The Impact of Climatic and Environmental Factors on $n$-Alkanes Indices in Southwestern Tibetan Plateau

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Abstract

$n$-Alkanes are widely used in paleoenvironmental reconstructions. However, our understanding of changes in the distribution of $n$-alkanes with climatic and environmental factors remains unclear in arid/semi-arid regions. We sampled 26 surface sediments from three climatic zones across the southwestern Tibetan Plateau to evaluate the sensitivity of chain length distributions of $n$-alkanes to climatic and environmental parameters. Our observations demonstrate that average chain length (ACL), proportion of aquatic macrophyte (Paq), carbon preference index (CPI) and ratio of the contents of $n$C$_{27}$ and $n$C$_{31}$ ($n$C$_{27}$/nC$_{31}$) are all sensitive to hydroclimatic conditions. In contrast to commonly-adopted assumptions, the correlations between these indices and hydrological parameters are not always good, which indicates that the $n$-alkane indices have unique influences on the southwestern Tibetan Plateau. These might be related to the vegetation characteristics and seasonality of biological activity, and need to be considered in paleoclimatic reconstruction. The impact of seasonal precipitation on $n$-alkanes indices was also evaluated.

Key words: $n$-alkanes; ACL; Tibetan Plateau; climate; environment

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1. Introduction

In organic geochemistry, $n$-alkane proxies have been widely used for paleoenvironmental and paleoclimatic reconstruction as they are chemically stable during the degradation process, and can be used to trace particular source organisms (Lin et al., 2008; Pu et al., 2009, 2010; Castañeda and Schouten, 2011).
Many studies have tried to explain the distribution characteristics of $n$-alkanes in sediments (Rao et al., 2009; Bush and McInerney, 2015), but their interpretation is often difficult and depends on detailed insights gained from studies of living plants (Hoffmann et al., 2013). Based on the knowledge of $n$-alkanes in plants, $n$-alkane indices have been developed to infer climate-induced changes recorded in lake sediments and peat sequences (Zheng et al., 2009; Long et al., 2011; Liu et al., 2015). For example, average chain length (ACL) is commonly used to characterize the chain length distribution of $n$-alkanes. Studies of numerous living plants show mostly positive correlations between ACL and temperature (Tipple and Pagani, 2013; Badewien et al., 2015; Bush and McInerney, 2015; Feakins et al., 2016; Wang et al., 2018), but some have shown significant correlation with annual precipitation and humidity (Hoffmann et al., 2013; Diefendorf and Freimuth, 2017). In addition, the response characteristics of ACL to temperature or humidity vary between species: for example, Hoffmann et al. (2013) discovered that ACL of Eucalyptus and Acacia show different correlations with humidity, precipitation and aridity. These findings imply that paleoclimatic implications of the ACL index might be dependent on specific regional conditions, and that biochemical differences between species also lead to substantial compositional differences in $n$-alkanes.

The proportion of aquatic macrophyte (Paq) is a proxy used to estimate the contributions of $n$-alkanes from submerged/floating plants relative to the contributions from emerged and terrigenous plants (Ficken et al., 2000). This index is useful for assessing changes in lake level fluctuations, which are correlated with the effective humidity (Seki et al., 2009). Generally, higher Paq values indicate a greater contribution from submerged/floating plants, thus indicating lake expansion and higher moisture levels (Ficken et al., 2000; Sun et al., 2013); conversely, lower Paq values may indicate a lower lake level, hence a drier climate. The Carbon Preference Index (CPI) is an important parameter describing the molecular distribution characteristics (odd-to-even carbon number predominance) of long-chain $n$-alkanes, and has been widely used in late Quaternary paleoclimate reconstructions as a preservational indicator (Wang et al., 2004; Liang et al., 2005; Zheng et al., 2007; Yang et al., 2008; Hyun et al., 2017). Higher temperature and precipitation may favor microbial activity and degradation, resulting in lower CPI values in soil samples, while low temperature and precipitation may have the opposite effects (Yamada et al., 1999; Xie et al., 2004). In contrast, other studies have indicated that microbial diagenesis was inhibited under cool and humid conditions, which will yield relatively higher CPI values (Rao et al., 2009). Inconsistent results impede the application of $n$-alkane distributions in paleoclimatic reconstruction.

The implications of $n$-alkane indices vary between different regions, such that it is necessary to collect samples of modern conditions in each region. Therefore, we investigated the $n$-alkanes of surface sediments on the southwestern Tibetan Plateau to understand the influences of climatic and environmental factors on the composition of $n$-alkanes, thus providing a basis for paleoclimatic reconstruction using the $n$-alkanes proxy in this region.

1. Material and Methods

2.1. Site description and samples

The study area is located on the southwestern Tibetan Plateau (Fig. 1), which straddles three climate zones (North Qiangtang in the cold and arid climate zone, South Qiangtang in the cold and semi-arid climate zone, and Naqu in the sub-cold semi-humid climate zone). Average annual precipitation ranges from 66 to 465 mm, with maximum and minimum precipitation occurring in eastern Ando county and western Rito county, respectively. Average annual air temperature ranges from -0.4 to 2.1 °C. Average relative humidity and average annual evaporation range from 31 to 52% and 1749 to 2486 mm, respectively. The 26 surface sediments were collected from Tibetan lakes and puddles on June, 2012, and kept dry until analysis. Locations of the sampling sites are shown in Table 1.
**Fig. 1** Map showing the sampled lakes and puddles on the Tibetan Plateau

**Table 1** Locations of lakes and puddles used in this study, and corresponding $n$-alkane parameters.

<table>
<thead>
<tr>
<th>Number</th>
<th>Names of lakes and puddles</th>
<th>Latitude</th>
<th>Longitude</th>
<th>$C_{\text{max}}$</th>
<th>CPI$_{22-34}$</th>
<th>ACL$_{25-35}$</th>
<th>Paq</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Southwest Lake of Bangong Co</td>
<td>33.44°N</td>
<td>79.76°E</td>
<td>$nC_{23}$</td>
<td>4.45</td>
<td>29.15</td>
<td>0.63</td>
</tr>
<tr>
<td>2</td>
<td>Shiquan River</td>
<td>33.02°N</td>
<td>79.81°E</td>
<td>$nC_{31}$</td>
<td>4.63</td>
<td>29.63</td>
<td>0.42</td>
</tr>
<tr>
<td>3</td>
<td>Angla Co</td>
<td>33.57°N</td>
<td>79.95°E</td>
<td>$nC_{29}$</td>
<td>6.18</td>
<td>29.51</td>
<td>0.45</td>
</tr>
<tr>
<td>4</td>
<td>Cuoga Lake</td>
<td>33.12°N</td>
<td>80.24°E</td>
<td>$nC_{23}$</td>
<td>6.20</td>
<td>29.69</td>
<td>0.51</td>
</tr>
<tr>
<td>5</td>
<td>Kanzhong Lake</td>
<td>33.10°N</td>
<td>80.37°E</td>
<td>$nC_{31}$</td>
<td>6.34</td>
<td>30.03</td>
<td>0.30</td>
</tr>
<tr>
<td>6</td>
<td>East Lake of Bieruoze Co</td>
<td>32.42°N</td>
<td>83.01°E</td>
<td>$nC_{16}$</td>
<td>4.43</td>
<td>30.09</td>
<td>0.24</td>
</tr>
<tr>
<td>7</td>
<td>Wuma Co</td>
<td>32.44°N</td>
<td>83.20°E</td>
<td>$nC_{16}$</td>
<td>3.26</td>
<td>29.79</td>
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<tr>
<td>8</td>
<td>Darebu Co</td>
<td>32.44°N</td>
<td>83.21°E</td>
<td>$nC_{31}$</td>
<td>4.81</td>
<td>30.05</td>
<td>0.28</td>
