, and algal biomarkers, while C/N and TP were farther from algal biomarkers and the related OM parameters. The C/N ratios of FX and DC were shown in Table S3. The variation trend of C/N is not obvious, because the sources of carbon and nitrogen in sediments are complex, and are affected by various factors in the process of deposition and burial. For example, early diagenesis and microbial selective degradation of organic matter (protein components are easily degraded) will change the C/N ratio of the initial deposited organic matter (Meyres, 1997). In addition, the hydrodynamic sorting of sediment grain size will also affect the C/N ratio (Thompson and Eglinton, 1979). The C/N ratios in fine grained sediments are generally lower than those in the coarse sediments. Thus, it showed weak correlations with other parameters.

We noted that TP concentrations in the sediment cores of FX (>1.0 mg g^{-1}) and DC (>1.4 mg g^{-1}) were higher than those in other reported lake sediments in China (0.25-1.0 mg g^{-1}) (Wang et al., 2014). The weak correlations with P may be related to the high P concentrations derived from phosphorus ore and the phosphorus chemical industry in FX and DC. Moreover, DC is a shallow lake that is more sensitive to temperature increases. The temperature has been a key factor in controlling algal community distribution in recent years. For example, studies have shown that the functional groups of planktonic algae have shown the characteristics of reduced low-temperature tolerance functional groups and increased trophic functional groups in Fuxian Lake and Dianchi Lake since the 1960s (Dong et al., 2014). As shown in Figure 6, the factor scores of PC1 increased gradually after 1970, then decreased after 1995, and finally gently increased after 2000 in FX. This pattern was consistent with that of temperature at Yuxihongta station (Fig. 2), which indicated that climate change is a suitable interpretation for PC1 in FX. The factor scores of PC2 showed no obvious changes before 2010 but displayed a rapid increase after 2010 in FX. This trend was in line with the TN change trend caused by intensive nutrient input and its long water storage time since 1990 in FX (Ni et al., 2011). Thus, human activity is appropriate to explain PC2 in FX.

In DC, there was a similar trend to FX in PC1. We found a significant peak in PC2 factor scores around 2005 when the water quality deteriorated rapidly (Ni et al., 2011). The sharp reduction occurred between 2005 and 2015 when the local government increased scientific research and environmental protection in DC. This result indicated that pollution controlling measures have achieved a certain effect in recent years. As FX is a deep lake with 167 years of water storage, pollution control measures will have difficulty proceeding with algae blooms. Therefore, we should devote more attention to FX regarding nutrient input control because the increasing trend in PC2 scores reflects continuing human impacts on the lake.

Temperature and nutrients are the main factors affecting the growth of algae. Figure S6 and Figure S7 show the linear regression analysis of T_5 and TN, TP, and five algal biomarkers in FX and DC after the 1950s, respectively. In

FX, the TN showed a significant positive correlation with the algal biomarkers (R^2>0.8, p<0.01), while T_5 and TP showed weak correlations with the algal biomarkers, which suggested that TP and T_5 affected the growth of algae by multiple factors. In DC, TN showed a positive correlation with algal biomarkers (R^2>0.5, p<0.01). This result suggested that TN was the main factor controlling the growth of algae in FX and DC. We performed multiple regression analyses on biomarker MARs and T_5, TN, TP in FX (except TP, t-test of TN and TP failed) and DC. Table 3 shows the multiple regression equations, which confirmed that the temperature and nutrients were significant factors affecting algal growth and displayed different effects on individual algae (from F_1 to F_5). As the coefficients of TN were greater than those of T_5 and TP, TN played a key role in controlling algae growth. This implied that the control of nutrient inputs would improve and will be critical to avoiding algal blooms in plateau lakes.

