Lipid biomarkers in lacustrine sediments of subtropical northeastern Mexico and inferred ecosystem changes during the late Pleistocene and Holocene

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Abstract

Evolution of ecosystems in the northeastern Mexico since the Last Glacial Maximum (LGM) and through the Holocene are yet to be fully characterised, creating a gap in our understanding of the ecological response to climate change in this water scarce region. Here we explore the response of lacustrine and surrounding terrestrial habitats of this region to hydrological changes of the late Pleistocene and especially the Holocene. Biomarker-based proxy data from the El Potosi Basin indicates dynamic and variable input of organic matter (OM) into the basin, with sources being the surrounding vegetation, bacterial biomass and aquatic microfauna. Changes in these inputs reveal distinct stages of ecosystem development over the last 20,000 years. Overall low lipid abundances (as a proportion of TOC) from 20-19 cal kyr BP, mainly from aquatic/in-situ microbial biomass and degraded terrestrial OM, are attributed to relatively low runoff. Increasing lipid proportions during the deglaciation, from 19 to 15 cal kyr BP, were mostly derived from terrestrial sources like woodland vegetation, soil and wetland vegetation, and we attribute them to more rainfall and runoff. Subsequently, the wetland biomarkers disappeared, and woodland input began to dominate the OM assemblage from 15 to 11.7 cal kyr BP. During the early- and mid-Holocene, after about 11.7 cal kyr BP, putative woodland and grass inputs decreased and the dominant vegetation appeared to shift to subtropical desert shrub, which could have been due to increasing regional aridity. The onset of the dry late Holocene was characterized
by gradual environmental transition and ecosystem adaption, especially from 4.2 to 2.8 cal kyr BP. The
terrestrial vegetation comprised increasing proportions of C$_4$ grasses, documented by changes in leaf
wax carbon isotopic compositions, and potentially more open-vegetation, while the in-lake bacterial
production increased. With increasing desertification from 2.8 cal kyr BP, the terrestrial productivity
decreased substantially, the lake became shallower/ephemeral, and the surrounding soils became more
alkaline. Changes of the limnic habitat from algal towards microbial communities occurred ~300 years
after the onset of terrestrial habitat changes. During the last millennium, the C$_3$ components of the
vegetation again dominated. This implies an enhanced moisture supply, possibly from agricultural
activities. Overall, this work reveals the marked sensitivity of northeastern Mexico ecosystems to the
climatic shifts that occurred since the LGM, and this perhaps indicates their vulnerability to future
global warming.

Keywords: Organic geochemistry; Continental biomarkers; North America; Paleoclimateology;
Paleolimnology; Holocene

1. Introduction

The prevailing vegetation of a given region is directly influenced by atmospheric temperature,
evaporation and precipitation, and the terrestrial biosphere can also release or absorb greenhouse gases.
Thus, it has an important role in regulating atmospheric composition and climate (e.g. Gifford and
Howden, 2001; Justino et al., 2016). Paleovegetation reconstruction has played an important role in
understanding the nature and influence of past climate systems on different ecosystems (e.g. Lozano-
García and Ortega-Guerrero, 1998; Metcalfe et al., 2000; Ortega-Rosas et al., 2016), but these records
are also crucial for improving the understanding of ecological responses to future environmental
conditions.

Paleovegetation records from subtropical northeast Mexico are scarce and poorly dated. The
first study focused on sediments from the Cuatro Ciénegas Basin (Figure 1) and represented the last 30
kyr BP (4 radiocarbon dates; Meyer, 1973). This fossil record suggests a cooler regional climate and
wetter conditions during the late Pleistocene than at present. Climate became progressively warmer and
drier, with modern climate developing during the Holocene. However, gaps in the pollen record obscure the complete Holocene climatic evolution of the Cuatro Ciénegas Basin (Meyer, 1973). Subsequently, packrat midden analysis from Puerto de Ventanillas (Van Devender and Burgess, 1985; Figure 1) revealed that the woodland disappeared during the early Holocene. Similarly, packrat midden analysis from Cañon de la Fragua (Betancourt et al., 1990; Figure 1) also revealed that vegetation changed during the deglaciation, from woodland dominated by pinion and juniper to its disappearance. Beyond these studies, however, paleoenvironmental reconstruction of northeastern Mexico during the Holocene remains sparse.

In the southeastern USA, pollen records from Llano Estacado in Texas (Hafsten, 1961; Figure 1) document vegetation changes during the late Pleistocene and Holocene. The vegetation evolved from conifer woodland during the glacial, to scrub grassland during the deglaciation, and finally to the present grassland established during the Holocene. Packrat midden analysis from Maravillas Canyon (Wells, 1966; Figure 1) suggests a similar trend: from a late Pleistocene dominance of pinyon-juniper-oak woodland, with shrubs and desert succulents also present, to an early- and mid-Holocene appearance of subtropical desert shrub along with many grasses. The present grassland was established only during the late Holocene (Wells, 1966).

A recent study from El Potosí Basin suggests that this could be a critical additional archive of past climate and vegetation change. That work suggests that the paleohydrological conditions of the area were controlled by the sea-surface temperature (SST) of the Gulf of Mexico (GoM; Roy et al., 2016). The Ti abundance, interpreted as a runoff and precipitation record, shows a first order positive correlation with the June (summer) insolation and SST of the GoM (Flower et al., 2004; Ziegler et al., 2008) for the Last Glacial Maximum (LGM) and deglaciation, with enhanced moisture transported during warmer conditions, and vice versa (Roy et al., 2016). However, during the early- and mid-Holocene, the precipitation record and SST of the GoM became decoupled, and the authors suggested that further evaluation was necessary to understand this hydrological disconnection.
In this study, we present a paleoenvironmental and paleoecological reconstruction of the El Potosi Basin – based on molecular organic geochemical proxies – over the last 20 kyr with a particular focus on the Holocene. Molecular organic geochemical proxies can be used to reconstruct environmental conditions and organic matter inputs, commonly applied to modern lakes across the world (e.g. Meyers, 2003; Theissen et al., 2005; Xiong et al., 2010; Holtvoeth et al., 2016; Van Bree et al., 2018). Lipid biomarkers can distinguish between terrestrial and aquatic components, providing insight into environmental conditions in the water column and the surrounding watershed. For example, the long-chain fatty acids (n-FAs) derive nearly exclusively from leaf waxes of terrestrial plants (Eglinton and Hamilton, 1967), whereas the C\textsubscript{17} and C\textsubscript{19} n-alkanes are generally considered to be indicators of algae and photosynthetic bacteria (Han et al., 1968; Han and Calvin, 1969; Cranwell et al., 1987; Meyers, 2003). The C\textsubscript{27}, C\textsubscript{29} and C\textsubscript{31} n-alkanes are also leaf wax constituents of terrestrial plants, with the C\textsubscript{31} n-alkane frequently being the most abundant n-alkane in grasses (Maffei, 1996; Ficken et al., 2002). Microbial biomarkers include the branched FAs (Goossens et al., 1989) and the isoprenoidal (i) and branched (br) glycerol dialkyl glycerol tetraether (GDGT) lipids (Sinninghe Damsté et al., 2000). Because the iGDGT crenarchaeol derives from primarily aquatic Thaumarchaeota and brGDGTs derive primarily from soil bacteria, the ratio of these two compound classes can also be used to assess the varying contributions of aquatic vs. terrestrial organic matter, via the Branched and Isoprenoid Tetraether (BIT) index (Hopmans et al., 2004).

The carbon isotopic composition of biomarkers provide further insights into organic matter inputs; in particular, the carbon isotopic composition of the aforementioned leaf waxes can be used to distinguish between C\textsubscript{3} and C\textsubscript{4} plants (O’Leary, 1988; Leng and Henderson, 2013). C\textsubscript{3} plants, which represent approximately 85% of all plant species, dominate in temperate environments, whereas C\textsubscript{4} plants, largely but not exclusively grasses, grow in extreme environments with high light intensities, high temperatures and high aridity (Ehleringer et al., 1991). Crucially, C\textsubscript{4} plants are enriched in $^{13}$C relative to C\textsubscript{3} plants (O’Leary, 1988), such that leaf wax $\delta^{13}$C values can act as an environmental proxy, via the ecological response to climatic conditions. Moreover, the carbon isotopic composition of aquatic biomarkers – such as short- and mid-chain fatty acids – can be used to evaluate changes in lake
conditions; this is because their $\delta^{13}C$ values are governed by those of dissolved inorganic carbon (Hollander and McKenzie 1991; Leng and Marshall, 2004) as well as the range of apparent fractionation values arising during algal photosynthesis (e.g. Bidigare et al., 1997).

The application of lipid biomarkers for environmental reconstruction in arid regions is generally poorly developed, because the associated lacustrine sediments often lack significant quantities of organic matter (OM). Nonetheless, organic-poor sediments of a paleo-lake located within the Santiaguillo Basin did yield a variety of biomarkers, allowing us to reconstruct ecosystem changes of the Chihuahua Desert of Mexico over the late Quaternary (Chávez-Lara et al., 2018). This provided insight into the temporal evolution of this lacustrine system and its catchment area through changes the aquatic and terrestrial OM inputs.

Figure 1 The El Potosi Basin (red star) is located in central-northern Mexico. The location of other records used here for comparison are presented as circles. Mean monthly temperature and precipitation from 1981 to 2010 AD are calculated from data obtained from the nearest meteorological station at El Potosi hills.