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<tr>
<td>9</td>
<td>Northwest Lake of Pudang Co</td>
<td>32.36°N</td>
<td>83.70°E</td>
<td>$nC_{31}$</td>
<td>6.03</td>
<td>30.11</td>
<td>0.09</td>
</tr>
<tr>
<td>10</td>
<td>Pudang Co</td>
<td>32.34°N</td>
<td>83.73°E</td>
<td>$nC_{31}$</td>
<td>7.48</td>
<td>30.09</td>
<td>0.13</td>
</tr>
<tr>
<td>11</td>
<td>Lagkor Co</td>
<td>32.03°N</td>
<td>84.12°E</td>
<td>$nC_{31}$</td>
<td>8.72</td>
<td>30.01</td>
<td>0.11</td>
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<tr>
<td>12</td>
<td>Tong Tso</td>
<td>31.18°N</td>
<td>84.68°E</td>
<td>$nC_{21}$</td>
<td>7.80</td>
<td>29.83</td>
<td>0.34</td>
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<tr>
<td>13</td>
<td>West Lake of Selin Co</td>
<td>31.79°N</td>
<td>88.45°E</td>
<td>$nC_{16}$</td>
<td>3.52</td>
<td>30.42</td>
<td>0.14</td>
</tr>
<tr>
<td>14</td>
<td>Southwest Lake of Selin Co</td>
<td>31.67°N</td>
<td>88.82°E</td>
<td>$nC_{31}$</td>
<td>10.52</td>
<td>30.20</td>
<td>0.20</td>
</tr>
<tr>
<td>15</td>
<td>South Lake of Selin Co</td>
<td>31.54°N</td>
<td>88.87°E</td>
<td>$nC_{31}$</td>
<td>4.41</td>
<td>30.17</td>
<td>0.22</td>
</tr>
<tr>
<td>16</td>
<td>East Lake of Bangkog Co</td>
<td>31.62°N</td>
<td>89.60°E</td>
<td>$nC_{23}$</td>
<td>3.59</td>
<td>29.90</td>
<td>0.45</td>
</tr>
<tr>
<td>17</td>
<td>East puddle of Bangkog Co</td>
<td>31.61°N</td>
<td>89.61°E</td>
<td>$nC_{31}$</td>
<td>12.63</td>
<td>30.44</td>
<td>0.16</td>
</tr>
<tr>
<td>18</td>
<td>West puddle of Lamu Co</td>
<td>31.47°N</td>
<td>89.81°E</td>
<td>$nC_{31}$</td>
<td>7.84</td>
<td>29.98</td>
<td>0.36</td>
</tr>
<tr>
<td>19</td>
<td>Cimagu Lake</td>
<td>31.48°N</td>
<td>89.87°E</td>
<td>$nC_{31}$</td>
<td>10.44</td>
<td>30.31</td>
<td>0.30</td>
</tr>
<tr>
<td>20</td>
<td>Cuoqiong Lake</td>
<td>31.47°N</td>
<td>89.89°E</td>
<td>$nC_{31}$</td>
<td>9.04</td>
<td>30.28</td>
<td>0.25</td>
</tr>
</tbody>
</table>

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2.2. Laboratory methods

All the analyses were conducted at the National Research Center for Geoanalysis, China. After the removal of modern rootlets and gravels via a 40 mesh sieve, each sample was Soxhlet extracted with 9:1 (v/v) dichloromethane:methanol for 48 h. Total extracts were filtered with cotton in funnels and evaporated under \( \text{N}_2 \). The alkanes were eluted with \( \text{n-} \)pentane from the total lipid extracts over an activated silica column. The eluent was concentrated and ready for analysis by gas chromatography (GC).

GC analyses were performed using a Shimadzu 2010 series instrument equipped with an Agilent DB-1MS GC column (30 m × 0.25 mm × 0.25 μm) and flame ionization detector (FID). For \( \text{n-} \)alkanes quantification, peak areas were compared with those of an external \( \text{n-} \)alkanes standard mixture (C7-C40).

