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Influence of aquatic plants on the hydrogen isotope composition of sedimentary long-chain *n*-alkanes in the Lake Qinghai region, Qinghai-Tibet Plateau

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Abstract The hydrogen isotopic composition (δD) of leaf wax long-chain *n*-alkanes (C_{27}, C_{29}, and C_{31}) from lacustrine sediments has been widely applied to reconstruct terrestrial paleoclimatic and paleohydrological changes. However, few studies have addressed whether the aquatic-derived *n*-alkanes can affect the δD values of lake sedimentary long-chain *n*-alkanes, which are usually regarded as a recorder of the terrestrial hydrological signals. Here we systematically investigated δD values of long-chain *n*-alkanes from modern aquatic plants, both near-shore and off-shore surface sediments, surrounding terrestrial plant litters, as well as river water and lake water in Lake Qinghai and its satellite lakes on the northeastern Qinghai-Tibet Plateau. Our data showed that (i) δD values of long-chain *n*-alkanes from aquatic plants varied from −184‰ to −132‰ for *n*-C_{27}, from −183‰ to −138‰ for *n*-C_{29}, and from −189‰ to −130‰ for *n*-C_{31}, respectively, with no significant differences among the three *n*-alkanes homologues; (ii) δD values of long-chain *n*-alkanes from aquatic plants were generally more positive than those from surrounding terrestrial plants, possibly because that they recorded the D-enrichment of lake water in this semi-arid region; (iii) δD values of long-chain *n*-alkanes from surface sediments showed significant differences among the three *n*-alkanes homologues, due to the larger aquatic input of *n*-C_{27} to the sedimentary lipid pool than that of *n*-C_{31}, and (iv) *n*-C_{27} δD values of near-shore aquatic plants and near-shore sediments are more negative than those from off-shore as a result of lower δD values of near-shore lake water. Our findings indicate that in this region (i) the offset between sedimentary *n*-C_{27} and *n*-C_{31} δD values ($\Delta\delta D_{C27\text{-}C31}$) could potentially be used to evaluate if sedimentary long-chain *n*-alkanes are derived from a single source; (ii) while δD values of *n*-C_{27} may be influenced by lake water hydrological changes, sedimentary *n*-C_{31} is derived predominantly from terrestrial plants and thus its δD can serve as a relatively reliable indicator for terrestrial paleoclimatic and paleohydrological reconstructions.

Keywords Hydrogen isotope, Long-chain *n*-alkanes, Aquatic plants, Paleohydrology proxy, Lake Qinghai

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1. Introduction

The hydrogen isotope composition (δD) of terrestrial plant long-chain *n*-alkanes recovered from lacustrine sediments is emerging as a powerful proxy for paleoenvironmental reconstructions, especially for terrestrial hydrological changes (Sessions et al., 1999; Castañeda and Schouten, 2011; Wang et al., 2013; Bird et al., 2014; Schmidt et al., 2014; Günther et al., 2015). For example, for an 11000-year δD record of long-chain *n*-alkanes from Lake Paru Co on the southeastern Qinghai-Tibet Plateau (QTP), Bird et al. (2014) interpreted the variability of this record as reflecting large-scale processes associated with regional Indian summer monsoon (ISM) dynamics. Together with other proxies, the δD record of long-chain *n*-alkanes revealed that maximum ISM rainfall occurred at ca. 10–5 ka and then ISM trended toward drier conditions to the present (Bird et al., 2014). Günther et al. (2015) regarded δD values of C_{29} *n*-alkanes (*n*-C_{29}) from the sediments of Lake Nam Co (QTP) as an appropriate paleohydrological proxy, displaying the influence of Indian Ocean summer monsoon in the Holocene. Their results showed that the interplay of different air masses seems to be primarily controlled by solar insolation in the investigated study areas.

The foundations of the above-mentioned studies concerning δD values of leaf waxes are based on the assumption that *n*-alkanes (at least for long-chain *n*-alkanes *n*-C_{27}, *n*-C_{29}, and *n*-C_{31}) from lacustrine sediments are predominantly originated from terrestrial plants. Consequently, the δD signals of long-chain *n*-alkanes retrieved from lake sediments are believed to have recorded hydrological variations (or changes in relative humidity) in terrestrial ecosystems. However, with the accumulating knowledge on the origin of *n*-alkanes in lake sediments and their stable isotope behaviors (Ficken et al., 2000; Mügler et al., 2008; Gao et al., 2011; Duan et al., 2011; Duan and Xu, 2012; Guenther et al., 2013), potential biases in quantitative reconstruction of paleoenvironment using lacustrine sedimentary long-chain *n*-alkanes have been the subject of some recent studies (Aichner et al., 2010a, 2010b; Liu et al., 2015). It has been shown that aquatic plants may contribute significant amounts of mid-chain *n*-alkanes to the lacustrine sedimentary *n*-alkane pool, particularly in relatively shallow lakes or the near-shore areas of lakes (Ficken et al., 2000; Aichner et al., 2010a, 2010b; Gao et al., 2011; Liu et al., 2015), affecting or controlling δD and δ^{13}C values of sedimentary mid-chain *n*-alkanes (Mügler et al., 2008; Aichner et al., 2010b; Gao et al., 2011; Guenther et al., 2013). Furthermore, Aichner et al. (2010b) observed that the correlation coefficients between δD values of individual *n*-alkanes and δD values of summer meteoric water increased with the increase of chain length in lakes at the QTP; they assumed that this was possibly due to the proportional contribution of aquatic organisms to C_{23}–C_{31} *n*-alkanes in sediments decreased with increasing chain length. Recently, we found that aquatic plants are flourishing in the Lake Qinghai region (particularly at the lake bottom), and have analyzed δ^{13}C values of leaf wax *n*-alkanes from dominating aquatic plants (Liu et al., 2015). The results showed that submerged aquatic plants can produce considerable amount of long-chain *n*-alkanes, and more importantly, *n*-alkane δ^{13}C values of submerged aquatic plants are similar to those of terrestrial C_4 plants, thus impacting on the quantification of historical C_4/C_3 ratios (Liu et al., 2015).