2. El Potosi Basin
The El Potosi Basin is located in subtropical northeast Mexico (Nuevo Leon State), in the rain shadow of the Sierra Madre Oriental Mountains (Figure 1). There was an endorheic and ephemeral lacustrine basin within this semi-graben (24°50'25'' N and 100°20'08'' W; 1,890 masl), but it has been dry for the last three decades. This is probably due to over-exploitation of groundwater from this drought-prone basin and agricultural practices, including burning the surface plants to prepare the land for cultivation, both of which have caused subsidence and sub-surface peat fire (Roy et al., 2014). The Jurassic to Neogene sedimentary bedrock of the watershed includes limestone, sandstone, siltstone and conglomerate (Eguiluz et al., 2000; Servicio Geológico Mexicano, 2000).

A nearby meteorological station on the El Potosi hills (~10 km east of the basin margin) provides mean monthly temperature and precipitation data from 1981 to 2010 AD (Source: Servicio Meteorológico Nacional, Mexico). It recorded an average annual temperature of ~16 °C (Figure 1). The average annual precipitation was 330 mm and most of it (~250 mm) occurred between April and October, with a bimodal distribution peaking in May and August. Precipitation for the rest of the year was 83 mm. Most of the modern day vegetation has been altered by agricultural activities, and the unaffected vegetation consists of xeric shrubland and halophilic grassland, including juniper (Juniperus monosperma), yuca (Yuca sp.), mesquite (Prosopis glandulosa), creosote bush (Larrea tridentata), prickly pear (Opuntia sp.), club chollas (Cylindropuntia sp.), lechuguilla (Agave lechuguilla), maguey (Agave sp.) and grasses (Oordeas sp., Bouteloa sp., Aristida sp.) (Amezcua-Torres, 2003).

3. Sediment and analysis

Sediment samples were collected up to 310 cm depth in a pit dug at the eastern border of the basin, in a natural part that had been unaffected by subsidence and peat fire. This sequence was previously studied for inorganic geochemistry, as well as total organic carbon (TOC), in order to reconstruct paleohydrological conditions (Roy et al., 2016). This profile includes a unit of clay at the bottom (310-200 cm depth) that includes a 42-cm section of organic rich clay (282-240 cm). Overlying the clay is a calcareous silt unit, from 200-48 cm depth, and then an upper silty-sand unit, from 48-0 cm depth. Both the silt and silty-sand units contain ~3-10 cm long desiccation fissures (Figure 2).
Sediments have TOC contents varying from 0.02 to 27.5 %, with the higher values (7.1-27.5 %) associated with the organic rich clay at 282-240 cm (Roy et al., 2016).

The chronology of the sequence is based on 9 different radiocarbon (AMS) dates previously reported by Roy et al. (2016) (Table 1). The radiocarbon values were calibrated by the online software Calib version 7.0.2 (Reimer et al., 2013), and the dates of highest probability within a 2σ interval were used for the chronological control (age vs. depth model shown in Figure 2). Collectively, the sediment sequence down to 310 cm depth represents the last 20,000 calendar years (20 cal kyr). Samples of 2 cm interval, therefore, represent 60 to 145 years average depositional history.

![Figure 2](image-url)  
**Figure 2** Stratigraphy of sedimentary sequence from the El Potosi Basin and radiocarbon dates at different depths (black boxes). The age model is constructed using calibrated values and it indicates the depositional history of last 20,000 years.

**Table 1** Radiocarbon dates of bulk sediment organic matter samples from different depths of the sedimentary profile, El Potosi Basin.
Total nitrogen (TN) contents were measured in 30 samples in duplicate (0.004 mean std. deviation) using a Thermo Scientific Flash Smart Organic Elemental Analyser at the School of Environmental Sciences of the University of Liverpool. Lipid biomarker analysis and their semi-quantification were carried out as described by Chávez-Lara et al. (2018). A total of 31 samples were collected at 10 cm intervals down to 301 cm depth. The samples were freeze-dried, homogenized, microwave extracted, transmethylated and derivatised prior to gas chromatography-mass spectrometry (GC-MS) analysis.

Biomarker ratios used in this paper include the BIT index (Hopmans et al., 2004), carbon preference index of n-alkyl leaf wax constituents (CPI; Bray and Evans, 1961), and total iGDGTs to total brGDGTs ratio (Ri/b; Xie et al., 2012). As explained above, the BIT index can be used to quantify the relative contribution of terrestrial (soil) vs aquatic (Thaumarchaeota) inputs, and it is defined as:

\[
BIT = \frac{GDGT1a + GDGT2a + GDGT3a}{crenarchaeol + GDGT1a + GDGT2a + GDGT3a}
\]

The related Ri/b can be used as a proxy for dry periods, where maximum values are indicative of the occurrence of severe drought and alkaline deposits. This ratio was calculated based on the equation (Xie et al., 2012):

\[
Ri/b = \frac{\sum iGDGTs}{\sum iGDGTs + \sum brGDGTs}
\]
The CPI of \( n \)-alkanes and \( n \)-FAs can be used to explore the nature and degradation of terrigenous inputs. Sediments containing non-degraded and immature organic matter have high indices, reflecting the primary biological signature, whereas low CPIs indicate that the inherited biological signature has been altered by secondary processes, such as degradation (Bray and Evans, 1961). It was calculated according to the following equation, where the numbers reflect the number of atoms in the \( n \)-FA carbon chain:

\[
\text{CPI} = \frac{C_{22} + C_{24} + C_{26} + C_{28}}{C_{21} + C_{23} + C_{25} + C_{27}} + \frac{C_{22} + C_{24} + C_{26} + C_{28}}{C_{23} + C_{25} + C_{27} + C_{29}}
\]

For compound specific carbon isotope analysis, total lipid extracts (TLEs) were fractionated by transferring into a silica (activated with 5% H\(_2\)O) column (1.25 g, 60-120 mesh, column length 132 mm). Based on the increasing polarity of 7 solvent mixtures (3.5 ml of each), each TLE was separated into 7 fractions: \( n \)-hexane, \( n \)-hexane: toluene (75:25), \( n \)-hexane: toluene (50:50), \( n \)-hexane: ethyl acetate (95:5), \( n \)-hexane: ethyl acetate (90:10), \( n \)-hexane: ethyl acetate (85:15) and \( n \)-hexane: ethyl acetate (80:20). Fractions were dried under a gentle flow of nitrogen and dissolved in hexane prior to their analysis by gas chromatography-combustion-isotope ratio mass spectrometry (GC-C-IRMS). Stable carbon isotopes of the fatty acids (analysed as fatty acid methyl esters, FAMEs) were determined using an Agilent Industries 7890A gas chromatograph coupled to an IsoPrime 100 mass spectrometer. Samples were automatically injected in splitless mode and helium was used as a carrier gas. The GC oven temperature programme was set to hold at 40°C for 2 min, followed by an increase to 300°C at a rate of 10°C min\(^{-1}\). The oven temperature was held at 315°C for 10 minutes. The combustion furnace contained a copper and silver wool reactor maintained at 850 °C. A standard FAME mixture (\( C_{11}, C_{13}, C_{16}, C_{21} \) and \( C_{23} \)) of known carbon isotopic composition was used to determine the instrument accuracy. Samples were analysed in duplicate, with data processing carried out using Ion Vantage software (version 1.5.6.0, IsoPrime). The \( \delta^{13}C \) values of individual fatty acids (\( n \)-FAs) were corrected for the carbon atoms added during methylation using the mass balance equation of Rieley (1994). Corrected \( \delta^{13}C \) values are expressed relative to the international VPDB (Vienna Pee Dee Belemnite) standard.
For GDGT analyses, a second TLE aliquot was dissolved in hexane:iso-propanol (IPA) (99:1 v/v) and passed through a 0.45 μm polytetrafluoroethylene (PTFE) filter. GDGTs were detected with HPLC-MS using an Accela LC system equipped with an automatic injector and coupled to a Thermo Scientific TSQ Quantum Access MS. Separation was achieved with an Alltech Prevail Cyan column (2.1 mm; 150 mm; 3 μm i.d.) with a flow rate of 0.2 ml/min. The solvent mix hexane:IPA (99:1 v/v) was eluted isocratically for 5 min, followed by a change in solvent polarity via a gradient to 1.8% IPA over 45 min (Hopmans et al., 2000). Ionisation was performed at atmospheric pressure, and select m/z: 1302, 1300, 1298, 1296, 1292, 1022, 1020, 1018, 1036, 1034, 1032, 1050, 1048, 1046 (Schouten et al., 2013) were scanned to increase sensitivity and reproducibility. No response factors have been determined as we only focus on GDGT proxy ratios such as Branched and Isoprenoid Tetraether (BIT) index (Hopmans et al., 2004), rather than GDGT concentrations.

4. Results

4.1. TOC contents, TOC/TN ratios and lipid concentration

The TOC concentrations are highly variable, and the highest percentages (7.1-27.5 %) are associated with organic rich clay at depths between 282 and 240 cm. Clay sediments between 240 and 200 cm have intermediate TOC concentrations (1.5-4.8%). Silt and silty-sand sediments have the lowest concentrations (< 2.1 %). The TOC percentages are taken from Roy et al. (2016).

TOC/TN ratios range from 6.7 to 23 (Figure 3). Clay sediments at the bottom-most part of the sediment archive (301-282 cm, 20-19.2 cal kyr) have the lowest ratios (6.7-7.9), and the organic rich clay sediments (282-240 cm, 19.2-15.5 cal kyr) have the highest ratios (18-23). In the rest of the sediment archive (240-0 cm, last 15.5 cal kyr), TOC/TN ratios range between 8.8 and 18.

The quantified lipid content is < 3.9 % relative to the total organic carbon (% TOC) and has an average of 0.7 % (Figure 3). Higher concentrations (0.5-3.9 %) occur in the organic rich clay unit (282-240 cm, 19.2-15.5 cal kyr BP) and the overlying clay unit at 240-200 cm (15.5-11.8 cal kyr BP). The bottom-most clay unit (301-282 cm, 20-19.2 cal kyr BP) and the sediments of the upper 91 cm (last 3.3
cal kyr) have lower lipid proportions (<0.3 %), indicating that a significant proportion of the TOC is recalcitrant and potentially reworked.
Figure 3 Stratigraphic profile with sample depths (grey boxes), geochemical data from elemental (TOC, total organic carbon content in weight%) and TOC to total nitrogen (TN, ratio) and biomarker analyses (BIT index; total iGDGTs to total brGDGTs ratio (Ri/b); GDGT-0 to crenarchaeol ratio; lipid concentration relative to TOC; lipid composition: bar diagram) over depth. Note that the total lipid concentration (%TOC) is presented on a logarithmic scale. The record is divided into seven units (grey bars) based on geochemical characteristics as described in section 5.
4.2. GDGTs

BIT indices range from 0.5 to 1 with an average of 0.9 (Figure 3). Only the uppermost sediments (51-0 cm, last 2.5 cal kyr) and a single horizon at 111 cm depth (3.7 cal kyr BP) have values below 0.8, whereas samples from the rest of the sediment archive have high values (0.8-1), indicating a dominance of either allochthonous soil inputs or a lack of Thaumarchaeotal production. The BIT index includes only crenarchaeol among the isoprenoidal GDGTs, but other isoprenoidal GDGTs do occur; nonetheless, the ratio of total iGDGTs to total brGDGTs (Ri/b) mirrors the BIT profile. GDGT-0 is the most significant iGDGT, even over crenarchaeol (high GDGT-0/cren ratio; Figure 3), and it could originate from lake surface-dwelling crenarchaeota as well as from methanogenic archaea residing in the deeper and anoxic part of the water column (Blaga et al., 2009; Sinninghe Damsté et al., 2009).

Cyclopentane-bearing GDGTs also occur; typically, this is GDGT-1 (i.e. a single ring) but in some sediments the proportions of GDGT-2 are relatively higher than GDGT-1. However, total abundances of iGDGTs that include these other components are still low compared to total abundances of brGDGTs (Figure 4).

Figure 4 Representative total ion current (TIC) of the HPLC/APCI/MS chromatogram of a representative sample (121 cm depth), showing both br- and iGDGTs. Note that the brGDGTs are particularly dominant over the iGDGTs.
The high BIT indices preclude application of the TEX$_{86}$ proxy (Weijers et al., 2006; Schouten et al., 2013). The MBT’ and CBT ratios, used for estimating the mean annual air temperature and pH (Weijers et al., 2007; Peterse et al., 2012), could be determined (see supplement) but are also deemed unreliable despite the dominance of brGDGTs, because they indicate LGM temperatures that are greater than those of the Holocene. This could reflect seasonal or other impacts, but we suggest that it arises from changes in aridity and soil moisture, which are known to strongly impact the MBT’ proxy (Xie et al., 2012).

4.4. Lipid composition (compound class inventory)

Amounts of individual lipids are presented as percentages of the sum of all quantified lipids ($\%_{lipids}$). Saturated $n$-fatty acids, mono- and poly-unsaturated fatty acids, hydroxy fatty acids, branched fatty acids, $n$-alcohols, $n$-alkanes, methyl ketones, sterols, and a range of miscellaneous compounds including $\alpha$-amyrin and $\beta$-amyrin are semi-quantified (summary in Table 2) and presented in Figure 3 (complete compound list is in the supplement). In general, these represent the vast majority of GC-amenable compounds in the TLEs. The lipid record is divided into seven units based on geochemical characteristics and biomarker distributions as discussed in section 5.

Saturated $n$-fatty acids ($n$-FAs) represent the major lipid group, and their summed concentration fluctuates between 29 to 62 $\%_{lipids}$, albeit with no clear trend with depth or among units (average 46 $\%_{lipids}$). Hydroxy fatty acids (OH-FAs) comprise the second major lipid group, and their concentration fluctuates between 0.8 and 36 $\%_{lipids}$ (average 19 $\%_{lipids}$), with that range largely arising from low abundances at the base of the section (Unit 1) and in the shallowest sediments (Units 6 and 7). The concentration of monounsaturated FAs (MUFAs) is highly variable, up to 37 $\%_{lipids}$ (average 9.3 $\%_{lipids}$), with the highest concentration at the base of the record (Unit 1) and in the shallowest sediments (Units 6 and 7). Polyunsaturated FA (PUFAs) concentration is < 3.2 $\%_{lipids}$ (average 0.8 $\%_{lipids}$) with the highest concentration in the deepest sediments (Unit 1). Branched FA – mainly anteiso-$C_{15}$, iso-$C_{16}$ and iso- and anteiso-$C_{17}$ components – concentration is < 14 $\%_{lipids}$ (average 3.4 $\%_{lipids}$), with that value decreasing from top (Units 6 and 7) to bottom (Unit 1) sediments. The $n$-alkane concentration varies
from 0.6 %\textsubscript{lipids} and 9.7 %\textsubscript{lipids} (average 2.3 %\textsubscript{lipids}), with the highest concentration in sediments from Units 1 and 7.

The concentrations of other compound groups vary but do not exhibit any clear trends with depth or among units: the \textit{n}-alcohol (\textit{n}-OH) concentration varies from 2.3 to 14 %\textsubscript{lipids} (average 6.7 %\textsubscript{lipids}), the methyl ketone concentration is < 4.5 %\textsubscript{lipids} (average 2.1 %\textsubscript{lipids}), and the concentration of summed sterols – mainly sitosterol – is < 2.7 %\textsubscript{lipids} (average 0.3 %\textsubscript{lipids}). Finally, the concentration of other identified compounds – mainly amyrins – is < 28 %\textsubscript{lipids} (average 12 %\textsubscript{lipids}), varying significantly through Units 1 to 6 and being absent in the uppermost Unit 7.