The oven temperature for analyzing alkanes was programmed from 60 to 320 °C at 3 °C/min and then remained isothermal for 40 min. Reproducibility of \( \text{n-} \)alkanes concentrations was better than 5%.

2.3. Data analysis

Using the concentration data, various indices were used to characterize the \( \text{n-} \)alkane distributions. ACL\(_{27-35}\), CPI\(_{22-34}\), and Paq were calculated using the following equations:

\[
\text{ACL}_{27-35} = \frac{27 \times C_{27} + 29 \times C_{29} + 31 \times C_{31} + 33 \times C_{33} + 35 \times C_{35}}{C_{27} + C_{29} + C_{31} + C_{33} + C_{35}}
\]

\[
\text{Paq} = \frac{C_{23}}{C_{23} + C_{31} + C_{33} + C_{35}}
\]

\[
\text{CPI}_{22-34} = 0.5 \times \left( \frac{\sum C_{23} \cdot C_{33} \text{ (odd)}}{\sum C_{24} \cdot C_{34} \text{ (even)}} \right) + \left( \frac{\sum C_{23} \cdot C_{33} \text{ (odd)}}{\sum C_{22} \cdot C_{32} \text{ (even)}} \right)
\]

Here, \( C_i \) denotes the concentration of \( \text{n-} \)alkanes whose carbon chain length is \( i \).

2.4. Climate data

Climate data for the meteorological stations was obtained from https://en.climate-data.org for cities worldwide and from the meteorological data center of the China Meteorological Administration (http://data.cma.cn). The climate data for the sampling sites include mean annual precipitation (MAP), mean annual spring precipitation (MAP-spr), mean annual summer precipitation (MAP-sum), mean annual precipitation (MAP-sum), and mean annual temperature (MAP-tem).
autumn precipitation (MAP-aut), mean annual winter precipitation (MAP-win), mean annual temperature (MAT), mean annual evaporation (MAE) and relative humidity (RH) were estimated by meteorological interpolation using the software ArcGIS (Supplementary Data 1).

2. Results and discussion

3.1. Distribution of the \( n \)-alkanes

\( n \)-Alkanes from \( C_{15} \) to \( C_{35} \) were identified in the sediments at concentrations ranging from 0.003 to 10.8 \( \mu g/g \). The \( n \)-alkane pattern of most surface samples is dominated by mid-chain \( n \)-alkanes from submerged macrophytes and/or long chain \( n \)-alkanes from emergent macrophytes or terrestrial vegetation (Lakes 1-5, 9, 11, 12, 14-19, 21-24, 26; Fig. 2a and 2b). In contrast, short chain homologues occur in significant amounts only in two lakes (Lakes 6, 7; Fig. 2c). In the other five lakes, both short and long chain \( n \)-alkanes are dominant (Lakes 8, 10, 13, 20, 25; Fig. 2d).

Table 1 provides some parameters describing \( n \)-alkane distributions in the surface sediments of lakes sampled in Tibet. All samples showed strong odd-numbered carbon dominance with CPI\(_{22-34}\) values ranging from 3.26 to 12.63 (Table 1). ACL\(_{27-35}\), Paq and \( nC_{27}/nC_{31} \) values vary from 29.15 to 30.67, 0.07 to 0.63 and 0.2 to 1.6, respectively.

![Fig. 2 Molecular distributions of \( n \)-alkanes in the lakes and puddles sampled.](image)

3.2 The relationship between ACL and climatic parameters

We performed redundancy analysis (RDA) and correlation analysis using Canoco and SPSS on the \( n \)-alkane proxies (ACL, CPI, Paq, \( nC_{27}/nC_{31} \)) and environmental parameters to determine which factors potentially affect \( n \)-alkane proxies in lakes and puddles on the southwestern Tibetan Plateau. All variables were standardized before performing RDA. The result of a Monte Carlo test with \( P < 0.002 \) shows that the effects of climate and environment on \( n \)-alkane proxies reached a very high significance level.