These results lead us to speculate that whether or not, and to what extent, are the δD values of sedimentary long-chain *n*-alkanes affected by aquatic organisms. One important issue is that, in terrestrial ecosystems the variations in δD values of soil water are directly controlled by changes in precipitation and the relative humidity (Barnes and Allison, 1983; Tang and Feng, 2001; Darling, 2004), while the δD values of lake water are related to many factors such as the source water, evaporation, lake size, local hydrological settings, etc. (Craig and Gordon, 1965; Dansgaard, 1964; Gat and Levy, 1978; Gonfiantini, 1986; Leng and Anderson, 2003; Gibson et al., 2005). If that is the case, it's quite necessary to evaluate the geochemical implications of sedimentary long-chain leaf wax *n*-alkanes in more details.

In the Lake Qinghai region, Duan et al. (2011, 2012) have preliminary investigated the distribution and δD values of *n*-alkanes in terrestrial and aquatic plants and lake sediments. However, we note that in their studies, the surface sediments and aquatic plants were all collected near the lakeside, with no samples from relatively deeper water areas. Consequently, although their results showed that aquatic plants can produce long-chain *n*-alkanes, the conclusion that *n*-alkanes in the sediments of Lake Qinghai are mainly sourced from terrestrial plants is quite general. In fact, our recent study concerning molecular carbon isotope (δ^{13}C) of the Lake Qinghai region has demonstrated that aquatic plants may significantly affect the δ^{13}C of long-chain *n*-alkanes preserved in lake sediments, especially for *n*-C_{27} and *n*-C_{29} (Liu et al., 2015). This reminds us that it is necessary to further explore the *n*-alkane δD values of different types of samples for the Lake Qinghai region, and to discuss how to reasonably use the δD values of sedimentary long-chain *n*-alkanes in paleoclimatic reconstructions on the QTP. In this study, therefore, we systematically collected aquatic plants and surface sediments at various depths, surrounding terrestrial plant litters, and lake and river water samples in the Lake Qinghai area. By the detailed investigation of δD values of individual sedimentary long-chain *n*-alkanes derived from different sources, we aim to evaluate different sources of lipids and their different contributions to individual sedimentary long-chain *n*-alkanes and the hydrogen isotope signals. Furthermore, we will also discuss the implications of the heterogeneous sources to the applications of sedimentary long-chain *n*-alkanes δD values in palaeolimnology studies.

2. Materials and methods

2.1 Study site and samples

Lake Qinghai is the largest inland brackish lake on the QTP and is of wide interest to paleoclimatologists due to its sensitivity to regional climate variations in response to monsoon variation and global change (Shen et al., 2005; Colman et al., 2007; Henderson and Holmes, 2009; An et al., 2012). Located in a semi-arid, cold and high altitude (ca. 3200 m) climate zone on the northeastern QTP, it is surrounded by mountains such as Datongshan, Riyueshan, and Nanshan (Liu et al., 2011). The lake is now hydrologically closed with an area of ~4260 km^2, a maximum water depth of 27 m and an average water depth of 21 m (Xiao et al., 2012). The regional annual mean temperature is ca. 1.2°C with higher temperature of 10.4–15.2°C in July (Jin et al., 2010). The mean annual precipitation is ca. 400 mm, whereas evaporation (800–1200 mm) greatly exceeds precipitation in the lake. In the northeastern and southeastern area of Lake Qinghai, several small lakes (e.g. Lake Gahai) have formed because the water level of Lake Qinghai has decreased in the recent centuries (Li et al., 1996).

Under a cold highland climate regime, the terrestrial flora of its catchment is characterized by alpine meadows and steppes (Duan and Xu, 2012; Wang and Liu, 2012), dominated by C_3 plants (Liu et al., 2015). As for aquatic vegetation in the lake, *Potamogeton* L. and *Ruppia* L., dominate the shallow water (<9 m) area, whereas the green alga *Cladophora* Kützing was found to cover the sediment surface extensively in offshore settings (Liu et al., 2013, 2015).

We collected water samples from lakes and rivers, leaf samples from aquatic plants and surrounding terrestrial plant litters, and sedimentary samples from corresponding surface sediments in the Lake Qinghai region during several field trips (Figure 1). Most of the sediment and aquatic plant samples are the same as those reported in a previous study concerning molecular carbon isotope (Liu et al., 2015). Surface sediments and aquatic plants at various locations and depths of Lake Qinghai and Lake Gahai were collected using a grab sampler, with aquatic plants and sediments carefully separated. The collected aquatic plants included *Cladophora* and some submerged plants, which were cleaned with distilled water to remove sediments or dust particles and then freeze-dried. Plant litters were collected in paper bags and air dried. Water samples were placed in small plastic bottles and stored at 4°C until analyzed.