\begin{table}
\centering
\begin{tabular}{cccccccccccc}
\hline
Depth (cm) & Age (cal kyr BP) & \textit{n}-FAs & short \textit{n}-FA & mid \textit{n}-FA & long \textit{n}-FA & \textit{a}-OH-FAs & branched FAs & MUFAs & PUFA & \textit{n}-Ohs & methyl ketones & sterols & others \\
\hline
1 & 0.1 & 40 & 13 & 7.9 & 19 & 1.9 & 1.2 & 0.6 & 1.7 & 35 & 1.2 & 8.1 & 9.7 & 2.7 & - \\
11 & 0.7 & 41 & 12 & 10 & 19 & 1.0 & 0.1 & 0.5 & 5.1 & 29 & 0.7 & 9.4 & 9.7 & 4.5 & 0.4 & - \\
21 & 1.3 & 29 & 18 & 9.2 & 14.8 & 1.6 & 1.3 & 1.0 & 26 & 0.5 & 7.2 & 3.0 & 0.4 & 24 & - \\
31 & 1.8 & 45 & 26 & 14 & 4.9 & 4.5 & 2.9 & 1.6 & 10 & 19 & 0.6 & 8.4 & 1.6 & 0.7 & - & 9.6 \\
41 & 2.3 & 48 & 24 & 21 & 3.1 & 1.3 & 0.9 & 0.5 & 4.2 & 34 & 0.6 & 3.9 & 1.2 & 0.4 & - & 6.0 \\
51 & 2.5 & 35 & 18 & 13 & 4.2 & 9.2 & 3.0 & 5.9 & 14 & 15 & - & 14 & 2.1 & 0.9 & 1.6 & 8.2 \\
61 & 2.7 & 49 & 27 & 19 & 3.0 & 3.1 & 2.3 & 0.9 & 14 & 25 & 0.2 & 2.9 & 1.1 & 0.4 & - & 4.5 \\
71 & 2.9 & 45 & 9.6 & 12 & 23 & 18 & 0.4 & 18 & 6.8 & 8.5 & - & 7.8 & 0.7 & 0.6 & 1.3 & 12 \\
81 & 3.0 & 38 & 6.0 & 13 & 20 & 24 & - & 24 & 6.7 & 2.3 & - & 5.9 & 1.3 & 0.9 & - & 21 \\
91 & 3.3 & 44 & 4.4 & 16 & 24 & 24 & 0.2 & 24 & 3.8 & 1.7 & - & 5.5 & 0.8 & 0.6 & - & 19 \\
101 & 3.5 & 43 & 4.3 & 15 & 24 & 18 & 0.1 & 18 & 2.5 & 1.2 & - & 5.3 & 0.6 & 1.4 & - & 28 \\
111 & 3.7 & 55 & 8.7 & 24 & 25 & 15 & - & 15 & 3.7 & 0.9 & - & 4.0 & 1.4 & 1.6 & 0.4 & 16 \\
121 & 3.9 & 39 & 4.5 & 13 & 21 & 21 & 0.1 & 20 & 4.1 & 2.1 & - & 6.8 & 1.0 & 2.6 & - & 24 \\
131 & 4.1 & 47 & 5.0 & 18 & 24 & 32 & 0.1 & 32 & 3.9 & 1.9 & 6.1 & 0.1 & 6.3 & 0.8 & 23 & 0.2 & 6.1 \\
141 & 4.3 & 50 & 5.7 & 21 & 23 & 19 & 0.1 & 19 & 2.6 & 1.5 & - & 6.0 & 1.4 & 3.1 & - & 16 \\
151 & 5.2 & 62 & 3.7 & 25 & 34 & 15 & - & 15 & 1.8 & 1.2 & - & 4.7 & 2.1 & 3.9 & 0.6 & 8.0 \\
161 & 6.1 & 51 & 4.7 & 20 & 26 & 25 & - & 25 & 2.9 & 2.5 & - & 7.7 & 1.6 & 4.4 & - & 5.4 \\
171 & 7.0 & 49 & 3.5 & 18 & 28 & 31 & - & 31 & 2.3 & 1.2 & - & 7.2 & 1.6 & 3.8 & 0.5 & 3.1 \\
181 & 8.4 & 50 & 3.1 & 19 & 28 & 30 & 0.1 & 30 & 1.9 & 0.8 & - & 7.2 & 1.1 & 3.6 & - & 5.7 \\
191 & 10.2 & 49 & 3.6 & 17 & 28 & 28 & 0.1 & 28 & 1.7 & 0.6 & - & 9.1 & 1.6 & 1.9 & - & 8.1 \\
201 & 12.0 & 55 & 3.3 & 17 & 35 & 24 & - & 24 & 0.9 & 0.2 & - & 5.5 & 2.2 & 2.6 & - & 9.0 \\
211 & 13.0 & 55 & 2.7 & 18 & 35 & 23 & 0.3 & 22 & 0.3 & 0.0 & - & 4.5 & 1.7 & 2.1 & - & 14 \\
221 & 13.8 & 50 & 3.4 & 16 & 31 & 24 & 0.3 & 23 & 0.3 & - & 5.1 & 1.3 & 1.4 & - & 18 \\
231 & 14.7 & 49 & 2.3 & 17 & 30 & 26 & - & 26 & 0.4 & 0.1 & - & 6.2 & 1.7 & 1.8 & - & 15 \\
241 & 15.6 & 46 & 2.9 & 14 & 29 & 31 & 3.2 & 27 & 0.2 & - & 5.2 & 1.1 & 1.6 & - & 15 \\
251 & 16.5 & 44 & 6.9 & 15 & 22 & 31 & 0.7 & 30 & 0.6 & - & 3.8 & 1.2 & 1.4 & - & 18 \\
261 & 17.4 & 44 & 5.0 & 22 & 17 & 30 & 0.1 & 29 & 0.7 & 0.3 & - & 7.9 & 1.4 & 2.4 & 2.2 & 11 \\
271 & 18.3 & 45 & 3.3 & 13 & 29 & 36 & 0.7 & 35 & 0.5 & 0.1 & - & 6.4 & 1.0 & 1.2 & - & 10 \\
281 & 19.1 & 49 & 4.6 & 22 & 23 & 31 & 0.6 & 31 & 0.4 & 0.1 & - & 5.5 & 1.4 & 2.9 & - & 9.1 \\
291 & 19.9 & 48 & 12 & 10 & 26 & 4.1 & - & 4.1 & 0.4 & 14 & 0.3 & 12 & 9.1 & 3.9 & - & 8.3 \\
301 & 20.0 & 41 & 14 & 13 & 14 & 0.8 & - & 0.8 & 0.5 & 37 & 3.2 & 6.9 & 4.5 & 3.4 & - & 2.3 \\
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\caption{Summary of the quantified compound classes in 31 sediment samples collected from the El Potosi sedimentary record. The concentrations are expressed as %\textsubscript{lipids}.}
\end{table}

4.5. Carbon isotope composition

The carbon isotopic compositions of \textit{n}-FAs (δ\textsubscript{13}C\textsubscript{FA}, Figure 5, Table 3) vary significantly with both carbon number and depth. However, three general patterns of behaviour can be distinguished, although within each group there are intriguing variations: 1) short-chain C\textsubscript{16} and C\textsubscript{18} \textit{n}-FAs, which...
exhibit high variability in Units 3 and 4; 2) the C$_{20}$ n-FA, which is unexpectedly decoupled from other mid-chain n-FAs and is often the most $^{13}$C-enriched n-FA in the entire sequence; and 3) mid-chain C$_{22}$ and C$_{24}$ n-FAs, which intriguingly exhibit similar carbon isotopic trends as the long-chain even-numbered (C$_{26}$, C$_{28}$, C$_{30}$) n-FAs. The odd-chain C$_{23}$, C$_{25}$ and C$_{27}$ n-FAs appear to exhibit similar behaviour to those in group (3), suggesting a similar source and suggesting that they derive from diagenetic alteration (Meyers and Ishiwatari, 1993).

Short-chain C$_{16}$ and C$_{18}$ n-FA $^{13}$C values behave similarly in Unit 2 and from Unit 5 to 7, where the values range from -31 ‰ to -24.7 ‰. In Units 3 and 4, their $^{13}$C values exhibit profound variability and a larger range from -32.2 ‰ to -22.6 ‰. However, excluding Units 3 and 4, these short-chain compounds record a general trend of $^{13}$C-enrichment from the deepest sediments to the shallowest sediments (Figure 5).

Overall, mid-chain C$_{22}$ and C$_{24}$ n-FAs exhibit a similar isotopic composition among all the units, and their $^{13}$C values range from -31.3 ‰ to -25.3 ‰. Interestingly, the C$_{20}$ n-FA presents a unique trend, being more enriched in $^{13}$C with $^{13}$C values fluctuating from -30.2 ‰ to -19.2 ‰; the lower values are observed in Unit 2, gradually increasing in Unit 3 and remaining high from Unit 4 to 7. The $^{13}$C values of the C$_{22}$ FA are as high as -19.2 ‰ suggesting an aquatic (algal) source, which is supported by the covariation of the $^{13}$C values of the C$_{22}$ and C$_{16}$ FAs during the C$_{16}$ isotope excursion in Units 3 and 4 (Figure 5).

Long-chain C$_{26}$, C$_{28}$ and C$_{30}$ n-FAs $^{13}$C values are variable but generally low in Units 2 and 3 within a range from -32.6 ‰ to -30 ‰. In Unit 4, they exhibit a larger range (from -32.2 ‰ to -26 ‰) which increases to higher $^{13}$C values (from -33.8 ‰ to -21.2 ‰) in Unit 6. Generally, C$_{3}$ plants exhibit $^{13}$C bulk values between -35 and -21 ‰, whereas C$_{4}$ exhibit $^{13}$C bulk values between -20 and -9 ‰ (O’Leary, 1988). Most lipids found in plant tissue, such as leaf waxes, are depleted by up to 4-6 ‰ relative to C$_{3}$ plant bulk vegetation values and up to 8-10 ‰ relative to C$_{4}$ bulk values (Hobbie and Werner, 2004). Thus, $^{13}$C values in leaf waxes can range from -40 to -27 ‰ in C$_{3}$ plants and from -30 to -19 ‰ in C$_{4}$ plants. Accordingly, higher $^{13}$C values of some long-chain FAs suggest an increase in the proportion of $^{13}$C-enriched C$_{4}$ plants within the terrestrial plant community.
The dominant chain length of long-chain leaf wax FAs can vary between different plant species (e.g. Holtvoeth et al., 2016), and this means that mixing ratios between C₃ and C₄ members can differ for different FAs; this appears to be the case at El Potosi (Figure 5). In Unit 4, C₂₆ and C₃₀ FAs have elevated δ¹³C values; in Unit 5, mainly C₃₀ FA has an elevated δ¹³C value; and in Unit 6 it is only the C₂₆ FA and, in one case, the C₂₈ FA that has an elevated value. Collectively, this indicates that there were significant C₄ inputs in Units 4, 5 and especially 6, but the C₄ plant source appears to have varied. Long-chain n-FA δ¹³C values are lower in the shallowest unit (Unit 7) compared to previous units, with a range from -29.2 ‰ to -26.8 ‰.

**Figure 5** Stratigraphic profile with sample depths (grey boxes) and the carbon isotopic compositions of short-chain C₁₆ and C₁₈ n-FAs (circles), mid-chain C₂₀, C₂₂ and C₂₄ n-FAs (diamonds), and long-chain even-numbered C₂₆, C₂₈ and C₃₀ n-FAs (triangles) and odd-numbered C₂₃, C₂₅ and C₂₇ n-FAs (average, squares). The values are expressed as ‰ relative to the international Vienna Pee Dee Belemnite standard; δ¹³CFA values in the bottom-most clay unit (Unit 1) could not be determined due to low
concentrations. The record is divided into seven units (grey bars) based on geochemical characteristics and biomarker distributions as described in the discussion.

Table 3 Carbon isotopic composition of n-fatty acids for 31 sediments collected from the El Potosi sedimentary record. The values are expressed as % relative to the international Vienna Pee Dee Belemnite standard.