To understand the climatic implications of the ACL index, we compare ACL with climatic and environmental data. Fig. 3 shows that ACL is mainly affected by LAT, LOT, ALT, MAP, MAE, RH,
MAP-spr, MAP-sum, MAP-aut and MAP-win. ACL increases with increasing longitude from west to east, and as latitude decreases from north to south (Fig. 4). A study of deciduous leaf n-alkanes also showed that ACL values increased with decreasing latitude in Europe (Sachse et al., 2006). In addition, the correlations of environmental parameters with ACL$_{27-35}$ are better than those with ACL$_{27-33}$ (Fig. 4), perhaps because there are more grasses than trees on the southwestern Tibetan Plateau, with grasses being more likely to produce very long chain n-alkanes. This principle also applies to the correlation between Paq and environmental parameters in this region. Therefore, we suggest that very long-chain n-alkanes should be added to proxy formulas in the arid/semi-arid region.

**Fig. 3** RDA of ACL.

Environmental parameters include: LAT, latitude; LOT, longitude; ALT, altitude; WT, water temperature; Cond, conductivity; DO, dissolved oxygen; pH, MAP, mean annual precipitation; MAP-spr, mean spring precipitation; MAP-sum, mean summer precipitation; MAP-aut, mean autumn precipitation; MAP-win, mean winter precipitation; MAT, mean annual temperature; MAE, mean annual evaporation; RH, relative humidity.
Significant positive correlations were found between ACL values and MAP ($r=0.653^{**}$, $p < 0.001$), ACL values and MAE ($r=0.686^{**}$, $p < 0.001$), ACL values and RH ($r=0.664^{**}$, $p < 0.001$, Fig. 4). This indicates that water availability and evapotranspiration were the major drivers of leaf wax n-alkane chain length distribution on the southwestern Tibetan Plateau. It is widely believed that the main function of the plant’s epicuticular wax is to maintain water balance of the blade: long chain alkanes (with greater ACL) would be preferentially synthesized in leaf wax to increase the water-holding ability of the plants as the climate gets drier, such that humidity and ACL are negatively correlated (Schefuß et al., 2003). This contradicts our result that humidity and ACL are positively correlated, indicating that the climatic interpretation of ACL is not applicable to all regions and that an alternative may be needed in the arid/semi-arid regions. For example, the studies of Hu et al. (2014) and Jia et al. (2016) also showed positive correlations between ACL and annual precipitation in the surface lake sediments and soils on the Tibetan Plateau. Although the driving mechanism of this relationship is not yet understood, some plant-based evidence is available. Hoffmann et al. (2013) discovered that the ACL of Eucalyptus and Acacia are correlated significantly with variables reflecting the sample site hydrological conditions (RH, MAP and aridity), but in opposite directions. ACL for Eucalyptus n-alkanes decreased from the moist northern sites towards the arid south, but the opposite trend was observed for Acacia. The reason for the reversed n-alkane ACL vs. hydroclimate relationships between these two genera remains unknown but may be related to known evolutionary differences between Acacia and Eucalyptus.

There is an inverse correlation between ACL and annual winter precipitation (MAP-win) ($r=-0.597^{**}$, $p < 0.001$), and positive correlation between ACL and precipitation in spring, summer, autumn (MAP-spr, MAP-sum, MAP-aut) (Table 2, Fig. 5). This indicates that the influence of winter precipitation (snow melt water) on ACL follows expected patterns, i.e. the plants will synthesize more long-chain n-alkanes to maintain water when the melt water is limited. However, the opposite correlation in the ACL-MAP formula is due to the effects of spring, summer and autumn precipitation, probably because of the different physiological feedback mechanisms in plants on the arid/semi-arid Tibetan Plateau.
Table 2 Correlation coefficients between environmental viables and ACL, Paq, CPI, nC27/nC31