4.4 Historical Changes in Dinoflagellates, Diatoms, Eustigmatophyte, Cyanobacteria, and Chlorophyta

The results of studies on the evolution of eutrophication and the evolution characteristics of planktonic algae in the three typical lakes of Dianchi, Erhai, and Fuxian Lakes on the Yunnan-Guizhou Plateau showed that the eutrophication sequence and the succession trend of algae functional groups were similar in the two lakes. The succession characteristics of the community are a decrease in low temperature-tolerant species and an increase in trophic species (Ni et al., 2011; Dong et al., 2014). Figure 7 shows that Chlorophyta and Cyanobacteria were the main components of algae communities in the past 100 years. The increase in dinoflagellates and Eustigmatophyte was accompanied by a decrease in diatoms, which was in line with the trend of Lake Malawi in East Africa (Castaneda et al., 2011). Zhang et al. (2015) combined changes in algae biomass in water bodies and used sterol biomarkers in sediments of chlorophyta, dinoflagellates, and diatoms to reflect community changes and indicate changes in nutrient status in water bodies. In addition, the deposition record of total lipids showed higher accumulation rate in the past 100 years than before (Fig. 5). A few natural and anthropogenic factors can lead to an increase in algal biomass, including temperature changes and nutrient load increases. By comparing the MARs of individual algal biomarkers with temperature, TN, and TP (Fig. 3 and Fig. 5), we learned that, since 1980, with the increase in temperature and TN concentration the accumulation rate of algal biomarkers showed an increasing trend in FX. We also found that since 1990, as the temperature increased and the concentrations of TN and TP increased, the accumulation rates of algal biomarkers also showed an increasing trend in DC. Due to its rapid economic development and frequent human activities in recent years, FX became frangible in response to increasing nutrient inputs. In general, TN and temperature were the main factors influencing algal growth, and we should pay more attention to nutrient input control and climate warming in plateau lakes.

1. **Conclusions**

Our investigation revealed the historical changes in TOC, HI, S2, ^{13}C, TN, TP, and algal biomarkers in FX and DC. These results showed that the increased accumulation rates of the algae species were significantly positively correlated with TN and temperature, indicating that the increase in temperature and nutrient load led to increasing primary productivity. This implied that anthropogenic factors were the main driving force influencing lacustrine community changes. The contents of TP, TN, and algal biomarkers have reduced in recent years with efforts by the government's investment in scientific research and concomitant environmental protection. Thus, we should continue to monitor the nutrient inputs and take prevention and control measures in plateau lakes. Moreover, we observed strong positive correlations between HI and algal biomarkers in oligotrophic FX and mesotrophic DC, suggesting that HI was a reliable index for algal productivity in lacustrine sediments. We will investigate more temperature proxies and other geochemical proxies and further study changes in lacustrine ecosystems caused by temperature changes and human activities to provide a scientific basis and advice on organic burial, global warming, and environmental management.

Supporting Information:

The water columns' physicochemical parameters, methods for the instrumental analysis of sterols, and sediment distribution of Pb-210, data tables of biomarker contents, TN, TP, and OM parameters and ratios of C/N, and plots of linear correlation analysis among biomarker contents, organic matter parameters, and nutrients are presented. Other data could be requested from the corresponding authors.

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Tables

Table 1. Sterol (cholesterol, -Sitosterol, brassicasterol, and dinosterol) concentrations in this study and others' reports.

Table 2. Correlations among bulk parameters, T_5, and biomarkers in FX and DC.

Table 3. Multiple regression equations between biomarker mass accumulation rates and T_5, TN, TP in FX and DC.

Figures

Figure 1. Sampling sites.

Figure 2. Five-year average moving temperature and the annual average temperature at Yuxihongta station and Kunming station.

Figure 3. Historical changes in OM parameters in the sediment cores from FX (a) and DC (b). The ^{13}C values corrected for the Suess effect were indicated by hollow circles.

Figure 4. Scatterplots of ^{13}C vs. C/N ratios (a), plankton OM record (b), and the proportional contributions of OM from different end members (c: FX, d: DC) for sediments in FX and DC.

Figure 5. Historical changes in mass accumulation rates of biomarkers from sediment cores in FX (a) and the DC (b).

Figure 6. PCA analysis for T_5, TN, TP, OM parameters, and algal biomarkers in FX and DC.