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5. Discussion

The dramatic changes in biomarker assemblages reveal complex and multiple controls on OM input into the El Potosi Basin. These reflect changes in terrestrial ecosystems as well as relative aquatic vs. terrestrial inputs. They also reflect the degree of degradation and alteration, especially of terrigenous material that has been delivered to the lacustrine basin. We identified 7 major units based on biomarker distributions (Figure 3, see supplement for principal component analysis). The lowermost Unit 1 is characterised by higher proportions of n-alkanes and MUFAs. Unit 2 and Unit 3 have similar biomarker distributions to each other, but they were further split based on their organic carbon content with the former being an organic rich interval and the latter being more organic lean. Units 4 and 5 are
characterised by methyl ketones and other identified compounds, including $\alpha$- and $\beta$-amyrin. Moreover, the boundary between the 3rd and 4th Unit is also characterised by a sedimentary change from clay to silt. Unit 6 is characterised by branched FAs as principal component. Intriguingly, the uppermost Unit 7 has similar characteristics as Unit 1, using only lipid class-based PCA, but these two intervals differ in a variety of other biomarker and isotopic features as discussed below. Below, we first examine the changes in biomarker distributions (5.1), focusing particularly but not exclusively on the distribution of terrigenous lipids that likely reflect the changes in terrestrial environment. We then consider those changes in the context of wider local and regional environmental change in section 5.2.

5.1. Ecosystem evolution

The sediment archive is characterised by change in texture from clay to silt at 200 cm depth and silt to silty-sand at 48 cm depth. The clay rich sediments in the lower part of the archive contained more TOC, whereas both the silt and silty-sand units in the middle and upper parts of the sediment contain desiccation fissures and lower TOC contents. This suggests that the depositional environment in the basin generally changed from low-energy mostly perennial conditions during the latest LGM and deglaciation to high-energy ephemeral conditions with periodic desiccation over the Holocene. We use these observations, as well as the seven different geochemical units described above, to interpret the millennial-scale changes that occurred since the LGM (in chronological order).
Figure 6 Stratigraphic profile of the sedimentary record (boxes on side of profile are sampled layers) alongside lipid biomarker distributions over time. Key compositional changes (%) of \( n \)-fatty acids (\( n \)-FAs), monounsaturated FAs (MUFAs), hydroxy acids (\( \omega \)-OH-FAs), branched FAs, \( n \)-alkanes and amyrins are shown, as well as units defined in the text: Unit 1 (20-19 cal kyr BP), Unit 2 (19-15 cal kyr BP), Unit 3 (15-11.7 cal kyr BP), Unit 4 (11.7-4.2 cal kyr BP), Unit 5 (4.2-2.8 cal kyr BP), Unit 6 (2.8-1 cal kyr BP) and Unit 7 (last 1 cal kyr). For \( n \)-alkyl components, \( s \) = short-chain (C\(_{16}\) to C\(_{19}\)), \( m \) = mid-chain (C\(_{20}\) to C\(_{25}\)), and \( l \) = long-chain (C\(_{26}\) to C\(_{32}\)) homologues.
**Figure 7** Averaged (by unit) chain length distributions of \( n \)-fatty acids, \( \omega \)-hydroxy acids, \( n \)-alkanes and \( n \)-alcohols from Unit 1 (20-19 cal kyr BP), Unit 2 (19-15 cal kyr BP), Unit 3 (15-11.7 cal kyr BP), Unit 4 (11.7-4.2 cal kyr BP), Unit 5 (4.2-2.8 cal kyr BP), Unit 6 (2.8-1 cal kyr BP) and Unit 7 (last 1 cal kyr).

Average values (y axis) are percentages of the total amount of each compound class, i.e. \( \% n \)-FAs, \( \% \omega \)-OH-FAs, etc.

5.1.1 Unit 1 (20-19 cal kyr BP, \( n = 2 \))

This unit is contemporary to the latest phase of the LGM and is characterized by very low lipid concentrations. Compound class distributions exhibit high proportions of MUFAs (C\( _{18:1} \) and C\( _{22:1} \)) and \( n \)-alkanes; among the \( n \)-FAs, the short-chain homologues are elevated relative to mid- and long-chain ones. The C\( _{22:1} \) MUFA could derive from zooplanktonic copepods that produce this compound as part
of protective wax esters (Arts et al., 2001). The proportion of ω-OH-FA, on the other hand, is very low. These compounds may result from in-situ microbial oxidation of fatty acids (Eglinton et al., 1968; Cranwell, 1982), in which case they would be expected to show a distribution similar to the fatty acids. However, the distributions of n-FAs and ω-OH-FA appear unrelated in this unit. The unusually high relative amounts of MUFAs and presence of some PUFAs in one of the samples suggest an in-situ source since unsaturated compounds are more susceptible to microbial degradation (electrophile attack on double bonds) compared to saturated compounds. The high proportions of C_{18:1} MUFA could be related to the comparably enhanced proportions of short-chain n-FAs, notably the C_{18} n-FA. This makes a plant source seem unlikely as this would typically be associated with elevated amounts of C_{16} n-FA as the main fatty acid in plant tissue (e.g., Matsuda and Koyama, 1977; Desvillettes et al., 1997; Holtvoeth et al., 2010). Low TOC/TN ratios are also consistent with a contribution from in-situ bacterial and/or algal biomass (TOC/TN: 4-6; Nagata, 1986; Lee and Fuhrman, 1987), and low BIT indices (Figure 8) suggest some contribution of archaeal isoprenoidal GDGTs from the water column. Terrestrial inputs are evident but are dominated by more recalcitrant components. In particular, the low proportion of long-chain ω-OH-FA and long-chain n-FAs and enhanced proportions of long-chain n-alkanes (1 n-alkanes) suggests that terrestrial OM was degraded on land, i.e. before being exported towards the sediment. The dominance of the C_{31} n-alkane suggests input from a grassy environment since grasses tend to show a distribution maximum at this chain length (Rommerskirchen et al., 2006; Cui et al., 2008; Holtvoeth et al., 2016; Bliedtner et al., 2018). The n-alcohols have a trimodal distribution, peaking at C_{18}, C_{28} and C_{32}, with the latter compounds indicating input of terrestrial plant leaf waxes (Eglinton and Hamilton, 1967; Řezanka and Sigler, 2009) from two distinct sources. This implies that the asymmetrical distribution of the long-chain n-FAs potentially also results from input of n-FAs from two sources. Overall, Unit 1 appears to represent a period with low organic matter burial in the lake, with production and/or input of terrestrial OM being relatively low and degraded and the contribution of lipids from aquatic/in-situ microbial biomass being relatively higher.

5.1.2 Unit 2 (19-15 cal kyr BP, n = 5)
Unit 2, by contrast, is characterized by significantly higher lipid concentrations, with higher proportions of mid- and long-chain n-FAs, ω-OH-FAs and long-chain OHs. Mid- and long-chain n-FAs derive nearly exclusively from leaf waxes of terrestrial plants, as indicated by their low δ13C values (Figure 8). The ω-OH-FA distribution in this unit appears to match that of the n-FAs, suggesting that, unlike in Unit 1, the ω-OH-FAs are mainly in-situ degradation products of n-FAs. Moreover, this unit shows enhanced proportions of odd-numbered n-FAs, peaking at C25; based on their carbon isotopic compositions, they also appear to be of terrestrial provenance, suggesting OM input from a peculiar terrestrial source with unusually high proportions of odd-numbered n-FAs or enhanced degradation of the FAs. The n-alkane distribution in this unit is bimodal with pronounced peaks at the C23 and C31 n-alkanes. The C23 n-alkane is the major n-alkane in many Sphagnum species (Baas et al., 2000; Nott et al., 2000) and also occurs in the roots of sedges (Ronkainen et al., 2013). It is also a constituent of submerged and floating aquatic plants, although the n-alkane distribution of these plants is usually unimodal and typically dominated by the C25 component (Ficken et al., 2000). Thus, we suggest its abundance in Unit 2 could be indicative of a wetland environment within the catchment of the lake. The C31 n-alkane is typically associated with grasses (Rommerskirchen et al., 2006; Cui et al., 2008; Holtvoeth et al., 2016; Bliedtner et al., 2018), which could have flourished in a wetland environment as well as in the hinterland. The n-alcohol distribution differs significantly from Unit 1, with the long-chain n-OHs now peaking at C26 and significant contributions of the mid-chain C22 and C24 n-OHs. The latter can derive from suberin, a biopolyester and major compound in root material (Molina et al., 2006), thus, representing inputs of soil OM (Holtvoeth et al., 2016).

Regardless of those nuanced biomarker interpretations, Unit 2 clearly represents a stage of significantly higher terrestrial OM input to the lake sediments compared to Unit 1, with the biomarkers evidently deriving from a range of terrestrial materials including leaf waxes, degradation products of macromolecules (suberin and cutin) and wetland vegetation. Such an interpretation is also consistent with high TOC/TN ratios and BIT indices (Figure 8).

5.1.3 Unit 3 (15-11.7 cal kyr BP, n = 4)
Sediments of Unit 3 represent the deglaciation and the Pleistocene-Holocene transition. Although the general lipid composition in Unit 3 is similar to the previous Unit 2 (Figures 3 and 6), the TOC content is much lower and there are meaningful differences in the chain-length distributions of the individual alkyl compound classes (Figure 7) as well as in the isotopic composition of the C_{20} n-FA. FAs are still dominated by the long-chain homologues, peaking at C_{26}, but the proportion of odd-numbered n-FAs, specifically C_{23}, C_{25} and C_{27} n-FA (peaking at C_{25}), continues to increase leading to slightly lower n-FA CPIs (Figure 8). Slightly elevated abundances of C_{20} n-FA result in a trimodal FA distribution that is also recognisable in the distribution of ω-OH-FAs, corroborating the assumption that the ω-OH-FAs result from in-situ degradation of n-FAs. However, the chain-length distribution maximum shifts from C_{26} to C_{28} ω-OH-FA, thus diverging from the n-FA distribution, peaking at C_{26}. This could result from different susceptibility of the mixture of plant tissue types to microbial degradation. As in Unit 2, the n-alcohols are mainly long-chain homologues, derived from terrestrial wax esters. However, a shift towards longer chain lengths occurs, with the dominant compounds now being C_{28} and C_{30} n-OH. The distribution suggests a supply of n-OHs from a range of sources, which could again include suberin (C_{22} n-OH) and possibly reeds with high proportions of the C_{30} and C_{28} n-OH on leaves (Holtvoeth et al., 2016). In contrast to Unit 2, the pronounced C_{23} n-alkane peak is nearly absent, leaving the C_{31} n-alkanes as the main, probably grass-derived compound. Finally, the δ^{13}C values of the C_{16} and C_{20} n-FAs increase during this stage, suggesting an increasing supply of these short-chain compounds from a ^{13}C-enriched aquatic source (Hollander and McKenzie 1991; Leng and Marshall 2004).

The organic matter of Unit 3, therefore, and like that of Unit 2, is dominated by terrigenous inputs. However, the distribution of terrestrial and littoral habitats appears to have changed, with the loss of wetlands but persistence of grasses. In addition, the C_{20} n-FA carbon isotopic shift indicates the emergence of a distinct aquatic yet unidentified source, and the shift in C_{16} n-FAs δ^{13}C values provides additional evidence for an increase in aquatic contributions.

5.1.4 Unit 4 (11.7-4.2 cal kyr BP, n = 6)
Unit 4 comprises sediments deposited during the early and middle Holocene. There, the proportion of the aquatic C_{20} n-FA further increases relative to the long-chain terrestrial n-FAs (Figure 8). The ω-OH-FA distribution is also similar to that of the n-FAs, again suggesting that the former are degradation products of the latter. The abundances of odd-numbered n-FAs also increases, again resulting in low CPIs (Figure 8); higher proportions of odd-chain C_{23}, C_{25} and C_{27} alcohols provide additional evidence for increased degradation of leaf waxes. The odd-numbered FAs and the C_{28} n-FA appear to derive from a common terrestrial source(s) as indicated by their δ^{13}C values (Figure 8), but the δ^{13}C values of the C_{28} and C_{30} n-FA exhibit slightly different profiles and become variable in this interval. This suggests that there are at least two terrestrial long-chain n-FA sources: one with variable δ^{13}C values, contributing mainly C_{26} and C_{30} FA, and another with non-variable δ^{13}C values, providing the C_{28} n-FA and the odd-numbered n-FAs (Figure 8).

The n-alkane distribution exhibits a remarkable decrease in the amount of the C_{31} n-alkane, suggesting a decrease in grass inputs. At the same time, the amount of β-amyрин relative to α-amyрин increases in Unit 4, expressed as the sharp drop in the α/β-amyрин ratio (Figure 8). This also indicates a change in the type of terrestrial plant tissue supplied to the lake which could result from a change in the composition of the terrestrial vegetation. In land plant tissue, β-amyрин is typically found in higher proportions in bark tissue, whereas α-amyрин is the major triterpenoid in resin (Hernández-Vázquez et al., 2012). Thus, a decrease in the α/β-amyрин ratio implies a shift towards a type of vegetation that contains less resinous material and produces relatively more bark litter.

The δ^{13}C values of the C_{16} and C_{20} n-FAs become even higher in the lower part of Unit 4, confirming the persistence of their aquatic source. Assuming that this increase no longer represents a change in a source mixing ratio, i.e. from a ^{13}C-depleted higher plant source to a ^{13}C-enriched aquatic one, and that these values reflect solely the aquatic end-member, then the increase in δ^{13}C values could reflect a combination of low dissolved carbon dioxide in the lake, more ^{13}C-enriched dissolved inorganic carbon and/or higher algal growth rates (Leng and Marshall., 2004). We attribute the increase in δ^{13}C values to an increase in algal growth, although a change in source cannot be precluded.
Intriguingly, in the upper part of Unit 4, the C$_{16}$ and C$_{20}$ n-FA δ$^{13}$C values become decoupled, with the former decreasing to values similar to those of the putative higher plant long-chain n-FAs.

This unit also contains increased proportions of short- and mid-chain n-OHs, dominated by the C$_{16}$ and C$_{20}$ homologues that possibly derive from phytoplankton and bacteria (Fukushima and Ishiwatari, 1984). The C$_{18:1}$ and C$_{22:1}$ MUFAs, indicative of phytoplankton and bacteria (e.g. Bobbie and White, 1980; Kattner et al., 1983; Ahlgren et al., 1992), are slightly more abundant, consistent with higher proportions of bacteria-derived branched FAs (Goossens et al., 1989). The mid-chain n-alkanes, notably, are dominated by the even-numbered C$_{24}$ n-alkane. Elevated proportions of even-numbered n-alkanes are typically attributed to bacterial sources (Grimalt et al., 1986; Grimalt and Albaigés, 1987).

At the same time, the GDGT-0 to crenarchaeol ratio decreases, which could reflect either higher temperatures (Schouten et al., 2002) or a change in archaeal assemblages, with lower abundances of methanogens associated with lower TOC contents.

Altogether, the supply of terrestrial OM appears to have decreased relative to aquatic/bacterial biomass in Unit 4. This is also indicated by lower TOC/TN values and slightly lower BIT indices (Figure 8). Furthermore, the composition of the terrestrial OM sources appears to have changed compared to Unit 3, with the relative contribution of the C$_{31}$ n-alkane from grasses decreasing and the change in the α/β-amyrin ratio suggesting a lower proportional input from resinous plant inputs. The terrestrial OM fraction also appears to be more degraded, with fatty acid and n-alcohols characterised by low CPIs.

5.1.5 Unit 5 (4.2-2.8 cal kyr BP, n = 7)

The transition to Unit 5 marks the onset of the late Holocene. Sediments of this unit contain slightly higher proportions of short-chain C$_{16}$ and C$_{18}$ n-FA relative to the long-chain terrestrial n-FAs, which could indicate greater proportions of aquatic OM sources. However, as discussed above, their δ$^{13}$C values converge somewhat, such that both could be of terrestrial provenance. The average n-FA distribution of this unit shows a distinct shift in the dominant compound from C$_{26}$ to C$_{28}$ n-FA, indicating decreasing n-FA supply from the terrestrial source characterised by variable δ$^{13}$C values of the C$_{26}$ and...
C$_{30}$ n-FAs (Figure 8). The odd-numbered terrestrial n-FAs are still present in this unit as well as their odd-chain C$_{23}$, C$_{25}$ and C$_{27}$ n-alcohol counterparts, albeit in slightly lower relative abundance compared to Unit 4. Thus, the CPI FA$_{22-28}$ values increase. The $\alpha/\beta$-amyrin ratio sharply increases, suggesting that the proportions of resin-derived $\alpha$-amyrin increases relative to $\beta$-amyrin from bark-type plant tissue.

The $\delta^{13}$C values of the C$_{28}$, C$_{30}$ and especially C$_{26}$ n-FAs increase through Unit 5, which could be due to a shift between C$_{3}$ and C$_{4}$ vegetation. The large increase in the C$_{26}$ n-FA $\delta^{13}$C value, especially at the top of Unit 5 (-24.1 ‰) and into Unit 6, provides particularly strong evidence for the presence of C$_{4}$ plants in the catchment.

In general, the biomarker data of this unit reflects a period of gradual environmental transition and ecosystem adaption during the first 1.5 kyr of the late Holocene. The findings imply a phase of gradual change in the terrestrial vegetation, including a higher proportion of C$_{4}$ grasses and potentially more open vegetation, as the overall terrestrial input decreases relative to bacterial/aquatic input. The latter is also indicated by slightly lower TOC/TN ratios. The sample at 3.7 kyr appears to represent a short interval of enhanced aquatic productivity as indicated by enhanced proportions of C$_{20}$ n-FA, C$_{20}$ $\omega$-OH-FA and isoprenoidal GDGTs (low BIT index, Figure 8).

### 5.1.6 Unit 6 (2.8-1 cal kyr BP, n = 5)

The most pronounced change in the overall character of OM input occurs from 2.8 kyr, apparently suggesting significant ecosystem shifts. The input of soil bacteria-derived branched GDGTs decreases abruptly relative to aquatic isoprenoidal GDGTs, as reflected by the BIT index (Figure 8), due to either a decrease in branched GDGT supply and/or enhanced production of isoprenoidal GDGTs. However, we note that an increase in the ratio of isoprenoidal to branched GDGTs in soils also occurs in alkaline soils formed under particularly arid conditions (Ri/b ratio; Xie et al., 2012). Increased soil alkalinity seems an additional or alternative explanation for the observed trends in BIT.

Further evidence for the shift towards a predominantly aquatic source of the extractable OM is the fact that Unit 6 is the only time slice where the C$_{20}$ n-FA is far more abundant than the long-chain leaf-wax derived n-FAs (high C$_{20}$/C$_{28}$ n-FAs ratio; Figure 8). Furthermore, the proportion of MUFAs
(C\textsubscript{18:1} and C\textsubscript{22:1}) increases significantly. High C\textsubscript{18:1} MUFA concentrations could reflect contributions from bacterial biomass, which is corroborated by enhanced proportions of microbial branched FAs and slightly higher amounts of the C\textsubscript{18:1} trans-isomer that tends to be more abundant in bacteria (Bobbie and White, 1980). The C\textsubscript{22:1} MUFA could derive from copepods (Arts \textit{et al}., 2001). The total proportions of \(\omega\)-OH-FAs – particularly of long-chain \(\omega\)-OH-FAs – decrease markedly, also in line with reduced terrestrial OM supply.

The now dominant C\textsubscript{16} \(\omega\)-OH-FA is likely to be of bacterial origin rather than a degradation product of C\textsubscript{16} n-FA. This is supported by enhanced proportions of C\textsubscript{16} \(\alpha\)-OH-FA (Table 2), which also probably derives from an \textit{in-situ} bacterial source (Eglinton \textit{et al}., 1968; Yano \textit{et al}., 1971; Fukushima \textit{et al}., 1992). Leaf wax-derived long-chain n-FAs not only have become sparse but also appear to have been significantly degraded (low I n-FA/I OH-FA ratio; Figure 8), especially at the base of Unit 6, suggesting reduced productivity and deterioration of the vegetation cover. Similarly, FA CPIs decrease.

Changes in vegetation, as inferred from biomarker distributions, appear to be complex. The \(\alpha/\beta\)-amyrin ratio fluctuates as do the n-OH distributions. Such fluctuations are not observed in the n-alkane distributions, but the upper three samples of Unit 6 are dominated by the C\textsubscript{27} n-alkane, which was largely absent in Units 3-5. Moreover, there is isotopic evidence that the C\textsubscript{26} n-FA derives from a \textit{C}_4 plant source. Intriguingly, the short-chain C\textsubscript{16} and C\textsubscript{18} n-FA \(\delta^{13}\)C values shift to slightly lower values of -26.7 and -27.6 ‰, respectively, deviating from those of the C\textsubscript{20} n-FA of presumed aquatic origin (-22.3 ‰) towards the \(\delta^{13}\)C values of long-chain n-FAs. Thus, these also could derive from degraded terrestrial inputs. Collectively, this suggests a general change in the terrestrial vegetation inputs, but it is unclear if this reflects ecosystem change or variability in delivery mechanism.

Overall, the proxy data in Unit 6 reflects an ecosystem with decreasing and variable terrestrial OM inputs, and associated variability in the character of those inputs. The ecosystem could have been near a transition state, making the supply of OM from various sources sensitive to low-amplitude climatic fluctuations. This could be expected for a shallow or ephemeral water body, with a limited catchment; indeed, evidence for a smaller and shallower lake comes from coarser lithogenic material (change from silt to silty sand), although the lithogenic change appears to have lagged those recorded
by the biomarkers by about 700 years. It is also consistent with high Ri/b ratios, potentially indicating very arid conditions and alkaline soils. This change in lacustrine conditions did not appear to adversely impact aquatic production, as the OM is still associated with persistent inputs from presumably aquatic (algal and microbial) sources. However, it is possible that the production became more microbially driven, as suggested by the decreased contribution of aquatic (algal) sources to the short-chain FAs (as reflected in their δ\(^{13}\)C values).

5.1.7 Unit 7 (last 1 cal kyr, \(n = 2\))

The uppermost and most recent unit contains higher lipid concentrations compared to the previous unit; it also appears, like Unit 6, to be dominated by aquatic inputs although the changes in higher plant inputs are complex and contradictory (although we note that Unit 1 comprises only two samples). The major changes with regard to lipid composition are the re-occurrence of abundant leaf wax-derived (long-chain) fatty acids and the highest proportions of long-chain \(n\)-alkanes, dominated again by the \(C_{31}\) \(n\)-alkane, but also the absence of the amyrins. BIT indices have their lowest values in the entire sequence, reflecting a combination of persistent aquatic inputs and low soil OM inputs – or highly alkaline soils. The δ\(^{13}\)C values of terrestrial \(n\)-FAs are slightly lower than in the previous unit, specifically for the \(C_{26}\) and \(C_{30}\) \(n\)-FA, suggesting a decreased \(C_4\) plant contribution to both and especially the \(C_{26}\) \(n\)-FA. The short-chain FAs, on the other hand, now seem to originate primarily from an aquatic source, whereas in Unit 6 they appeared to be of terrestrial origin.

It is possible that the contradictory terrestrial plant biomarker trends (i.e. the complete absence of amyrins and the minimum amounts of long-chain \(\omega\)-OH-FAs but the highest proportions of long-chain \(n\)-alkanes and \(1\)-FAs) arises from a low quality of the terrestrial OM, potentially related to OM degradation during soil storage or transport to the sediments. However, evidence for the preservation state of the OM is equivocal. The \(1\) \(n\)-FA/I OH-FA ratio increases, suggesting better preservation of leaf wax-derived \(n\)-FAs (Figure 8), but those ratios are not as high as in the fine-grained lower sections of the sediment core. Moreover, higher proportions of short chain \(\omega\)-OH-FAs peaking at \(C_{20}\) indicate enhanced \textit{in situ} degradation of the aquatic \(C_{20}\) \(n\)-FA, which now is present in significantly lower
proportions; however, it also has a lighter isotopic composition (Figure 8), implying an increasing contribution from terrestrial sources.

Evidence for significant aquatic inputs comes from the abundant short-chain FAs, with high δ13C values that are clearly distinct from those of the long-chain FAs, as well as low BIT indices and the maximum relative amounts of the C18:1 MUFA in the entire section, with higher proportions of the trans-isomer.

In general, the lipid composition of Unit 7 appears to reflect a combination of aquatic and minimal terrestrial inputs. The findings imply an ecosystem with some aquatic/bacterial productivity and degraded terrestrial vegetation shifting from C4 to C3 type. Moreover, the putative terrestrial source(s) for resinous material and bark litter (α- and β-amyris) seems to have been lost.

5.2 Ecosystem response to changing environments and regional hydroclimate

It has been argued that the hydroclimate of the El Potosí Basin was controlled by sea-surface temperature (SST) of the Gulf of Mexico (GoM), with enhanced moisture transported during warmer conditions, and vice versa (Roy et al., 2016). It influenced the evolution of the limnic ecosystem as well as the surrounding terrestrial habitats. Seven different units have been distinguished, based on biomarker assemblages and representing different stages of the ecosystem development. We compare the ecosystem changes inferred from the biomarker proxies with the previously published Ti-based runoff record (Roy et al., 2016) for the late Pleistocene as well as Holocene in Figure 8. Some of the fossil pollen and midden-based paleovegetation records from the southeastern USA and northeastern Mexico (Figure 1) are also incorporated into our interpretation (Hafsten, 1961; Wells, 1966; Van Devender and Burgess, 1985; Betancourt et al., 1990; Van Devender, 1990).
Figure 8 Proxy record comparison of a) inorganic terrestrial runoff (Ti; Roy et al., 2016), b) total organic carbon to total nitrogen ratio, c) branched and isoprenoid tetraether (BIT) index, d) lipid concentration relative to the total organic carbon (%TOC), e) long chain n-fatty acids to long chain hydroxy acids ratio, f) carbon preference index from C_{22} to C_{28} n-fatty acids, g) C_{20} to C_{28} n-fatty acid ratio and C_{20} to C_{28} ω-hydroxy acid ratio, h) α-amyrin to β-amyrin ratio and i) δ^{13}C values of n-fatty acids. The record is divided into seven units (grey bars) as defined in the text: Unit 1 (20-19 cal kyr BP), Unit 2 (19-15 cal kyr BP), Unit 3 (15-11.7 cal kyr BP), Unit 4 (11.7-4.2 cal kyr BP), Unit 5 (4.2-2.8 cal kyr BP), Unit 6 (2.8-1 cal kyr BP) and Unit 7 (last 1 cal kyr).
During the final stage of the LGM (20-19 cal kyr BP; Unit 1), dry conditions are inferred from low terrestrial runoff input as indicated by low Ti concentration (Roy et al., 2016). Moreover, lipid biomarkers suggest a period with relatively low terrestrial OM production and evidence for degraded terrestrial biomass (unrelated distributions of $n$-FAs and $\omega$-OH-FAs; low $l$/$n$-FAs/$l$ OH-FAs ratio). However, the lake did seem well developed, with a strong contribution of aquatic/in-situ microbial biomass ($C_{18:1}$ MUFA, TOC/TN, BIT index), as well as inferred copepod abundance which are highly adapted to survive periods of droughts (Hastison and Walton, 1986).

During the deglaciation, the SST of the GoM increased and concurrently runoff to the El Potosi basin increased between 19 and 12 cal kyr BP (Roy et al., 2016). The paleovegetation record – based on packrat middens – suggests abundant woodland species including pinyon, juniper and some succulents (Wells, 1966; Betancourt et al., 1990). These findings match the lipid results from El Potosi Basin. During the earlier part of the wetter deglaciation (19-15 cal kyr BP; Unit 2), the lipid concentration increased significantly. Crucially, it appears to have been derived mostly from terrestrial materials (woodland) such as protective leaf wax esters and cutin (mid- and long-chain $n$-FAs), wetland vegetation and grasses ($C_{23}$ and $C_{31}$ $n$-alkane, respectively) and potentially suberin from soil OM ($C_{22}$ and $C_{24}$ $n$-OH). Moreover, there was a high contribution of terrestrial in-situ degradation products ($\omega$-OH-FAs), and the in-lake productivity seems to have been diluted. Thus, warming and increased rainfall in the El Potosi Basin during the deglaciation brought about the growth of extensive and diverse terrestrial ecosystems and associated runoff that flushed that OM into the ancient lake.

During the latter part of deglaciation (15-11.7 cal kyr BP; Unit 3), the contribution of wetland material disappeared, whereas the proportions of leaf wax esters, cutin and soil OM remain high, reflecting the woodland influence. This could reflect somewhat wetter conditions, especially as it is associated with increased lipid preservation. Moreover, the aquatic contributions to the $C_{16}$ and $C_{20}$ $n$-FA appear to have been proportionally higher, even after 13 cal kyr BP, although their specific source cannot be discerned. We suggest that more runoff into the El Potosi Basin maintained locally wet conditions that allowed the lake productivity to increase after 13 cal kyr BP. The lipid record does not
exhibit significant changes during the YD event and the changes occurred only after 11.7 cal kyr BP (discussed below). However, the YD is represented by only one sample in our lipid biomarker record. We suggest that analysis of sedimentary records with higher rates of deposition from this basin and other nearby basins is necessary for interpreting the ecological response to this and other short-duration global climatic events.

5.2.2 Holocene

The early- and mid-Holocene represent a drier period in the El Potosi Basin. Reduced runoff after 13 cal kyr BP was possibly due to lower SST in the Gulf of Mexico (Flower et al., 2004; Ziegler et al., 2008; Roy et al., 2016). Alternatively or additionally, intensification of El Niño Southern Oscillation activity could have caused an increase in aridity of the El Potosi Basin (e.g. Barron et al., 2005). The decrease in moisture evidently affected the vegetation cover and runoff into the basin. Fossil pollen and plant remains of packrat middens suggest the woodland disappeared from the Llano Estacado and Maravillas Canyon (southern USA; Figure 1) from 11.2 to 10 cal kyr BP (Hafsten, 1961; Wells, 1966). Paleovegetation records from the Canyon de la Fragua, Puerto de Ventanilas and Sierra de la Misericordia suggest that the woodlands also disappeared in northeastern Mexico from 12.6 to 8.7 cal kyr BP (Van Devender and Burgess, 1985; Betancourt et al., 1990). Based on lower lipid concentrations and a changing terrestrial vegetation biomarker distribution ($C_{29}/C_{28} \omega$-OH-FA, $\alpha/\beta$-amyrin ratio, $\delta^{13}C_{FA}$ values), we suggest the woodland withdrew from the El Potosi Basin after 11.7 kyr (Unit 4). The inland vegetation became less resinous, but produced relatively more bark litter during 11.7-4.2 cal kyr BP. The abundance of grasses was evidently lower than during the deglaciation period, but an increase in long-chain $n$-FA $\delta^{13}C$ values suggests an increasing proportion of C$_4$ plants. Coincident with these terrestrial ecosystem changes, the proportion of aquatic OM increased. During 10.3-4.6 cal kyr BP the paleovegetation record from the Maravillas Canyon indicates an interval of dominant subtropical desert shrub with many grasses (Wells, 1966); despite the apparent lack of biomarker evidence for grasses, compositional changes in the terrestrial vegetation of the El Potosi Basin might also be the result of a subtropical desert shrub ecosystem.
During the late Holocene, aridity increased in the El Potosi Basin, possibly as a result of intensification of the El Niño Southern Oscillation activity and a relatively cooler GoM (Flower et al., 2004; Ziegler et al., 2008; Roy et al., 2016). Moreover, during El Niño years in modern times, summer precipitation decreases significantly in the north of Mexico (Magaña et al., 2003). This considerable reduction in the moisture flux triggered a shift in the vegetation type to a more xeric habitat in the Chihuahua Desert (e.g. Van Devender, 1990; Pérez-Cruz, 2006; Holmgren et al., 2007; Chávez-Lara et al., 2018), characterised by the appearance of Big Bend silver leaf and C₄ chino grass at the Maravillas Canyon at 4.6 cal kyr BP (Wells, 1966).

The lipid biomarker data also indicate a period of gradual environmental transition and ecosystem adaption from 4.2 to 2.8 cal kyr BP (Unit 5). The terrestrial vegetation shifted gradually (α/β-amyrin ratio, CPI FA₂₂-₂₈, δ¹³C values) to enhanced proportions of C₄ grasses and potentially more open vegetation. Runoff continued to decrease as indicated by lower Ti concentrations and decreasing proportions of terrigenous relative to inferred aquatic OM (Figure 8). Slightly enhanced terrestrial mineral runoff at ~3.5-3 cal kyr BP, indicated by enhanced Ti concentrations, could have resulted from temporarily destabilised soils during vegetation recession. However, some parts of northwestern Mexico experienced more humid winters as a result of increased SST in the north eastern Pacific (Ropelewski and Halpert, 1987), as well as increased inflow of humid air masses from tropical Pacific cyclones during autumn (Reyes and Mejia-Trejo, 1991; Rodgers et al., 2000; Englehart and Douglas, 2001; Jáuregui, 2003; Magaña et al., 2003; Larson et al., 2005). Similarly, a recent climate model simulation reveals warming of central and/or eastern Pacific SST during ENSO phase, triggering increased precipitation in western North America (Barr et al., 2019). The enhanced moisture supply during autumn and winter could have supported the expansion of C₄ grasses, as these grasses strongly depend on seasonal precipitation (Throop et al., 2012; Báez et al., 2013).

After 2.8 cal kyr BP (Unit 6), as climate continued to dry, terrestrial productivity decreased substantially and the lake became shallower and ephemeral, with OM characterised by high contributions from microbes (C₁₈:₁ MUFA, branch FAs, isoGDGTs) and possibly copepods (C₂₂:₁ MUFA), both of which are resistant to drought. Periodic drying is also indicated by the presence of
desiccation fissures in the sedimentary record. At least two types of vegetation, the relative contributions of which vary, occur in Unit 6: one with enhanced proportions of long-chain C$_{30}$ and C$_{32}$ n-OH and reduced amounts of β-amyrin, and the other with higher amounts of β-amyrin and degraded FA distributions (low CPI). The fluctuations could reflect changes in the climatically controlled supply mechanisms, including episodic runoff through transient and poorly connected fluvial systems or an increased role for aeolian input under these drier conditions. Such variability is supported by higher concentrations of Si-bearing sediments with higher amplitude changes after ~2.7 cal kyr BP (Roy et al., 2016) as well as coarser, sandy sediments.

The last millennium (Unit 7) represents a period of relatively higher lipid concentration, better preservation of leaf wax-derived compounds and terrestrial vegetation with lighter isotopic composition (C$_{3}$). All of this suggests enhanced moisture supply. Likewise, the vegetation of Maravillas Canyon became more mesic during the last thousand years (Wells, 1966). However, terrestrial mineral runoff (Ti) remains low (Roy et al., 2016), and it is unclear what the natural forcing mechanism would be for a reversal in the long-term Holocene drying trend. One possible explanation for these somewhat divergent characteristics is modern human influence. During the pre-Columbian era, the north of Mexico (Aridoamerica) was occupied by the Guachichiles, nomadic and non-agrarian people (Powell, 1945). Hence, the agricultural activity in the El Potosi area is relatively recent and started during the Spanish conquest about 400 years ago (SEGOB, 1988), and currently most of the modern vegetation has been altered (for tomato, chili and onion farming; SAGARPA, 2016). Agriculture could also explain the loss of amyrins, possibly derived from the xeric shrubland, from the sedimentary record and the enhanced proportions of the C$_{31}$ n-alkane. Determination of the biomarker distributions in modern day vegetation in the El Potosi Basin would help explore this hypothesis.

6. Conclusions

This study represents the paleoecological reconstruction of subtropical northeastern Mexico spanning the last 20,000 years and it is based on the newly studied lipid biomarkers in sediments from the El Potosi Basin. The biomarker-based proxy data reflect seven units that represent the environmental transition of this basin during the Late Pleistocene and Holocene. They also represent the first Holocene
vegetation reconstruction of the northeastern Mexico. Our findings complement previous studies on paleohydrological and the paleovegetation reconstructions from this region as well as from the southeastern USA. Generally dry conditions with a stable water body in the basin are reflected by low lipid concentration, enhanced contribution of aquatic/in-situ microbial biomass and degraded terrestrial OM during 20-19 cal kyr BP. The wetter deglaciation was characterized by increasing lipid concentrations in lake sediments mostly derived from terrestrial vegetation such as woodland, soil and wetland from 19 cal kyr BP to 15 cal kyr BP. After this period, the wetland disappeared, and woodland input dominated the organic material from 15 to 11.7 cal kyr BP. Aridity increased and the woodland habitat possibly disappeared after 11.7 kyr. The proportion of grasses decreased during the early- and mid-Holocene, and the dominant vegetation shifted to subtropical desert shrub with higher proportions of bark litter during 11.7-4.2 cal kyr BP. The onset of the dry late Holocene is characterized by gradual environmental transition and ecosystem adaption from 4.2 to 2.8 cal kyr BP. The terrestrial vegetation shifted to enhanced proportions of C₄ grasses and potentially more open-vegetation, and the in-lake productivity increased. After 2.8 cal kyr BP, terrestrial productivity decreased substantially and the lake became shallower/ephemeral and more sensitive to changes in the climatically controlled supply mechanisms. Changes of the limnic habitat from algal towards microbial communities occurred ~300 years after the onset of terrestrial habitat changes. Finally, during the last thousand years the vegetation shifted back to C₃ conditions, and the lipid concentration and preservation increased, implying enhanced moisture supply due to anthropogenic agricultural activities. Collectively, these observation reveal the profound sensitivity of northeastern Mexico to climate change.

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