2.2 Analysis of *n*-alkanes

The extraction and quantification of *n*-alkanes were described in detail in Liu et al. (2015). Briefly, plant samples were extracted ultrasonically by dichloromethane (DCM), whereas finely grounded sediments were extracted ultrasonically using DCM/MeOH (9∶1). All the samples were extracted 4 times with 15 min each extraction. The hydrocarbon fractions containing *n*-alkanes were isolated using silica column chromatography. An Agilent 6890 gas chromatography (GC) instrument with flame ionization detector was used to quantify *n*-alkanes. The samples were injected in a split mode, with an inlet temperature of 310°C and a flow rate of carrier gas of 1.2 mL/min. The oven temperature program was: 40°C (1 min) to 150°C at 10°C/min, and

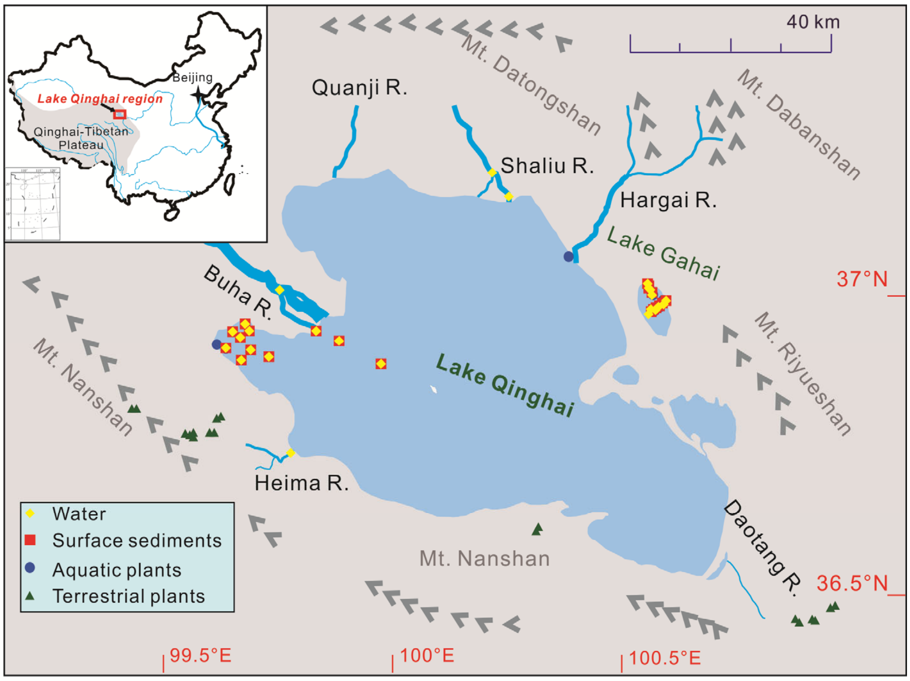

Figure 1 Geographical map showing the Lake Qinghai region and sampling sites in this study.

then to 310°C (20 min) at 6°C/min. Peak areas from individual *n*-alkanes were compared with those of an external standard with known amounts of individual *n*-alkanes to calculate the concentration of *n*-alkanes for each sample.

The P_{aq} index, a proxy for the relative contribution of *n*-alkanes from submerged/floating aquatic macrophytes versus emergent and terrestrial plants (Ficken et al., 2000), was calculated as follows:

$$P_{aq} = (C_{23} + C_{25}) / (C_{23} + C_{25} + C_{29} + C_{31}).$$

The *δ*D values of the *n*-alkanes were determined using a Trace GC Ultra^{TM} gas chromatograph (Thermo Scientific, Waltham, MA, USA) coupled with a Delta V Advantage isotope ratio mass spectrometer (Thermo Scientific) via a high-temperature pyrolysis reactor operated at 1430°C. During this experiment, the H_3^+ factor was calculated daily using the same H_2 reference gas. The reproducibility and accuracy were evaluated by measuring *n*-alkane standards (C_{21}, C_{25}, C_{27}, C_{29}, C_{31}, and C_{33} *n*-alkanes, purity $\geqslant$99.5%, Fluka Inc., Buchs, Switzerland) between every five measured samples, and the standard deviation of *δ*D values of *n*-alkanes standards was generally <3‰. All reported *δ*D values (‰) are relative to VSMOW (0).

2.3 Analysis of water *δ*D values

*δ*D values of water samples were analyzed using Isotope Water Analyzer (Picarro L2130-i, USA), and the values were normalized to VSMOW using lab standards. The standard deviation of the *δ*D measurements was <3‰.

3. Results

3.1 *δ*D values of long-chain *n*-alkanes in plant and surface sediment samples

*δ*D values of long-chain *n*-alkanes from collected aquatic plants varied from −184‰ to −132‰ with a mean value of −160‰ for *n*-C_{27}, from −183‰ to −138‰ with a mean value of −158‰ for *n*-C_{29}, and from −189‰ to −130‰ with a mean value of −161‰ for *n*-C_{31} respectively (Table 1; Figure 2).

For the surrounding terrestrial plant litters, the range of *n*-alkane *δ*D values are −151– −190‰, −161– −200‰ and −158– −205‰ for *n*-C_{27}, *n*-$C_{29,}$ and *n*-C_{31}, respectively, while the average values are −167‰, −173‰ and −177‰, accordingly for the three compounds (Table 1; Figure 3). We analyzed *n*-alkane *δ*D values for plant litters instead of fresh plants because we think that the former may have integrated the *n*-alkane *δ*D signals of various plants, and thus a more accurate representation for the terrestrial *n*-alkane source.

For the surface sediments in Lake Qinghai and its satellite lakes, the *n*-C_{27} *δ*D values ranged from −145‰ to −172‰ (avg. −159‰), the *n*-C_{29} *δ*D values varied from −156‰ to −172‰ (avg. −165‰), and the *n*-C_{31} *δ*D values extended from −171‰ to −188‰ (avg. −179‰). Interestingly, *δ*D from *n*-C_{27} and *n*-C_{29} consistently exhibited systematic D-enrichment relative to *n*-C_{31} (Table 2; Figure 4). This is quite different from the *δ*D pattern for the long-chain *n*-alkanes of surrounding terrestrial plant litters (Figure 3).

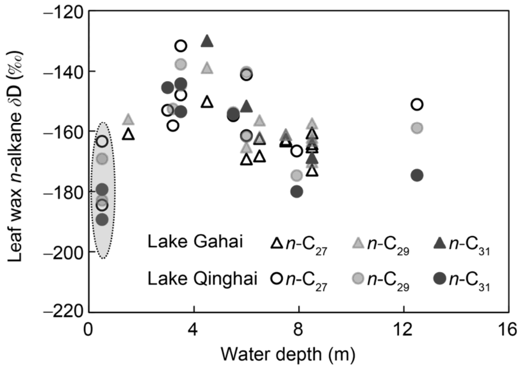

Figure 2 Long-chain *n*-alkane *δ*D values from aquatic plants at various water depths in the Lake Qinghai region. The shading highlights aquatic plants at shallower water depth (<1 m) which showed relatively negative *δ*D values than those from deeper water.

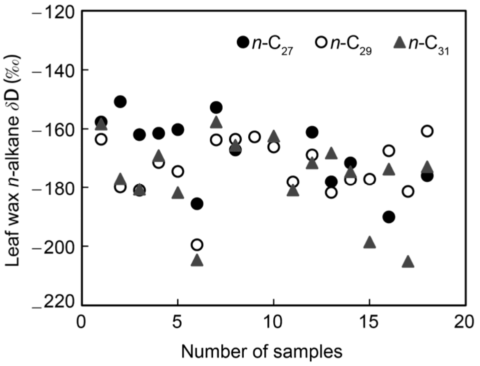

Figure 3 Long-chain *n*-alkane *δ*D values from terrestrial plant litters in the Lake Qinghai region.

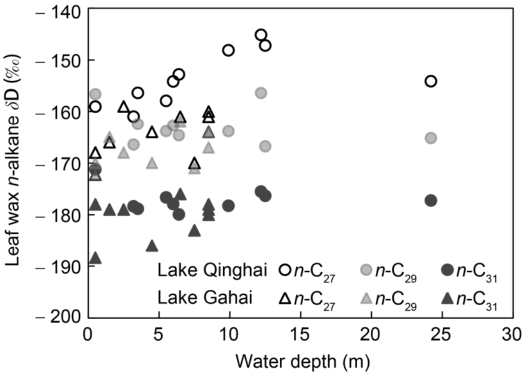

Figure 4 Long-chain *n*-alkane *δ*D values of surface sediments from Lake Qinghai and its satellite Lake Gahai with various water depths.

Table 1 Relative abundance (relative to the sum of C_{23}–C_{31}) and δD values of long-chain *n*-alkanes from aquatic plants and surrounding terrestrial plant litters in the Lake Qinghai region[a)]

Plant source	Latitude (N)	Longitude (E)	Water depth (m)	P_{aq}	Relative abundance (%)			δD values (VSMOW ‰)		
					C_{27}	C_{29}	C_{31}	C_{27}	C_{29}	C_{31}
Cladophora	36°56′32″	99°41′56″	5.5	0.76*	21.8*	14.7*	7.0*	−155	−154	−154
Cladophora	36°53′04″	99°40′44″	6	0.68*	21.0*	13.4*	6.5*	−141	−140	n.a.
Cladophora	36°53′29″	99°45′16″	12.5	0.00	23.3	35.1	33.7	−151	−159	−175
Cladophora	37°01′07″	100°35′27″	6.5	0.75	30.1	14.0	2.3	−162	−156	n.a.
Cladophora	37°02′38″	100°33′10″	4.5	0.82	16.7	10.2	4.6	−150	−139	−130
Cladophora	36°54′49″	99°37′19″	8	0.43*	16.4*	21.3*	19.5*	−167	−175	−180
Submerged plant	37°06′51″	100°22′07″	0.5	0.77*	34.9*	8.4*	5.7*	−163	−169	−179
Submerged plant	37°01′07″	100°35′12″	8.5	0.94*	13.8*	4.4*	0.4*	−173	−170	−169
Submerged plant	37°01′14″	100°35′24″	6.0	0.96*	12.7*	3.5*	0.0*	−169	−165	−152
Submerged plant	36°57′12″	99°41′36″	3.2	0.92*	17.8*	5.6*	0.5*	−158	−153	n.a.
Submerged plant	36°56′16″	99°39′08″	3	0.91*	10.7*	6.2*	2.0*	−153	−145	−145
Submerged plant	36°54′16″	99°38′33″	3.5	0.91*	10.3*	5.7*	2.3*	−148	−145	−153
Submerged plant	36°54′16″	99°38′33″	3.5	0.88*	14.8*	9.2*	4.4*	−132	−138	−144
Submerged plant	36°53′04″	99°40′44″	6	0.90*	20.8*	7.3*	0.7*	−161	−162	n.a.
Submerged plant	36°57′41″	99°49′53″	0.5	0.91*	20.6*	5.1*	0.9*	−184	−183	−189
Submerged plant	37° 00′27″	100°34′28″	8.5	0.88*	22.0*	8.0*	0.0*	−165	−163	n.a.
Submerged plant	37°00′37″	100°34′49″	8.5	0.94*	16.9*	4.9*	0.0*	−161	−157	n.a.
Submerged plant	37°00′50″	100°35′08″	8.5	0.93*	16.3*	5.4*	0.3*	−164	−162	n.a.
Submerged plant	37°01′07″	100°35′27″	6.5	0.89*	23.0*	7.2*	0.4*	−168	−162	n.a.
Submerged plant	37°02′09″	100°33′32″	7.5	0.90*	21.8*	6.9*	0.0*	−163	−161	n.a.
Submerged plant	37°01′21″	100°35′33″	1.5	0.95*	12.2*	3.8*	0.5*	−161	−156	n.a.
Submerged plant	37°02′09″	100°33′32″	7.5	0.84	23.4	11.1	0.0	−163	−161	n.a.
Terrestrial litter	36°45′00″	99°36′36″		0.23	5.2	15.1	27.9	−158	−164	−158
Terrestrial litter	36°45′00″	99°36′36″		0.31	3.3	18.2	27.9	−151	−180	−177
Terrestrial litter	36°45′00″	99°36′36″		0.07	3.9	22.1	35.1	−162	−181	−181
Terrestrial litter	36°45′00″	99°36′36″		0.11	4.2	18.2	27.1	−162	−171	−169
Terrestrial litter	36°45′00″	99°38′24″		0.04	6.4	28.1	38.0	−160	−174	−182
Terrestrial litter	36°45′00″	99°38′24″		0.08	6.9	18.2	39.3	−186	−200	−205
Terrestrial litter	36°46′12″	99°39′00″		0.12	3.3	14.4	24.1	−153	−164	−158
Terrestrial litter	36°46′12″	99°39′00″		0.18	6.9	20.0	24.0	−167	−164	−166
Terrestrial litter	36°46′48″	99°23′24″		0.20	6.0	43.7	9.4	n.a.	−163	n.a.
Terrestrial litter	36°46′48″	99°23′24″		0.15	2.9	19.1	11.8	n.a.	−166	−162
Terrestrial litter	36°37′12″	100°19′48″		0.09	2.9	16.9	35.2	n.a.	−178	−181
Terrestrial litter	36°36′58″	100°19′37″		0.10	4.7	19.5	34.1	−161	−169	−172
Terrestrial litter	36°26′17″	101°05′24″		0.10	7.6	25.1	11.9	−178	−182	−168
Terrestrial litter	36°26′17″	101°05′24″		0.14	6.1	17.2	11.5	−172	−177	−175
Terrestrial litter	36°26′49″	101°07′08″		0.05	3.9	27.1	32.7	n.a.	−177	−199
Terrestrial litter	36°26′49″	101°07′08″		0.09	7.9	20.2	31.2	−190	−167	−174
Terrestrial litter	36°28′26″	101°09′00″		0.06	3.8	24.9	44.7	n.a.	−181	−205
Terrestrial litter	36°28′26″	101°09′00″		0.08	10.8	43.0	19.4	−176	−161	−173

a) Data with * are reported by Liu et al. (2015); n.a.=not available.

3.2 δD values of river water and lake water

δD values of lake water varied from −2.7‰ to −24.6‰ with a mean value of −11.4‰. δD values of river water varied from −37‰ to −49‰ with a mean value of −45‰. It is noticed that δD values are much negative for river water and lake water at shallow areas (Figure 5).

4. Discussion

4.1 δD values of long-chain *n*-alkanes from aquatic plants

In general, δD values of the three long-chain *n*-alkanes homologues from aquatic plants in the Lake Qinghai region remain very similar (Figures 2 and 6). This is in agreement

Table 2 Relative abundance (reported by Liu et al., 2015) and δD values of long-chain n-alkanes from surface sediments in Lake Qinghai region[a]

Samples	Latitude (N)	Longitude (E)	Water depth (m)	P_{aq}	Relative abundance (%)			δD values (VSMOW ‰)			
					C_{27}	C_{29}	C_{31}	C_{27}	C_{29}	C_{31}	$\Delta\delta D_{C27-C31}$
QHS13-1	36°56'32"	99°41'56"	5.5	0.33	15	24	26	−158	−164	−177	19
QHS13-2	36°57'12"	99°41'36"	3.2	0.60	17	20	24	−161	−166	−178	17
QHS13-3	36°55'54"	99°40'16"	6.4	0.27	14	26	29	−153	−165	−180	27
QHS13-4	36°56'16"	99°39'08"	3	0.41	14	21	24	n.a.	n.a.	n.a.	n.a.
QHS13-5	36°54'16"	99°38'33"	3.5	0.44	13	20	24	−156	−162	−179	22
QHS13-6	36°53'04"	99°40'44"	6	0.23	13	28	31	−154	−163	−178	24
QHS13-7	36°54'07"	99°42'31"	9.9	0.23	13	28	30	−148	−164	−178	30
QHS13-8	36°53'29"	99°45'16"	12.5	0.23	13	28	31	−147	−167	−176	29
QHS13-9	36°53'09"	99°59'53"	24.2	0.19	13	28	34	−154	−165	−177	23
QHS13-10	36°56'24"	99°55'01"	12.2	0.22	14	29	30	−145	−156	−176	30
QHS13-12-1	36°57'41"	99°49'53"	0.5	0.26	15	31	25	−159	−157	−171	12
GHS13-0	37°01'19"	100°35'37"	0.5	0.38	13	22	29	−172	−172	−188	16
GHS13-1	37°00'27"	100°34'28"	8.5	0.15	14	31	34	−160	−167	−179	19
GHS13-2	37°00'37"	100°34'49"	8.5	0.22	16	30	29	−161	−164	−178	17
GHS13-3	37°00'50"	100°35'08"	8.5	0.19	16	31	30	−164	−164	−180	16
GHS13-4	37°01'07"	100°35'27"	6.5	0.20	16	28	30	−161	−162	−176	15
GHS13-5	37°03'10"	100°33'04"	0.5	0.27	18	26	27	−168	−170	−178	10
GHS13-6	37°02'55"	100°33'04"	2.5	0.23	16	27	27	−159	−168	−179	20
GHS13-7	37°02'38"	100°33'10"	4.5	0.20	14	28	31	−164	−170	−186	22
GHS13-8	37°02'09"	100°33'32"	7.5	0.19	15	30	31	−170	−171	−183	13
GHS13-9	37°01'21"	100°35'33"	1.5	0.33	16	26	23	−166	−165	−179	13

a) n.a. = not available.

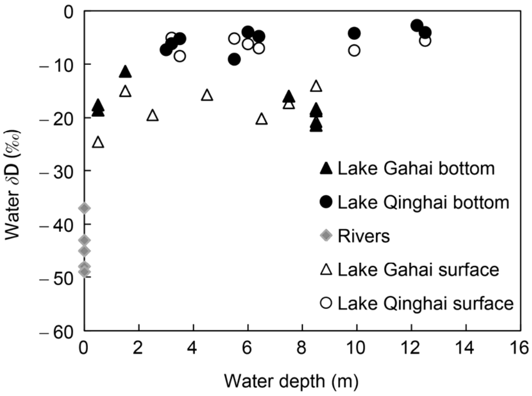

Figure 5 δD values of water samples from lakes and rivers with various water depths in the Lake Qinghai region.

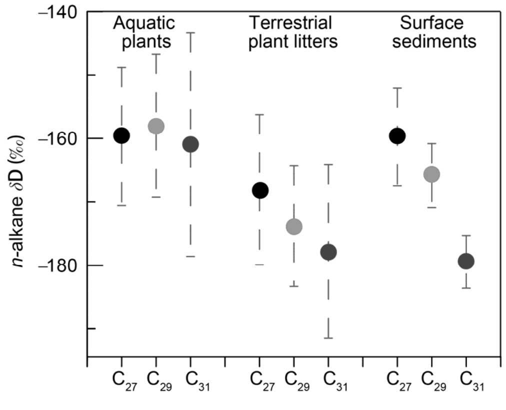

Figure 6 Mean δD values of individual n-alkanes (C_{27}, C_{29} and C_{31}) in sediments, aquatic plants, and terrestrial plant litters in the Lake Qinghai region. The vertical dotted lines (error bars) indicate standard deviations.

with previous observations that variations in n-alkane δD values within a single plant is negligible (Sachse et al., 2004, 2006; Mügler et al., 2008; Aichner et al., 2010b; Li et al., 2015).

For aquatic plants at different sites, however, long-chain n-alkane δD values showed considerable variations (Figure 2). The different *in situ* lake water δD values might account for the differences in δD values of long-chain n-alkanes between aquatic plants collected at different sites, as aquatic plants use lake water as their source water. Actually, the variation in long-chain n-alkanes produced by aquatic plants resembles the variation in lake water δD values (Figure 5). Particularly, for aquatic plants collected from near shore very shallow water (depth <1 m), they showed more negative long-chain n-alkane δD values than those from deeper water (Figure 2), possibly due to the fact that the lake water at very shallow areas was more influenced by the inflow water (e.g. river water) with relatively negative δD values (Figure 5). For another lake on the QTP, Lake Nam Co, Guenther et al. (2013) also observed that mean n-C_{23} δD values of submerged macrophytes collected near the shoreline were more negative than n-C_{23} δD values collected at other lake locations by Mügler et al. (2008). Hence, it is reasonable to believe that the δD values of individual long-chain n-alkanes produced by aquatic plants track variations in δD values of *in situ* lake water.

Moreover, the long-chain n-alkane δD values for aquatic plants are generally more positive than those for terrestrial plant litters (Figures 2, 3, and 6). For example, n-C_{29} of the aquatic plants is D-enriched by ~15‰. A preliminary investigation of *n*-alkane δD values in Lake Qinghai (Duan and Xu, 2012) also found that mean *n*-alkane δD values from aquatic plants collected near the lakeside are generally more positive than those from surrounding terrestrial herbaceous plants, such as *Kobresia* sp., *Poa* sp., *Oxytropis ochrocephala*, and *Leymus* sp., but the δD values of individual *n*-alkanes measured for a single plant sample varied quite significantly.

The difference of source water δD values for aquatic and terrestrial plants should predict different δD values of long-chain *n*-alkanes between aquatic plants and terrestrial plant litters for the Lake Qinghai region. Lake Qinghai and its satellite Lake Gahai are hydrologically closed saline lakes that are situated in a semi-arid climatic zone. The strong evaporation of D-depleted lake water and the reservoir effort for saline lakes can cause significant D-enrichment for the lake water relative to precipitation. Indeed, we observed much positive δD values for lake water (avg. −12‰) than those of the river water (avg. −45‰) (Figure 5), in agreement with Duan et al. (2012)'s report that δD values of lake water were ~50‰ more positive than those of river water in Lake Qinghai and consistent with Mügler et al. (2008) and Guenther et al. (2013)'s observations on the QTP. Moreover, we also noticed that from rivers to nearshore and to offshore settings, water δD values become more positive with the increase of water depth (Figure 5). These results indicate that the water δD values dominated by terrestrial precipitation and those dominated by evaporation are quite distinct in this region. Such differences of source water δD values must have resulted in the differences of long-chain *n*-alkane δD values between aquatic plants at nearshore and offshore settings, also between terrestrial plants and aquatic plants in the Lake Qinghai region.

As has been discussed previously, δD values of long-chain *n*-alkanes produced by aquatic plants can trace δD values of lake water. On the other hand, terrestrial-derived long-chain *n*-alkane δD values can generally record the precipitation δD signals at spatial scales (Smith and Freeman , 2006; Liu and Yang, 2008; Rao et al., 2009). Therefore, the D-enrichment of lake water relative to precipitation might be an important factor for the more positive long-chain *n*-alkanes δD values from aquatic plants than those from the terrestrial plants in Lake Qinghai region.

4.2 Influence of aquatic plants on the δD values of individual sedimentary long-chain *n*-alkanes

For δD values of long-chain *n*-alkanes from the surface sediments in the Lake Qinghai region, *n*-C_{27} and *n*-C_{29} consistently exhibited systematic D-enrichment by 20‰ and 14‰ relative to *n*-C_{31} (Figure 4). A further comparison of mean δD values of individual *n*-alkanes among C_{27}, C_{29} and C_{31} in sediments, aquatic plants, and terrestrial plant litters in the Lake Qinghai region shows that, the δD value of sedimentary *n*-C_{31} is similar to that of terrestrial *n*-C_{31} while the δD value of sedimentary *n*-C_{27} is consistent with that of aquatic *n*-C_{27}, and the value of sedimentary *n*-C_{29} is intermediate between those of aquatic plants and terrestrial plant litters (Figure 6).

It is highly likely that C_{27}, C_{29} and C_{31} *n*-alkanes in the sediments constitute different degrees of mixing between aquatic and terrestrial sources, and therefore they exhibit quite different δD values, departing from resembling values as they were from a single plant. Aquatic plants have generally more positive *n*-alkane δD values than those of surrounding terrestrial plants in the Lake Qinghai region (Figure 6), primarily because they record the D-enriched lake water through strong evaporation (Section 4.1). Additionally, aquatic plants can generally produce larger amounts of *n*-C_{27} relative to *n*-C_{31} (Liu et al., 2015), while long-chain *n*-alkanes derived from dominant terrestrial plants in this region are dominated by *n*-C_{31} (Liu et al., 2015; Table 1). Significant contribution of D-enriched, aquatic-derived *n*-alkanes to the sediments can thus result in more positive δD values of sedimentary long chain *n*-alkanes, especially for *n*-C_{27}. Therefore, the systematic D-enrichment in *n*-C_{27} and *n*-C_{29} relative to *n*-C_{31} observed in lake surface sediments in this region can be attributed to a larger input of aquatic *n*-C_{27} and *n*-C_{29} to the sediments, particularly for *n*-C_{27}. On the other hand, the sedimentary C_{31} *n*-alkane may contain only minor contribution from aquatic plants with the majority from the terrestrial plant sources. We also noticed that the results of Duan et al. (2011) did not show such effect of aquatic plants on the δD values of sedimentary long chain *n*-alkanes. This is possibly because that their surface sediments and core sediments were collected at the modern shoreline and mostly near river mouths, where large amount of terrestrial *n*-alkane input from surrounding wetland and rivers overwhelmed the effect of aquatic plants, and therefore, these sediments were less affected by aquatic plants living in the lake.

4.3 Implications for geochemical and palaeolimnological studies

(i) δD values of lacustrine sedimentary long-chain *n*-alkanes are widely believed to have recorded terrestrial hydrological information (e.g. Sachse et al., 2004; Mügler et al., 2008; Xia et al., 2008; Guenther et al., 2013; Yao et al., 2015), since these lipids are assumed to be predominantly originated from terrestrial higher plants (Eglinton and Hamilton, 1967; Rieley et al., 1991, Smith and Freeman, 2006; Feakins and Sessions, 2010; Castañeda and Schouten, 2011, Duan et al. 2011). In this study and a previous investigation (Liu et al., 2015), however, based on systematical investigation of individual long-chain *n*-alkanes in different types of samples, we confirmed that aquatic plants might contribute significantly to the sedimentary long chain *n*-C_{27} and *n*-C_{29} pool in Lake Qinghai and its satellite lakes. This suggests that the application of δD values of lacustrine sedimentary n-C$_{27}$ and n-C$_{29}$ (or the mean δD value of long-chain n-alkanes) for tracing terrestrial hydrological variations requires exercising cautions. On the other hand, δD values of sedimentary n-C$_{31}$ are similar to those of terrestrial n-C$_{31}$ (Figure 6) at the Lake Qinghai region. The new δD data support the idea that sedimentary n-C$_{31}$ might be a more reliable recorder of terrestrial climate changes compared with n-C$_{27}$ and n-C$_{29}$, as shown (suggested) in previous carbon and hydrogen isotope analyses (Aichner et al., 2010b; Liu et al., 2015).

(ii) In relatively arid regions, δD values of aquatic plant n-alkanes and some sedimentary long-chain n-alkanes (such as n-C$_{27}$ and n-C$_{29}$) may vary as a result of changing δD values of lake water, while the variation of lake water δD values can be strongly influenced by the distance from the shoreline or from river mouths. Consequently, variations in δD values of n-C$_{27}$ and n-C$_{29}$ in paleoclimate record might also be affected by the changing of geographic distance between the coring site and the inflow water, in addition to by variations in δD values of surface water or the whole lake water, or by the relative contributions of long-chain n-alkanes from aquatic plants.

(iii) As sedimentary n-C$_{31}$ is predominantly derived from terrestrial sources while sedimentary n-C$_{27}$ has inputs from both aquatic and terrestrial sources, we recommend that the intermolecular deviation of δD values between n-C$_{27}$ and n-C$_{31}$ ($\Delta\delta$D$_{\mathrm{C27–C31}}$) can be used roughly to judge if long-chain n-alkanes in lacustrine sediments are from a single source in this region. Given that the n-alkane δD values of aquatic plants are generally more positive than those of terrestrial plants in relatively arid regions (Mügler et al., 2008; Duan et al., 2012; Guenther et al., 2013), a large $\Delta\delta$D$_{\mathrm{C27–C31}}$ value thus may indicate considerable contribution of long-chain n-alkanes from aquatic plants to the sediments.

Recently, we observed large difference in δ^{13}C values between C$_{27}$ and C$_{31}$ n-alkane ($\Delta\delta^{13}$C$_{\mathrm{C27–C31}}$) in nearshore sediments and such offsets were reduced while moving away from the shoreline and eventually diminished in offshore sediments (Liu et al., 2015). The small $\Delta\delta^{13}$C$_{\mathrm{C27–C31}}$ values in deeper lake areas were tentatively attributed to the single terrestrial source for long-chain n-alkanes in the offshore settings. Based on our new n-alkane δD data, however, it is much more likely that long-chain n-alkanes from aquatic plants (such as *Cladophora*) also contributed to offshore sediments, as the $\Delta\delta$D$_{\mathrm{C27-C31}}$ values therein are still very large (>20‰. Figure 7) while the mean $\Delta\delta$D$_{\mathrm{C27–C31}}$ values are only 2‰ and 6‰ respectively for aquatic plants and terrestrial plant litters with available n-C$_{27}$ and n-C$_{31}$ δD data. Thus, the inter-molecular δD difference ($\Delta\delta$D$_{\mathrm{C27–C31}}$) might be a more sensitive source indicator than its carbon counterpart ($\Delta\delta^{13}$C$_{\mathrm{C27–C31}}$) when different plant sources have similar δ^{13}C values but distinct δD values for n-alkanes. The P_{aq} index has previously been proposed as a proxy for evaluating the relative contribution of n-alkanes from submerged/floating aquatic macrophytes to the lake sediments (Ficken et al., 2000). However, the evaluation based on multiple independent proxies is still necessary in organic geochemical investigations, particularly for samples with low P_{aq} values. For example, the range of P_{aq} for terrestrial plants is 0.01–0.23 in Ficken et al. (2000) while it is 0.04–0.31 in this study. Therefore, it might be hard to judge if aquatic plants contribute partly to long-chain n-alkanes in the offshore sediments of Lake Qinghai, based only on the P_{aq} index (the average is ca. 0.2 for samples collected at water depth >10 m). But when looking at the large $\Delta\delta$D$_{\mathrm{C27–C31}}$ (>20‰), it seems that aquatic plants also contribute to these offshore sediments.

It should be noted, however, for surface sediments at shallow lake area, relatively lower $\Delta\delta$D$_{\mathrm{C27–C31}}$ values are usually obtained than those from the deeper part (Figure 7). This is mainly because that aquatic plants grow in shallow areas have more negative n-alkane δD values due to the much D-depleted *in situ* lake water; therefore the n-C$_{27}$ δD values of aquatic plants are much close to those derived from terrestrial plants, a phenomenon that is not necessary contradict to the high aquatic plant input in shallow areas as indicated by large $\Delta\delta^{13}$C$_{\mathrm{C27–C31}}$ and P_{aq} values (Liu et al., 2015). Overall, therefore, our results highlight the importance of using both n-alkane δD and δ^{13}C data, as well as the distribution of n-alkanes (e.g. P_{aq}) for tracing lipid sources of sedimentary n-alkanes for organic geochemical studies using lacustrine sediments.

5. Conclusions

We presented long-chain n-alkane δD results from aquatic plants (*Cladophora* and submerged plants), surface sediments, surrounding terrestrial plant litters, and δD values of lake water and river water from the Lake Qinghai region on the northeastern QTP in China.

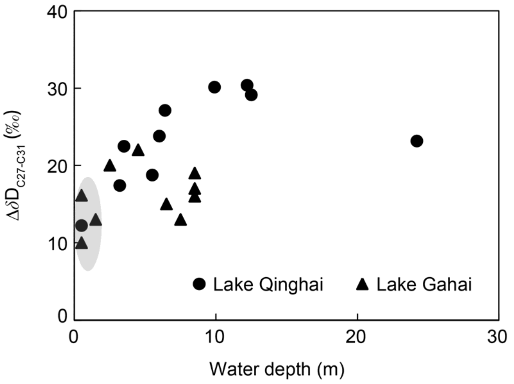

Figure 7 Changes in $\Delta\delta$D$_{\mathrm{C27–C31}}$ values of sedimentary n-alkanes with water depth from Lake Qinghai and Lake Gahai. The shading highlights surface sediments at shallow water depth (<1 m) which showed relatively smaller $\Delta\delta$D$_{\mathrm{C27–C31}}$ values than those from deeper water areas.

δD values of long-chain *n*-alkanes from aquatic plants showed no significant difference among the three homologues (n-C_{27}, n-C_{29} and n-C_{31}), but were more positive than those of surrounding terrestrial plants due to D-enrichment of strongly evaporated lake water in Lake Qinghai and its satellite lakes. In surface sediments, however, significant variations in δD values of the three long-chain homologues were detected, with n-C_{27} and n-C_{29} systematically exhibiting more D-enriched values than in n-C_{31}, indicating larger amounts of aquatic plant inputs to sediments for n-C_{27} and n-C_{29}. These results confirmed that aquatic plants can contribute considerably to the sedimentary long chain n-C_{27} and n-C_{29} pool in lakes on the QTP, whereas n-C_{31} might be predominantly from terrestrial sources, and thus δD values of n-C_{31} might be a relatively faithful proxy for terrestrial hydrological changes. Additionally, we also proposed a potential way to evaluate the contribution of lipids from aquatic plants to the sedimentary long-chain *n*-alkane pool based on the offset between δD values of n-C_{27} and n-C_{31} (i.e., $\Delta\delta D_{C27-C31}$) in lake systems with unchangeable regional terrestrial vegetation.

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