Figure 7. Historical changes of Dinoflagellates, Diatoms, Eustigmatophyte, Cyanobacteria, and Chlorophyta in FX (a) and DC (b).

Table 1. Sterol (cholesterol, -Sitosterol, brassicasterol, and dinosterol) concentrations in this study and others' reports.

	Lake	Cholesterol g g^{-1} dw	-Sitosterol	Brassicasterol	
Surface Sediment (0-1cm)	Baldegg	44.4	26.6	13.8	Ladd et al., 2018
	Greifen	35.2	18.7	16.0	
	Inkwil	14.3	13.8	3.0	
	Lucerne	4.3	6.4	3.9	
	Mauen	14.6	21.2	35.4	
	Rot	160.8	116.6	20.3	
	Sarnen	1.9	2.9	1.0	
	Soppen	93.9	81.8	53.1	
	Thun	1.2	2.9	1.1	
0-2 cm	FX	7.46	9.34	2.38	This study
	DC	25.7	13.9	3.80	
	Lake	Cholesterol g g^{-1} TOC	-Sitosterol	Dinosterol	
Surface Sediment (0-4cm)	TIZO	310	530	620	Schwab et al., 2015
	TABE	280	400	50	
	BALE	130	200	500	
	MANE	90	400	100	
	BARO	90	300	50	
	DEBU	100	260	260	
	OSSA	20	410	-	
2-4 cm	FX	115	121	82.0	This study
	DC	253	216	24.2	

Table 2. Correlations among bulk parameters, T_5, and biomarkers in FX and DC.

	TOC FX	HI	S2	T_5	TN	TP	Chlorophyta	Cyanobacteria
TOC	1	0.996**	0.983**	0.151	0.992**	-0.244	0.983**	0.944**
HI		1	0.969**	0.126	0.993**	-0.247	0.987**	0.933**
S2			1	0.229	0.967**	-0.183	0.948**	0.933**
T_5				1	0.082	-0.308	0.105	0.194
TN					1	-0.222	0.970**	0.909**
TP						1	-0.261	-0.252
Chlorophyta							1	0.969**

Cyanobacteria								1
Eustigmatophyte								
Diatoms								
Dinoflagellates								
	DC							
TOC	1	0.988**	0.981**	0.784**	0.996**	0.837**	0.842**	0.851**
HI		1	0.989**	0.716**	0.985**	0.834**	0.856**	0.880**
S2			1	0.736**	0.972**	0.872**	0.825**	0.842**
T_5				1	0.779**	0.631*	0.561*	0.648**
TN					1	0.800**	0.870**	0.870**
TP						1	0.523*	0.593*
Chlorophyta							1	0.879**
Cyanobacteria								1
Eustigmatophyte								
Diatoms								
Dinoflagellates								

*Significant correlation at p<0.05 (Two-tailed); **Significant correlation at p<0.01 (Two-tailed).

Table 3. Multiple regression equations between biomarker mass accumulation rates and T_5, TN, TP in FX and DC.

Multiple regression equations		
	FX	DC
	T_5 (x_1); TN (x_2); TP (x_3)	
Chlorophyta (F_1)	F_1 = -0.27x_1+4.05x_2+4.03 (R^2 = 0.94, p < 0.01)	F_1 = 0.01x_1+7.91x_2-16.5
Cyanobacteria (F_2)	F_2 = -0.01x_1+1.77x_2+0.21 (R^2 = 0.84, p < 0.01)	F_2= 0.19x_1+4.66x_2-7.11
Eustigmatophyte (F_3)	F_3 = -0.29x_1+4.45x_2+4.22 (R^2 = 0.94, p < 0.01)	F_3 = -0.09x_1+0.22x_2+1.9
Diatoms (F_4)	F_4 = -0.12x_1+1.85x_2+1.75 (R^2 = 0.92, p < 0.01)	F_4 = -0.05x_1+0.97x_2-1.5
Dinoflagellates (F_5)	F_5 = -0.19x_1+2.33x_2+2.72 (R^2 = 0.95, p < 0.01)	F_5 = 0.03x_1+0.54x_2-1.05