<table>
<thead>
<tr>
<th>Environmental viables</th>
<th>Correlation coefficient</th>
<th>ACL</th>
<th>Paq</th>
<th>CPI</th>
<th>nC27/nC31</th>
</tr>
</thead>
<tbody>
<tr>
<td>LAT</td>
<td>-0.720**</td>
<td>0.569**</td>
<td>-0.484*</td>
<td>0.701**</td>
<td></td>
</tr>
<tr>
<td>LOT</td>
<td>0.725**</td>
<td>-0.532**</td>
<td>0.483*</td>
<td>-0.646**</td>
<td></td>
</tr>
<tr>
<td>ALT</td>
<td>0.682**</td>
<td>-0.400</td>
<td>0.455*</td>
<td>-0.599**</td>
<td></td>
</tr>
<tr>
<td>WT</td>
<td>-0.327</td>
<td>0.486*</td>
<td>-0.043</td>
<td>0.344</td>
<td></td>
</tr>
<tr>
<td>Cond</td>
<td>-0.131</td>
<td>0.445</td>
<td>-0.009</td>
<td>0.39</td>
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</tr>
<tr>
<td>DO</td>
<td>-0.497</td>
<td>0.523**</td>
<td>-0.146</td>
<td>0.423</td>
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<tr>
<td>pH</td>
<td>0.188</td>
<td>0.157</td>
<td>-0.061</td>
<td>0.033</td>
<td></td>
</tr>
<tr>
<td>MAP</td>
<td>0.654**</td>
<td>-0.496**</td>
<td>0.390</td>
<td>-0.572**</td>
<td></td>
</tr>
<tr>
<td>MAT</td>
<td>0.092</td>
<td>-0.199</td>
<td>-0.244</td>
<td>-0.117</td>
<td></td>
</tr>
<tr>
<td>MAE</td>
<td>-0.685**</td>
<td>0.539**</td>
<td>-0.460*</td>
<td>0.620**</td>
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</tr>
<tr>
<td>RH</td>
<td>0.664**</td>
<td>-0.471</td>
<td>0.399</td>
<td>-0.600**</td>
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<tr>
<td>MAP-spr</td>
<td>0.548**</td>
<td>-0.286</td>
<td>0.317</td>
<td>-0.406</td>
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<tr>
<td>MAP-sum</td>
<td>0.720**</td>
<td>-0.509**</td>
<td>0.460</td>
<td>-0.619**</td>
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<tr>
<td>MAP-aut</td>
<td>0.677**</td>
<td>-0.449</td>
<td>0.446</td>
<td>-0.567**</td>
<td></td>
</tr>
<tr>
<td>MAP-win</td>
<td>-0.597**</td>
<td>0.544**</td>
<td>-0.532**</td>
<td>0.615**</td>
<td></td>
</tr>
</tbody>
</table>

ACL has also been reported to be positively related to temperature, because plants prefer to biosynthesize longer-chain compounds with higher melting points for their waxy coatings in warm regions and shorter chain compounds in cooler regions (Bush and Mcinerney, 2015). However, our research shows that ACL values did not correlate with any temperature parameters (Fig. 3; Table 2). This is probably because humidity has a greater influence on n-alkanes ACL than temperature in the arid/semi-arid region. Indeed, at a global scale, temperature does not appear to be a strong control on ACL, likely because of differences in ACL among species (Diefendorf et al., 2017).

3.3 The relationship between Paq and climatic parameters

We now consider the Paq index, which our comparison suggests is best represented as nC27/(nC23+nC31+nC33+nC35). Fig. 6 shows that Paq is mainly affected by LAT, LOT, WT, DO, MAP, MAE, MAP-sum and MAP-win. There is negative correlation between Paq and MAP (r=-0.496**, p < 0.05, Fig. 7), and positive correlation between Paq and MAE (r=0.539**, p < 0.005, Fig. 7). This is inconsistent with previous assumptions that higher and lower Paq values indicate higher and lower humidity, respectively (Ficken et al., 2000; Sun et al., 2013). In the arid/semi-arid regions, underground water availability may increases as the climate gets drier, so Paq could be high even if mean annual precipitation is low; however, positive correlation was observed between winter precipitation (MAP-win) and Paq (Table 2), showing that the Paq index of n-alkanes on the southwestern Tibetan Plateau reflects the humidity in winter.

In addition to hydrological factors, Paq is weakly correlated with water temperature (WT) and dissolved oxygen (DO) (Fig. 7; Table 2). WT and DO of lakes and puddles all show positive correlation with the Paq of n-alkanes, i.e., Paq increases as temperature or dissolved oxygen increase.
3.4 The relationship between CPI and climatic parameters

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In this study, CPI\textsubscript{22-34} is mainly affected by LAT, LOT, ALT, MAE and MAP-win (Fig. 8). CPI\textsubscript{22-34} values of long chain \textit{n}-alkanes extracted from surface sediments across the southwestern Tibetan Plateau displayed a generally decreasing trend from low to high latitudes \((r=-0.484^*,~p<0.05,\) Fig. 8), and from high to low longitudes \((r=0.483^*,~p<0.05,\) Fig. 9). The correlation between surface sedimentary \textit{n}-alkanes CPI values and latitudes, longitudes may imply their environmental significance on the southwestern Tibetan Plateau. Moreover, CPI\textsubscript{22-34} values show weak positive correlation with MAP, RH and negative correlation with MAE (Fig. 9; Table 2), such that higher CPI values correspond to higher humidity and weaker evaporation: this is in contradiction with some previous research where, in general, higher CPI values correlate with cold and dry periods while lower values correlate with warm and wet periods (Xie et al., 2004; Liu and Huang, 2005; Zhang et al., 2006; Luo et al., 2012). This close relation between CPI and climate probably results from differences in the extent of microbial degradation of long-chain \textit{n}-alkanes. In the warm and humid conditions such as those in the southern peatlands, enhanced rates of microbial degradation will decrease the CPI values. However, other studies have indicated that microbial activity is inhibited in cool and humid conditions, a factor that will help preserve plant \textit{n}-alkanes and hence yield relatively higher CPI values (Rao et al., 2009). This is consistent with our research. Considering the arid climate of our study region (MAP ranges from 66 to 465 mm), microbial activities may be limited, such that the CPI of surface sedimentary \textit{n}-alkanes are more likely to maintain the molecular characteristics of the leaf waxes of overlying vegetation, and will be less strongly affected by microbial activities alone. Therefore, the spatial variations of CPI on the Tibet will certainly be affected by other factors in addition to microbial activities: these could include the plant community, the nutrient status of the sediments, and the local microbial community (Huang et al., 2016).

Likewise, the significant negative correlation between CPI and MAP-win (Table 2) indicates that winter precipitation (snow melt-water) had the strongest contribution to CPI index, similarly to the ACL and Paq indices. However, due to additional effects of MAP-spr, MAP-sum and MAP-aut, the relationship between CPI and climatic parameters for the whole year is different from generally accepted patterns.

![Fig. 8 RDA of CPI.](image)

Environmental parameters include: LAT, latitude; LOT, longitude; ALT, altitude; WT, water temperature; Cond, conductivity; DO, dissolved oxygen; pH; MAP, mean annual precipitation; MAP-spr, mean spring precipitation; MAP-sum, mean summer precipitation; MAP-aut, mean autumn precipitation; MAP-win, mean winter precipitation; MAT, mean annual temperature; MAE, mean annual evaporation; RH, relative
3.5 The relationship between $nC_{27}/nC_{31}$ and climatic parameters

The carbon number of the most abundant homologue has been used to indicate vegetation type. For example, the ratio of $nC_{27}/nC_{31}$ has been used to infer vegetation type (tree/grass) changes. The $nC_{27}/nC_{31}$ of n-alkanes in most Tibetan lakes and puddles is less than 1, which indicates that herbaceous plants are relatively dominant in this region. The one exception is the Southwest Lake of Bangong Co, where $nC_{27}/nC_{31}$ is 1.55, indicating the dominance of woody plants.

Fig. 10 shows that $nC_{27}/nC_{31}$ is mainly affected by LAT, LOT, ALT, MAP, MAE, RH, MAP-sum, MAP-aut and MAP-win. There is a significant correlation between $nC_{27}/nC_{31}$ index and hydrological factors, like MAP ($r=-0.572**$, $p<0.001$), MAE ($r=0.620**$, $p<0.001$) and RH ($r=-0.600**$, $p<0.001$), except for the Southwest Lake of Bangong Co (blue point in Fig. 11) which is a notable outlier in the data set. There appears to be a threshold $nC_{27}/nC_{31}$ index separating the contrasting relationships between climatic and environmental parameters. Specifically, when herbaceous plants are dominant in the region, they become more prosperous as the climate gets wetter. On the other hand, MAP-win shows positive correlation with $nC_{27}/nC_{31}$ index ($r=0.615**$, $p<0.001$), which is consistent with the widely-held view that herbaceous plants become more abundant as the humidity decreases.
**Fig. 10** RDA of $nC_{27}/nC_{31}$.

Environmental parameters include: LAT, latitude; LOT, longitude; ALT, altitude; WT, water temperature; Cond, conductivity; DO, dissolved oxygen; pH; MAP, mean annual precipitation; MAP-spr, mean spring precipitation; MAP-sum, mean summer precipitation; MAP-aut, mean autumn precipitation; MAP-win, mean winter precipitation; MAT, mean annual temperature; MAE, mean annual evaporation; RH, relative humidity.

**Fig. 11** Linear correlation between $nC_{27}/nC_{31}$ and LAT (latitude), LOT (longitude), ALT (altitude), MAP (mean annual precipitation), MAE (mean annual evaporation), RH (relative humidity).
3.6 Implications for paleoclimatic studies

Our study shows that molecular distributions of n-alkanes are affected by environmental variables, especially the hydrological parameters. As a consequence, changes in distributions of n-alkanes in sediments could potentially be used as a proxy for paleoclimatic, paleoenvironmental and paleoaltitude reconstruction. However, the main drawbacks of these proxies are encountered in dry climates. For example, our results support the large-scale correlation between n-alkane indices and MAP-win, but differ from previous regional studies: instead, we observe a significant but reversed correlation between n-alkane indices and MAP. These reversed trends in the relationships of n-alkane indices with the climatic factors (Table 2) across the southwestern Tibetan Plateau imply that paleoclimatic implications of n-alkane indices might be dependent on specific regional conditions. Therefore, common assumptions on the variations in n-alkane indices under different climatic and environmental conditions are not robust features for all regions, necessitating caution when employing ACL, Paq, CPI and nC27/nC31 as climate proxies. Studies that have combined n-alkane concentrations with other indices appear to the most successful for assessing changes in the interpretation of proxies during paleoclimate reconstruction.

4. Conclusions

We present an analysis of n-alkanes in surface sediment samples from the southwestern Tibetan Plateau, covering a large geographical area that includes three climate zones. We conclude the following:

1. ACL, Paq, CPI, nC27/nC31 are all affected by LAT, LOT, ALT and hydrological factors, including MAP, MAE and RH. Hydrology is an important factor controlling the distribution of n-alkanes in sediments on the southwestern Tibetan Plateau. Paq is also influenced by WT and DO of water.

2. We observe a significant but opposing correlations between n-alkane indices and climatic factors, which may be caused by differences between species, seasonality and other reasons. The significant correlation between these indices and winter precipitation indicates that snow melt-water played a dominant role.

3. Care is needed when applying these indices as paleoclimatic proxies; for example, detailed information on vegetation structure is also needed. More studies are certainly required to better understand n-alkane proxies, because of the high variability in sources of n-alkanes in modern sediments and the unique climate of the arid/semi arid southwestern Tibetan Plateau.

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