

# Environmental change in subtropical South America for the last two millennia as shown by lacustrine pigments

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Received: 8 August 2013 / Accepted: 9 December 2014 / Published online: 21 December 2014  
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**Abstract** Organic matter accumulation and preservation in aquatic systems can be linked to variations in organic matter sources as well as primary productivity. These changes can be used to determine contemporaneous environmental variations in the catchment area. The source, quality and distribution of lacustrine organic matter (LOM) have been determined in a sedimentary core covering the last ~1,500 years from Laguna Mar Chiquita, a saline lake in central Argentina. Petrophysical, sedimentological and geochemical data along with results of high-resolution pigment analyses provide a unique dataset that allow characterization of both source and type of LOM. Climat-

ically triggered changes in the Laguna Mar Chiquita catchment led to changes in the water salinity and lake trophic state that in turn influenced primary productivity and thus organic matter accumulation. Distinctive high lake water levels and associated low salinity characterize the Medieval Climatic Anomaly (MCA) as well as the last quarter of the twentieth century and beginning of the twentyfirst century. Conversely, extremely low lake levels with resulting high salinity correspond with the Little Ice Age (LIA). High-resolution sedimentary pigment analyses in these two end-members (i.e., LIA and MCA) do not indicate major changes in the structure of phototrophic communities signifying that the biota survives a large range of salinity and temperature. High lake stands (low salinity) correspond with increased primary productivity as shown by high pigment concentrations along with a decrease in authigenic carbonates and evaporites. These high lake level intervals have been previously linked to a warmer and more humid climate. Conversely, low lake levels (hyper saline waters) correlate with decreasing lake productivity and precipitation of both authigenic carbonates and evaporites. These sediments correspond to cooler intervals with a negative moisture balance. The relative similarity between LOM indicated by the pigment stratigraphy for both intervals show no clear evidence of a linkage between human impact and lake productivity. Hence, Laguna Mar Chiquita has been naturally productive even prior to agriculture expansion by the end of the twentieth century.

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**Keywords** Subtropical South America · Central Argentina · Saline lake · Organic matter · HPLC · Fossil pigments

## Introduction

In recent years increasing limnogeological research over southern South America has produced critical new data that are improving our understanding of past Southern Hemisphere atmospheric circulation and its impact at a regional and global scale (Valero-Garcés et al. 2003; Gilli et al. 2005; Piovano et al. 2006; Whitlock et al. 2006; Ariztegui et al. 2008; Piovano et al. 2009; Villalba et al. 2009; Neukom et al. 2011; Recasens et al. 2012; Stutz et al. 2012). The Pampean plains of central Argentina are particularly interesting to study late Quaternary paleoclimatic variability since they have undergone pronounced hydrological changes in very recent years (Peñalba and Vargas 2004; Pasquini et al. 2006; Piovano et al. 2009; Leroy et al. 2010; Troin et al. 2010, 2012). Severe climatic oscillations consisting of alternating wet and dry periods have been historically and instrumentally recorded along a broad region of southeastern South America (Piovano et al. 2002; Fonseca and Cavalcanti 2012). In particular, a conspicuous hydrological change affected central Argentina during the twentieth century, more precisely after the 1970s, triggering the onset of the largest instrumentally recorded humid phase, equivalent in magnitude to a humid period dated around 1.1 cal Ka BP (Piovano et al. 2009).

Laguna Mar Chiquita, the target of this study, is a terminal lake within a closed basin located in central Argentina. The lake catchment has undergone a substantial increase in available moisture since the second half of the twentieth century resulting in high lake water levels. Hydrological modeling indicated that the dramatic rise in the water-level of Laguna Mar Chiquita in the early 1970s can be fully explained by increased runoff, especially in the upper northern catchment, suggesting a tropical climatic influence on the lake water balance (Troin et al. 2010). Throughout the twentieth century, the salinity has fluctuated between 27 and 360 g l<sup>-1</sup>, a range 139 % greater than the widest range of salinities recorded in a series of the largest salt lakes of the world (Williams 1993). The associated variations in water chemistry triggered

major changes in both abundance and composition of aquatic communities producing in turn either enrichment or depletion in organic matter production and preservation (Martinez 1995; Reati et al. 1996; Piovano et al. 2004). Therefore, the study of organic by products such as the pigments in Laguna Mar Chiquita sediments can serve to refine previous reconstructions of lake evolution throughout time as well as the causes behind it.

Preserved sedimentary pigments in closed lacustrine basins provide an organic proxy for changes in algal communities and other syn- and/or post-sedimentary redox related processes (Guilizzoni et al. 2000; Ariztegui et al. 2001; Guilizzoni and Lami 2002). Fossil pigments in modern saline lakes are highly sensitive to natural and human-induced environmental changes such as salinity, ionic composition, pH, nutrient fluxes and therefore are suitable for paleoenvironmental investigations (Sanger 1988; Pienitz et al. 1992; Fritz et al. 1993; