



Biomarker seasonality study in Lake Van, Turkey

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ABSTRACT

The endorheic Lake Van in eastern Anatolia (Turkey) is the world's largest soda lake and it is an important site in paleoclimate studies to understand past continental conditions in western Asia. In order to gain further insights into the biomarker signatures in Lake Van's sediments we have analyzed particulate material in sediment traps deployed between August 2006 and July 2007. The biomarkers used were long chain alkenones (LCAs C₃₇–C₃₉, haptophyte lipids), isoprenoid glycerol dialkyl glycerol tetraethers (GDGTs, Archaea membrane lipids) and pigments (chlorins and fucoxanthin). The biomarker fluxes indicate a strong seasonality in export primary productivity and the phytoplankton community structure. The highest total mass and organic carbon fluxes were found in summer, coupled to strong stratification while the lowest mass fluxes occurred in winter at the time of water column mixing. With increasing temperatures in early spring, phytoplankton export productivity grew, coupled with an increase of total mass flux and organic carbon, which might be associated to enhanced nutrient input from snowmelt runoff. The percentage of C_{37:4} shows some correspondence with observed seasonal changes in Lake Van's stratification structure. We also evaluated the potential applicability of molecular temperature proxies derived from Archaea and haptophyte lipids. The use of the TEX₈₆ proxy was precluded by low GDGT abundances. Estimated LCA temperatures were consistent with temperatures in the photic zone but no seasonality changes were observed despite the wide annual temperature range measured at Lake Van.

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1. Introduction

Understanding past changes in Earth's climate requires the reconstruction of climatic patterns in both marine and continental settings. Presently, continental climate records are often incomplete. However, lakes generally display higher production and sedimentation rates than oceans and contain paleoclimatic and paleoenvironmental information on the local–regional continental response to global changes (e.g. Meyers, 2003; Litt et al., 2009). Temperature is one of the key environmental factors to understand climate changes, two molecular proxies initially developed in marine environments also have specific lake calibrations, i.e. the long chain alkenones (LCAs) unsaturation index (U₃₇^K) and the TEX₈₆ index based on isoprenoid glycerol dialkyl glycerol tetraethers (GDGTs).

LCAs are a group of lipids comprising C₃₇–C₄₀ di-, tri- and tetra-unsaturated methyl and ethyl ketones, which are key biomarkers for haptophytes. They were originally found in marine environments, but later discovered to be present also in lakes (e.g. Marlowe et al., 1984; Cranwell, 1988; Zink et al., 2001; Chu et al., 2005; Pearson et al., 2008; Toney et al., 2010). In marine

environments, alkenone production is dominated by *Emiliania huxleyi* and *Gephyrocapsa oceanica*, but lakes contain other species, like *Isochrysis galbana* and *Chrysothila lamellosa* (e.g. Marlowe et al., 1984). Previously LCA distributions and specifically the C₃₇/C₃₈ ratio have been used as indicators of haptophyte species identity (e.g. Chu et al., 2005; Liu et al., 2008; Toney et al., 2010), but a recent study revealed no clear correlation between LCA ratios and phylogenetic placement (Theroux et al., 2010). Thus, even though it is known that lake species belong to the order Isochrysoideales, LCA sources in specific lakes are still largely unknown (Theroux et al., 2010).

A marine sediment core study showed that the ratio of LCAs is sensitive to climatic changes (Brassell et al., 1986), and studies using laboratory cultures of *E. huxleyi* proved that the extent of unsaturation changed with growth temperatures (e.g., Marlowe et al., 1984). Based on this finding, the alkenone indices U₃₇^K and U₃₇^K were proposed and confirmed as sea surface temperature (SST) proxies by culture studies of *E. huxleyi* (Prahl and Wakeham, 1987; Prahl et al., 1988) and global core-top studies (e.g. Müller et al., 1998; Conte et al., 2006). In contrast, the use of LCA ratios to reconstruct water temperatures in lacustrine settings is a more recent topic of study. Specific lake calibrations had to be developed (e.g. Chu et al., 2005; Toney et al., 2010) as LCA distribution in lakes is different than the one found in marine settings, for instance

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usually displaying a dominance of C_{37:4} and absence of ethyl alkenones. In fact, until recently the appropriate use of LCA indices to quantitatively reconstruct lake temperature was uncertain. In Lake Van, for example, Thiel et al. (1997) suggested that the LCA distributions were unrelated to temperature, but the lake was later successfully included in an Asian lake calibration study by Chu et al. (2005).

Another molecular temperature proxy that is also applied in lakes, is the TEX₈₆ index based on archaeal isoprenoid GDGTs (e.g. Powers et al., 2004, 2010; Blaga et al., 2009). A number of Archaea have been shown to change the relative proportion of GDGTs with growth temperature, i.e. higher temperatures result in an increase in the relative amounts of GDGTs with two or more cyclopentane moieties and thus higher TEX₈₆ (Schouten et al., 2002; Wuchter et al., 2004). By measuring the TEX₈₆, the temperature at which Archaea lived when they produced their membranes can be determined. Archaea ubiquitously occur in the marine water column and are one of the dominant prokaryotic groups in the modern oceans (Karner et al., 2001), but they are also found in lakes (e.g. Schleper et al., 1997; Hicks, 2003; Casamayor and Borrego, 2009). Core-top studies have provided a linear regression equation to convert TEX₈₆ values into SSTs (Schouten et al., 2002; Kim et al., 2010) or lake surface temperatures (Powers et al., 2004, 2010).

Although Lake Van has a relatively low sedimentation rate, the varved deposition and its endhoreic nature make it an ideal location to obtain paleoclimatic data (Litt et al., 2009). With the aim of investigating continental paleoclimate, a record spanning multiple glacial–interglacial cycles was recovered from Lake Van in 2010, within the framework of the International Scientific Continental Drilling Program (ICDP) project PALEOVAN (Litt et al., 2009; Fig. 1). Evaluating the environmental information stored in sedimentary records firstly depends on the knowledge about the ecosystem and understanding of present day link between environmental variability and lake response. Here we collected settling particles with sequential sediment traps between August 2006 and July 2007 to study the seasonal biomarker fluxes. Biomarkers in lakes have often been used to reconstruct the paleoenvironment surrounding the lake and the surface water column conditions

(e.g. Cranwell, 1988; Thiel et al., 1997; Meyers, 2003; Blaga et al., 2009). In this paper we report data on chlorophyll a derivatives as indicators of total export primary productivity (e.g. Villanueva et al., 1994; Leavitt and Hodgson, 2001; Walker and Keely, 2004), fucoxanthin as indicators for fucoxanthin-containing algae such as diatoms, chrysophytes and haptophytes (e.g. Jeffrey et al., 1997), LCAs as indicators for haptophytes (e.g. Marlowe et al., 1984) and isoprenoid GDGTs as indicators for Archaea (e.g. Schouten et al., 2002). We also evaluate the potential use of paleo-temperature proxies derived from LCAs and GDGTs.

2. Material and methods

2.1. Regional setting

Lake Van is situated in eastern Anatolia (Turkey) at 1648 m above sea level and it has an area of 3570 km², a maximum depth of 460 m, pH ~9.5–9.9, ~21–24‰ salinity and 155 m eq/l alkalinity (Litt et al., 2009; Reimer et al., 2009; Kaden et al., 2010). The lake receives water mainly through precipitation and snowmelt inflow from a catchment area estimated to be 12,500 km² and loses it through evaporation (Kadioğlu et al., 1997; Fig. 1).

The climate in eastern Anatolia is strongly influenced by changes in the position of the westerly jet stream, the extension of the subtropical low pressure belt and Siberian high pressure area (Wick et al., 2003; Reimer et al., 2009). The study area experiences relatively warm summers (above 20 °C) and cold winters (below 0 °C), but, due to the high salinity and the great depth of the lake, no ice forms on the surface. Annual precipitation in the city of Van is about 379 mm, with highest precipitation occurring in April and October. Surface water temperatures recorded during the study ranged from 3.4–23 °C (Stockhecke, 2008). From May to October Lake Van is stratified with surface temperatures of 11–23 °C (Table 2). In January, cooling of the surface water and impact of winds induces mixing of the upper 70 m of the water column, generating a homogeneously cold water column at 3.4 °C. Below 70 m the water temperature ranges between 3.2 °C and 3.7 °C throughout the year (Stockhecke, 2008). Lake Van particles are usually deposited in annual varve

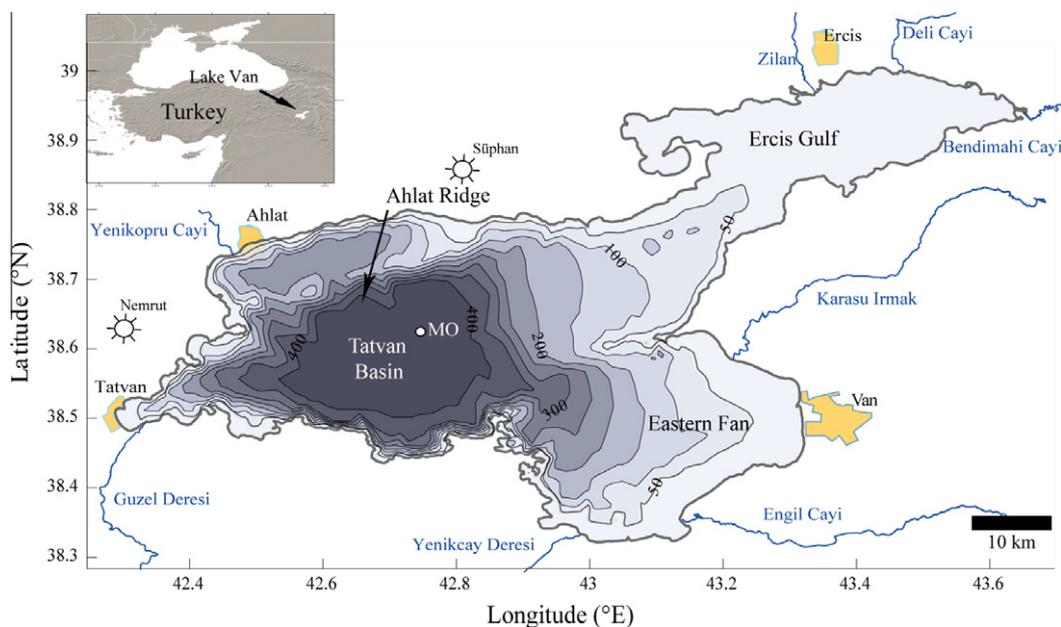


Fig. 1. Bathymetric map of Lake Van with major tributaries, settlements and location of the sediment trap mooring site (MO). Two semi-active volcanic systems, Nemrut and Süphan, border the lake.

couplets of light carbonate (spring–summer–autumn) and dark organic rich (winter) laminae (Stockhecke, 2008; Reimer et al., 2009). This change is governed by the CaCO₃ precipitation that occurs when the surface fresh water rich in calcium starts to mix with the underlying salty water resulting in supersaturation (Landmann and Kempe, 2005; Reimer et al., 2009). Thus seasonality can be observed in the sedimentary record.

2.2. Samples

Sediment trap samples were obtained from a mooring deployed in the Tatvan Basin in July 2006 at a water depth of 440 m (38°38.1'N, 42°46.1'E; Fig. 1), 10 m above the lake bottom. The sequential trap system (TECHNICAP-PPS4/3) had 12 cups with individually controlled exposure times (21–50 days) and a funnel shaped inlet, which ensures that no settled material is resuspended from the bottom of the trap (Stockhecke, 2008). The integrating traps (Eawag-130 cylinder) had two collecting cylinders each with an aspect ratio of 8. The upper integrating trap, referred to as Z1, was placed at 35 m below the lake surface, while Z2 was 10 m above the lake bottom (440 m depth). All traps were recovered in July 2007.

After recovery the sampling cups were stored in a cool room (4 °C) for 48 h to ensure particle settlement. The supernatant water was decanted and samples were freeze dried and weighed, a fraction of approximately 1 g per sample was used in this study. The amount of salt present in the samples' standing water was subtracted from the sample mass to subsequently determine the net mass fluxes (see Stockhecke, 2008 for details).

2.3. Sample extraction

Freeze dried sediment samples were extracted by sonication first with methanol (MeOH), then a mixture (1:1; v:v) of MeOH and dichloromethane (DCM), and lastly with pure DCM, three times each for 5 min. Organic extracts were combined, centrifuged at 3500 rpm and the supernatants decanted, taken to near dryness and eluted through anhydrous sodium sulphate. An internal standard (2-nonadecanone, Fluka Chemika) was added to the samples before extraction.

An aliquot of the total extract was taken to analyze pigments as described below. The remaining extract was divided into apolar, intermediate and polar fractions using a small glass column filled with activated silica and eluted with hexane:DCM (9:1; v:v), hexane:DCM (1:1; v:v) and DCM:MeOH (1:1; v:v).

An internal standard (a synthetic tetraether abbreviated GR, see Rethoré et al., 2007 for details) to quantify the GDGTs was added to the polar fraction after extraction (cf. Huguet et al., 2006). Polar fractions were hydrolyzed with HCl:MeOH (5%) for 4 h at 70 °C. On completion MilliQ water was added to the mixture, which was then extracted four times with DCM. The combined DCM extracts were rinsed with MilliQ water six times in order to eliminate possible leftover acid (Huguet et al., 2010).

2.4. Pigment analysis

Aliquots of the total extracts, stored dry in the fridge were redissolved in acetone prior to instrumental analysis. To quantify the total abundance of chlorophyll pigments (i.e. chlorins) we used a Thermo Surveyor high performance liquid chromatograph (HPLC), with 100% acetone as mobile phase, a pressure restrictor instead of a chromatographic column and a photodiode array detector (Thermo Surveyor). For quantification the absorbance was monitored at 662 nm using pyropheophorbide a as an external standard.

For the identification and quantification of individual pigments the total extracts were analyzed with the setup described above equipped with a Genesis C18 column (250 × 4.6 mm, 4 μm; Grace). Mobile phase composition changed from MeOH:acetonitrile:0.5 M aq. ammonium acetate (40:40:20, v:v:v) to solvent acetonitrile:acetone (45:55 v:v) at 1 ml/min flow rate was used. Pigments were identified by their relative retention time and absorption spectra. In this paper we only use the fucoxanthin versus chlorin ratio, as a marker for diatom and chrysophyte contribution to total phytoplankton (e.g. Jeffrey et al., 1997).

2.5. Alkenone analysis

The intermediate fraction (hexane:DCM (1:1; v:v)) containing LCAs were dried with N₂ and redissolved in isoctane. Samples were analyzed using a Thermo Trace gas chromatograph equipped with a flame ionization detector (GC-FID), in splitless injection mode and using helium as carrier gas at 1.5 ml/min with constant flux. After injection of 2 μl of sample, compounds were separated through an Agilent HP-1 capillary column (60 m length × 0.25 mm i.d., 25 μm film thickness) with a 5 m pre-column. Oven temperature was held at 80 °C for 1 min, increased to 120 °C at a rate of 20 °C/min, then to 320 °C at 6 °C/min and held at this value for 20 min. Absolute abundances were determined using the 2-nona-decanone (Fluka Chemika) internal standard.

The GC-FID analysis showed the presence of the methyl LCAs C₃₇–C₃₉ (Fig. 2) but absence of ethyl homologues. Alkenone identity was confirmed with an Agilent gas chromatograph coupled to a mass spectrometer (GC-MS). After injection of 1 μl of sample, in split/splitless mode, compounds were separated through an Agilent DB-5MS capillary column (30 m × 0.25 mm i.d. × 25 μm film thickness) with a 5 m precolumn. Oven temperature was held at 80 °C for 1 min, increased to 120 °C at a rate of 20 °C/min, then to 320 °C at 6 °C/min and held at this value for 30 min. Helium was used as carrier gas at a constant flow of 1.5 ml/min. The mass spectrometer parameters were set as follows to generate positive ion spectra: injector 310 °C, source 250 °C, MS Quad 150 °C and ionization energy 70 eV, scan range from 50–650 m/z.

Alkenone unsaturation indices U₃₇^K and U₃₇^{K'}, and U₃₈^K and U₃₇₃₈^K (Brassell et al., 1986; Prahl and Wakeham, 1987; Pearson et al., 2008) were calculated (Table 2) as follows:

$$U_{37}^K = ([C_{37:2}] - [C_{37:4}]) / ([C_{37:2}] + [C_{37:3}] + [C_{37:4}]) \quad (1)$$

$$U_{37}^{K'} = [C_{37:2}] / ([C_{37:2}] + [C_{37:3}]) \quad (2)$$

$$U_{38}^K = ([C_{38:2}] - [C_{38:4}]) / ([C_{38:2}] + [C_{38:3}] + [C_{38:4}]) \quad (3)$$

$$U_{3738}^K = ([C_{37:2}] - [C_{37:4}] + [C_{38:2}] - [C_{38:4}]) / ([C_{37:2}] + [C_{37:3}] + [C_{37:4}] + [C_{38:2}] + [C_{38:3}] + [C_{38:4}]) \quad (4)$$

2.6. Isoprenoid GDGT analysis

The polar GDGT fractions were evaporated, redissolved in hexane:*n*-propanol (99:1, v:v) and filtered through 0.45 μm PVDF filters prior to injection into the HPLC-MS. Analysis was performed using a Dionex P680 HPLC coupled to a Thermo Finnigan TSQ Quantum Discovery Max quadrupole mass spectrometer with an atmospheric pressure chemical ionization (APCI) interface set in positive mode. The target compounds were separated with a Tracer Excel CN column (40 mm diameter, 200 mm length, 3 μm particle size; Teknokroma) fitted with a precolumn filter and a guard column. The solvent program is derived and modified from Schouten et al. (2007) and Escala et al. (2009). The flow rate was set at 0.6 ml/min and the eluting program was as follows: 98.5% hexane

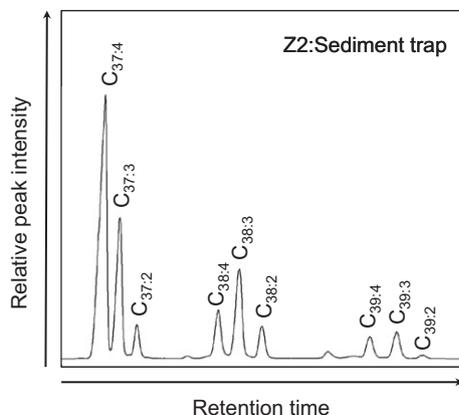


Fig. 2. Partial alkenone chromatogram showing the distribution of C₃₇, C₃₈ and C₃₉ alkenones in the integrating trap (Eawag-130 cylinder) Z2 placed 10 m above the lake bottom (440 m depth) that collected a full annual cycle 2006–2007.

and 1.5% *n*-propanol for 4 min, increased gradually to 5% *n*-propanol in 11 min. To clean the column the proportion of *n*-propanol was increased to 10% over a minute and held for 4 min. Finally the *n*-propanol was lowered to 1.5% in 1 min and held for 9 min in order to condition the column. The parameters of the APCI were set as follows to generate positive ion spectra: corona discharge 3 μ A, vaporizer temperature 400 °C, sheath gas pressure 49 mTorr, auxiliary gas (N₂) pressure 5 mTorr and capillary temperature 200 °C. GDGTs were detected in selected ion monitoring (SIM) mode of $[M+H]^+ \pm 0.5 m/z$ units. Absolute abundances were determined using the GR internal standard (Rethoré et al., 2007) and calculated as in Huguet et al. (2006).

3. Results and discussion

3.1. Seasonal changes in Lake Van

Lake Van is characterized by strong seasonal oscillations in temperature, precipitation, dissolved ions and nutrient input (e.g. Tuğrul et al., 1984; Thiel et al., 1997; Stockhecke, 2008; Litt et al., 2009; Kaden et al., 2010). The changes observed in biomarker abundances and fluxes are closely linked to these seasonal changes, especially increased nutrient loading triggered by snowmelt and precipitation. All time series of the analyzed compounds over the period August 2006–July 2007 are shown in Fig. 3. Generally, total mass fluxes were two orders of magnitude higher than those of organic carbon but both showed consistent changes through the annual cycle with higher summer and spring values and almost no flux in winter (Stockhecke, 2008; Fig. 3). However, while total mass fluxes were highest in August and July, the organic carbon flux was highest in spring, probably linked to phytoplankton blooms (Fig. 3a). All biomarkers display individual seasonal patterns but they all show a sharp winter decrease (Table 1; Fig. 3).

The integrating trap Z1, deployed at 35 m within the euphotic zone, has only half of most biomarker concentrations compared to Z2, deployed at 440 m near the lake bottom (Tables 1 and 2). The only exception of this is the chlorin abundance (Tables 1 and 2). Both, total mass and organic carbon fluxes are also lower in the upper trap sample with values of 0.24 g DM m⁻² d⁻¹ and 6.37 mg C_{org} m⁻² d⁻¹ for Z1, which increase to 0.30 g m⁻² d⁻¹ and 7.95 mg C_{org} m⁻² d⁻¹ for the bottom trap Z2. The higher fluxes and biomarker concentrations at the deeper trap can be due to material transport by lateral advection and/or sediment resuspension. As all biomarkers and fluxes show strong, but contrasting

seasonal patterns in the seasonal traps (at 440 m, same depth as Z2), we interpret such higher concentrations in Z2 samples as the result of lateral advection rather than sediment resuspension. If the signal was influenced by resuspension we would expect to see a uniform increase of all biomarkers, or at least a smoothed signal through the year. The deeper sample also naturally concentrates material from a wider water column area than the upper trap. Moreover, the upper trap (Z1) was deployed too shallow (35 m) to sample the entire photic zone, thus not incorporating all production collected at Z2.

3.1.1. Phytoplankton and pigments

Over 100 phytoplankton species have been recorded in the lake including flagellates, green algae, diatoms and cyanobacteria, with predominance of the latter two (Gessner, 1957). Diatom frustules were identified in all spring summer and autumn trap samples by Stockhecke (2008), but they were less abundant in winter when fluxes were at their minimum (Fig. 3c). Still little is known about biological productivity and seasonal species succession in Lake Van. Chlorin abundances ranged from 0.3–1.3 μ g/g DM. Previously chlorophyll a concentrations of 0.1–0.9 mg/l have been reported in Lake Van (Tuğrul et al., 1984). Our chlorin concentration (per gram sediment) and flux data show that export primary production peaks in August and also increases in early spring (Fig. 3b), while it is non-detectable in winter. This contrasts a previous study that showed higher summer but also autumn chlorophyll a concentrations (Tuğrul et al., 1984). The chlorin concentration and flux peaks in August coincide with peaks in total mass and organic carbon fluxes (Fig. 3a), thus decaying phytoplankton cells may represent a substantial portion of the organic matter flux. A small increase in chlorin concentration was observed in November arguably linked to an increase in haptophytes (as inferred by changes in alkenone fluxes; Fig. 3b and d). Slightly higher fluxes are observed in March, which coincides with the first increase of total mass and organic matter fluxes after almost complete cessation of fluxes during the winter months. At this time of the year, the runoff is highest because snowmelt and precipitation coincide (Reimer et al., 2009; Stockhecke, 2008), resulting in a significant input of nutrients into the lake and possibly causing the spring increase in phytoplankton production. The small difference in the chlorin content between Z1 and Z2 indicate that most chlorins are produced in the upper 35 m and hence are also trapped by the upper, Z1, trap. This is in agreement with the reported chlorophyll maximum at 30 m depth in summer (Stockhecke, 2008; Kaden et al., 2010).

The fucoxanthin/chlorin ratio is highest between July and September indicating major contributions from diatoms and, probably to a lesser extent, from haptophytes to the phytoplankton assemblage (Figs. 3 c and d). While the chlorin concentration decreases, the fucoxanthin/chlorin ratio stays high in September, matching an increase in biogenic silica flux and reflecting a substantial contribution of diatoms to the phytoplankton assemblage (Fig. 3c). However the highest silica flux was observed in November while the fucoxanthin/chlorin ratio decreased. This November silica peak could be related to chrysophyte cysts, which are identified all year round but which were particularly abundant in autumn (Stockhecke, 2008). In July 2007, fucoxanthin/chlorin ratio increased again, as it was found at the beginning of the monitoring in August and September 2006. However, this increase is not coupled to increased total phytoplankton productivity as it was in August 2006, suggesting a relative diatom increase over other phytoplankton organisms.

3.1.2. Alkenones

The trap samples contain methyl di-, tri- and tetra-unsaturated ketones with carbon chain lengths from C₃₇–C₃₉ (Fig. 2). Absence

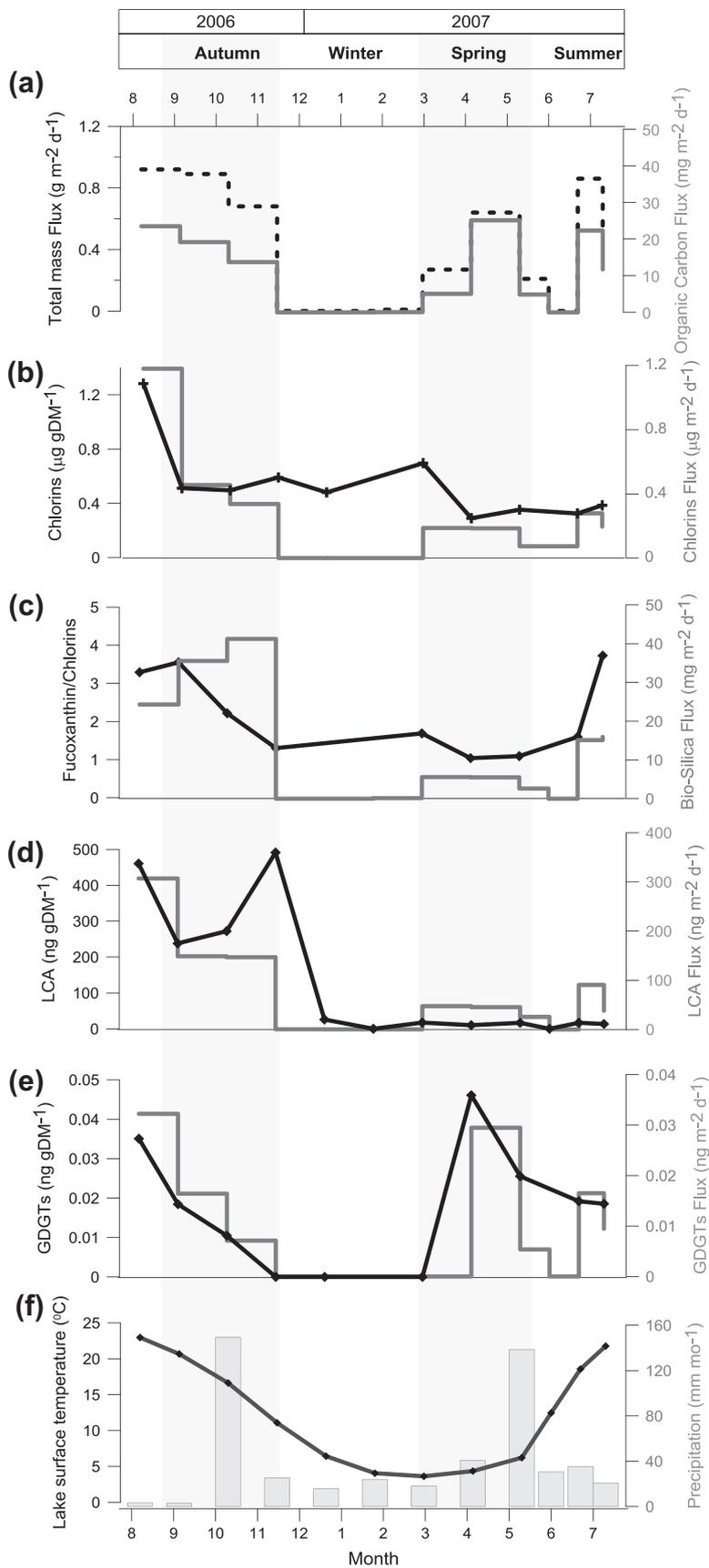


Fig. 3. Biomarker seasonality with (a) mass flux (dotted line) and organic carbon flux (grey line) see Stockhecke, 2008 for details; (b) chlorins abundance (black line) and flux (grey step plot); (c) fucoxanthin/chlorins ratio (black line) and biogenic silica flux (grey step plot; Stockhecke, 2008); (d) long chain alkenones (LCAs) abundance (black line) and flux (grey step plot); (e) isoprenoid GDGT abundance (black line) and flux (grey step plot); (f) lake surface temperature (black line), and precipitation (grey histogram).

Table 1
Sequential (S1–S12) average values (S_{average}) and integrating (Z1, Z2) sediment traps, sample dates, depths (m), chlorin concentrations ($\mu\text{g/g}$ dry matter (DM), indicating total export primary productivity), fucoxanthin/chlorin ratio (indicating contribution of fucoxanthin-containing algae include diatoms, chrysophytes and haptophytes), unsaturated alkenones concentrations (in ng/gDM ; haptophyte lipids) and isoprenoid glycerol dialkyl glycerol tetraethers lipids (GDGTs in ng/gDM ; as indicators of the presence of Archaea).

Sample	Date	Depth	Chlorins ($\mu\text{g/gDM}$)	Fuco/ chlo ($\mu\text{g/gDM}$)	$C_{37:4}$ (ng/gDM)	$C_{37:3}$ (ng/gDM)	$C_{37:2}$ (ng/gDM)	$C_{38:4}$ (ng/gDM)	$C_{38:3}$ (ng/gDM)	$C_{38:2}$ (ng/gDM)	$C_{39:4}$ (ng/gDM)	$C_{39:3}$ (ng/gDM)	$C_{39:2}$ (ng/gDM)	GDGTs (ng/gDM)
S1	Aug-06	440	1.3	3.3	200.0	85.4	19.5	32.5	65.9	22.7	14.1	17.8	2.5	0.04
S2	Sep-06	440	0.5	3.6	104.1	42.1	8.8	18.3	34.0	10.6	8.6	10.3	1.3	0.02
S3	Oct-06	440	0.5	2.2	125.2	51.3	10.7	18.1	35.2	10.5	8.6	11.2	1.3	0.01
S4	Nov-06	440	0.6	1.3	223.4	88.8	18.9	33.9	63.8	20.0	18.0	21.7	2.7	nd
S5	Dec-06	440	0.5	nd	10.4	5.2	1.3	2.0	3.5	1.3	1.0	1.2	0.2	nd
S6	Feb-07	440												
S7	Mar-07	440	0.7	1.7	6.9	3.7	0.6	1.8	2.4	0.8	0.4	0.6	0.1	nd
S8	Apr-07	440	0.3	1.0	4.0	2.2	0.4	1.1	1.4	0.4	0.2	0.4	0.0	0.05
S9	May-07	440	0.4	1.1	6.5	3.4	0.6	2.0	2.5	0.6	0.5	0.6	0.1	0.03
S10	Jun-07	440												
S11	Jun-07	440	0.3	1.6	6.4	3.6	0.6	1.8	2.5	0.7	0.4	0.6	0.1	0.02
S12	Jul-07	440	0.4	3.7	5.0	3.1	0.5	1.3	2.0	0.6	0.3	0.5	0.1	0.02
S_{average}	Aug-06–Jul-07	440	0.5	2.2	69.2	28.9	6.2	11.3	21.3	6.8	5.2	6.5	0.8	0.02
Z1	2006–2007	35	0.5	2.7	16.3	7.4	1.9	2.9	5.7	2.0	1.3	1.7	0.3	0.01
Z2	2006–2007	440	0.5	4.9	42.9	18.5	4.2	7.0	13.6	4.4	3.0	4.1	0.5	0.03

Table 2
Sequential (S1–S12) average values (S_{average}) and integrating (Z1, Z2) sediment traps, sample dates, depths (m), alkenone unsaturation indices, U_{37}^K , U_{38}^K and U_{3738}^K , U_{37}^K converted to surface temperature (ST) with calibrations by (a) Zink et al. (2001), (b) Sun et al. (2007), (c) Toney et al. (2010), (d) Chu et al. (2005), (e) Sun et al. (2007) and (f) Pearson et al. (2008). Instrumental lake surface temperatures ($^{\circ}\text{C}$) are also shown.

Sample	Date	Depth	U_{37}^K	$U_{37}^K\text{-ST}^a$	$U_{37}^K\text{-ST}^b$	$U_{37}^K\text{-ST}^c$	U_{37}^K	$U_{37}^K\text{-ST}^d$	$U_{37}^K\text{-ST}^e$	U_{38}^K	$U_{38}^K\text{-ST}^f$	U_{3738}^K	$U_{3738}^K\text{-ST}^f$	Measured ST
S1	Aug-06	440	-0.59	10.6	0.19	13.8	0.19	16.8	17.2	0.08	15.0	-0.32	6.4	22.95
S2	Sep-06	440	-0.61	9.9	-0.41	13.2	0.17	16.4	16.7	0.12	16.1	-0.33	6.2	20.66
S3	Oct-06	440	-0.61	10.0	-0.33	13.2	0.17	16.4	16.7	0.12	15.9	-0.36	5.6	16.63
S4	Nov-06	440	-0.62	9.8	-0.50	13.1	0.18	16.4	16.8	0.12	15.9	-0.36	5.6	11.07
S5	Dec-06	440	-0.54	12.3	1.56	15.3	0.20	17.1	17.6	0.11	15.8	-0.29	7.0	6.42
S6	Feb-07	440												
S7	Mar-07	440	-0.56	11.8	1.11	14.8	0.14	15.4	15.5	0.21	18.3	-0.28	7.2	3.62
S8	Apr-07	440	-0.54	12.2	1.47	15.2	0.15	15.6	15.7	0.22	18.6	-0.27	7.5	4.35
S9	May-07	440	-0.56	11.7	1.03	14.7	0.15	15.8	16.0	0.27	19.8	-0.26	7.8	6.21
S10	Jun-07	440	12.45											
S11	Jun-07	440	-0.54	12.2	1.52	15.2	0.15	15.6	15.7	0.22	18.4	-0.25	7.9	18.56
S12	Jul-07	440	-0.52	13.0	2.17	15.9	0.14	15.4	15.5	0.18	17.4	-0.25	8.0	21.77
S_{average}	Aug-06–Jul-07	440	-0.57	11.4	0.78	14.4	0.16	16.1	16.3	0.17	17.1	-0.30	6.9	13.15
Z1	2006–2007	35	-0.57	11.5	0.90	14.6	0.20	17.2	17.8	0.09	15.1	-0.29	7.0	13.15
Z2	2006–2007	440	-0.59	10.8	0.29	13.9	0.19	16.8	17.2	0.10	15.6	-0.32	6.3	12.39

of the ethyl homologues is in agreement with the previous observations by Thiel et al. (1997). Alkenone production is likely restricted to some haptophyte nanoplankton species of which lakes usually contain non-calcifying representatives (e.g. Cranwell, 1988; Chu et al., 2005; Toney et al., 2010). In fact the high alkalinity of Lake Van results in very low amounts of Ca^{2+} ions (Kempe et al., 1991), which does not permit the existence of calcifying haptophyte species (Thiel et al., 1997) as the incoming calcium is almost completely lost by precipitation of calcite and aragonite (Reimer et al., 2009). Some non-calcifying haptophytes have been identified in other lakes (e.g. Chu et al., 2005; Toney et al., 2010), but so far no haptophyte species have been described for Lake Van. Previous studies used the C_{37}/C_{38} ratio as an indicator of haptophyte species identity (e.g. Chu et al., 2005; Pearson et al., 2008; Toney et al., 2010). This ratio ranges in Lake Van from 0.67 to 0.75, which is relatively low compared to previously reported values (see Theroux et al., 2010 for compilation). Together with the presence of C_{38} methyl ketones, this value possibly rules out both *I. galbana* and *C. lamellosa* (e.g. Marlowe et al., 1984; Theroux et al., 2010) as sources of the LCAs in Lake Van. However, it should be noted that other physiological and environmental factors can also affect the C_{37}/C_{38} ratio (Liu et al., 2011) and that no clear correlation between LCA ratios and phylogenetic placement was found by Theroux et al. (2010).

Analysis of the trap samples revealed abundances of C_{37} (up to 250 ng/g DM), C_{38} (over 120 ng/g DM) and C_{39} (up to 90 ng/g DM) (Table 1; Fig. 3) within the usual range found in lakes (e.g. Chu et al., 2005; Toney et al., 2010). High LCA abundances (4.8–12.9 $\text{mg/g C}_{\text{org}}$) were reported from sediments in Lake Van, seemingly contributing up to half of the organic carbon present in an early Holocene sample (Thiel et al., 1997). Lowest concentrations are found in April and highest in November (Table 1 and Fig. 3). Two alkenone peaks are observed, one in August, which is linked to the overall high mass, organic carbon and chlorin fluxes, and a second in November (Fig. 3d). A substantial increase in precipitation in October, probably coupled to nutrient input through runoff, may have triggered the November peak in haptophytes (Fig. 3d), which is also linked to an increase in chlorins and silica flux. LCAs could thus be carried by settling diatoms to the lake bottom. These processes are in agreement with a previous study in Lake Van that showed LCAs to be most abundant during intervals of high fresh water input coupled to high nutrient loading (Thiel et al., 1997).

The observed dominance of the C_{37} tetra-unsaturated alkenone ($C_{37:4}$) over the tri- and di-unsaturated counterparts (Figs. 2 and 4) already reported by Thiel et al. (1997) is common in lacustrine settings (e.g. Chu et al., 2005; Toney et al., 2010). In culture

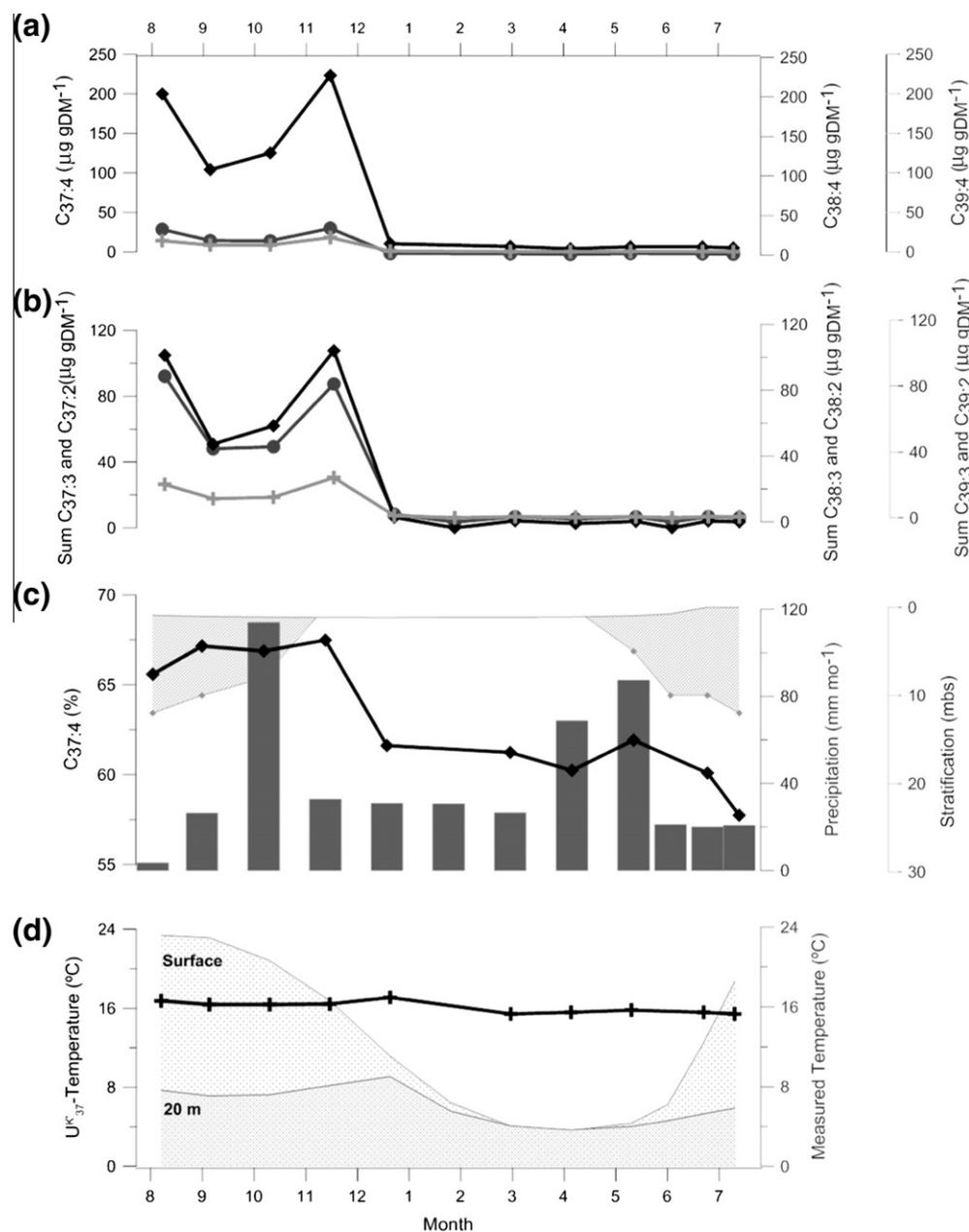


Fig. 4. Distribution of (a) tetra-unsaturated C₃₇ (black diamonds), C₃₈ (dark grey circles) and C₃₉ (light grey crosses) LCAs; (b) sum of tri and di-unsaturated C₃₇ (black diamonds), C₃₈ (dark grey circles) and C₃₉ (light grey crosses) LCAs; (c) percentage of C_{37:4} (black diamonds) compared to precipitation (grey histogram) and thermal stratification in meters below surface level (mbs, diamonds and filled with stripes), lakes level changed from 1648.82 m above sea level in December 2006 to 1650.005 m in June 2007 (Stockhecke, 2008); (d) U₃₇^K estimated temperatures (black crosses; according to Chu et al. (2005) calibration) and measured water temperature at surface and 20 m depth (grey, filled profiles).

experiments, the relative abundance of the C_{37:4} was shown to be linked to decreasing temperatures (Sun et al., 2007). In contrast, our data show highest relative C_{37:4} abundance during the warmer months (Table 2; Fig. 4), thus suggesting an alternative controlling factor. A relationship between %C_{37:4} and salinity/water mass changes has also been postulated for both marine and lacustrine settings (Sikes and Volkman, 1993; Rosell-Melé, 1998; Rosell-Melé et al., 2002; Sicre et al., 2002; Blanz et al., 2005; Bendle et al., 2005, 2009; Liu et al., 2008), even though in some cases no relationship is observed (Toney et al., 2010; Liu et al., 2011). The %C_{37:4}, is higher from August to November seemingly coupled to the development of a surface freshwater and high temperature stratification (Fig. 4c). Values decrease when the upper 70 m of the water column becomes mixed in January. We interpret the second increase in the %C_{37:4} to be linked to snowmelt and high precipitation in March and

April, which result in a lake level increase and stratification (Fig. 4c). Both temperature and salinity stabilize the surface stratification with reported 5‰ lower salinities in the surface layer than at greater depths (Kaden et al., 2010). As Lake Van is at a boundary area between the humid Mediterranean and continental climate, any changes in the westerly jet stream, the subtropical low pressure belt, or the Siberian high pressure area will result in changes in moisture (Wick et al., 2003) and will presumably be reflected by %C_{37:4} shifts. Some salinity changes have been reported in a late glacial–Holocene record from Lake Van, which reflects changes in moisture distribution and hence climatic patterns (Lemcke and Sturm, 1997; Wick et al., 2003). This suggests that the %C_{37:4} may be a useful proxy to detect climatic shifts at the study area.

The C₃₈ alkenones are dominated by the tri-unsaturated compound (Figs. 2 and 4, Table 1), contrasts previous studies showing

C_{38:4} dominance in lakes (Cranwell, 1988; Zink et al., 2001; Chu et al., 2005). However, dominance of C_{38:3} over its tetra- and di-unsaturated counterparts has been reported from other alkaline, evaporitic or saline lakes (e.g. Chu et al., 2005; Pearson et al., 2008; Toney et al., 2010), indicating that the LCA distribution in Lake Van (Fig. 2) is most likely related to changes in the haptophyte species composition, rather than to specific physico-chemical parameters. The C₃₉ alkenone series is characterized by considerably lower values than its C₃₈ and C₃₇ counterparts, and even though C_{39:3} produced the highest peak, tetra- and tri-unsaturated compounds present very similar concentrations (Figs. 2 and 4, Table 1). Similar LCA distributions were reported in a sediment core from Lake Van (Thiel et al., 1997), which may indicate the prevalence of a single source organism through sedimentary history. But Theroux et al. (2010) showed that lakes with multiple haptophyte taxa may display only one sedimentary signature, thus a molecular approach would be necessary to ascertain the origin of the LCAs.

3.1.3. Isoprenoid GDGTs

Isoprenoid GDGT abundances are very low and only two of the most common five mesophile Archaea lipids were detected (Fig. 3e; Table 1). The GDGTs detected are caldarchaeol (no moieties) and crenarchaeol (four cyclopentane and one cyclohexane moieties), which are universally found in Archaea of different origins and usually present in much higher concentrations than other GDGTs (Schouten et al., 2002). We observe higher GDGT concentrations and fluxes in August, corresponding to the phytoplankton bloom in stratified conditions, as well as in April after the slight increase of phytoplankton production, which might be explained by their possible metabolic dependence on phytoplankton-derived resources, such as ammonium (Könneke et al., 2005; Wuchter et al., 2006; Fietz et al., 2011). The delay of a month between phytoplankton and GDGT peaks is in agreement with previous seasonal studies on the phytoplankton and Archaea coupling (Wuchter et al., 2005; Herfort et al., 2006). However, their increased abundance also coincides with the periods of higher carbon flux so they could also have an allochthonous origin. Even though crenarchaeol usually derives from aquatic in situ production (Sinnighe-Damsté et al., 2002), it has also been found in terrigenous environments (Weijers et al., 2006). The presence of only low concentrations of non-specific GDGTs also points towards very low in situ production and towards a dominance of allochthonous material. As both detected types of GDGTs are widely distributed across aquatic and terrigenous environments it difficult to ascertain if in fact there is in situ production.

3.2. Possible applicability of molecular temperature proxies

While the TEX₈₆ has been successfully applied in lake sediments (Powers et al., 2004, 2010; Blaga et al., 2009), this is the first time its potential use is investigated in Lake Van. As the isoprenoid GDGTs used for the TEX₈₆ calculations (see Schouten et al., 2002 for details) were below detection limit, the index could not be calculated. Even though the use of the TEX₈₆ temperature proxy in trap samples was precluded by the low GDGT abundances, the proxy may still be applicable in sediments as they amplify the signal through accumulation. Provided that the aquatic origin of the isoprenoid GDGTs could be ascertained, sediment measurements should be done, before discarding the use of the TEX₈₆ proxy in Lake Van's sedimentary record.

In contrast, the U₃₇^K index had previously been evaluated in Lake Van and the temperature estimates were reported to be unreliable (Thiel et al., 1997). This is due to the use of marine calibrations in the Thiel et al. (1997) study, as we obtain similar values when applying the (Prah and Wakeham, 1987) marine calibrations (−11.3 °C for the U₃₇^K and 3–4 °C for U₃₇^K). If instead we use fresh

water calibrations (Table 2) most of the calculated temperatures ranged between −0.5 °C (U₃₇^K, Sun et al., 2007 and 17.2 °C (U₃₈^K, Pearson et al., 2008). The Chu et al. (2005) calibration was deemed the most adequate for this study as it includes Lake Van. Average derived temperature was 16 °C and it showed very little seasonal change (Fig. 4). This average is higher than the surface annual mean temperature (13 °C; Table 2) but within measured values in the upper 20 m of the water column at higher LCAs productive months (Figs. 3 and 4). To adjust for the marked LCAs seasonality we calculated the flux weighted measured surface temperature. However the obtained value of 19.7 °C is almost 4 °C above our sequential trap average (Table 2). This together with higher temperatures at the Z1 trap (17.2 °C) than at the Z2 deep trap (Table 2) suggest that the 440 m signal probably originates in the upper 35 m as well as from deeper water, not covered by the Z1 trap. The euphotic zone in Lake Van reaches up to 50 m and that means light penetrates below the depth of Z1 deployment, therefore haptophytes may grow and produce alkenones also below Z1 depth. Nonetheless, the temperature values obtained with the Chu et al. (2005) calibration displays values consistent with the Lake Van average temperatures and may possibly be used to evaluate climatic changes. Relatively stable values were reported for the Holocene record in Lake Van, but strong U₃₇^K shifts were observed in samples older than 1200 years (Thiel et al., 1997), underscoring the potential of the U₃₇^K proxy in the study area.

4. Conclusions

Our results show that all measured biomarker fluxes and concentrations follow a marked seasonality that can be used to track climatic shifts in the sedimentary record of Lake Van. Moreover we illustrate the importance of using trap data to calibrate sediment proxies. Changes observed in the %C_{37:4} are consistent with water column changes and thus may be used to detect past changes in freshwater input linked to different continental climatic conditions. The low GDGT concentrations precluded the use of the TEX₈₆ index in trap samples, however, we cannot rule out its use in downcore records. Despite strong seasonal shifts in LCA abundance no seasonal changes were observed in the ratios, in contrast with the marked seasonality observed in the measured temperature. Using an Asian lake calibration, which includes Lake Van, we derived temperatures between 15.4 and 17.2 °C, indicating LCAs production in the photic zone and highlighting the potential of the U₃₇^K as a paleotemperature proxy in the study area.

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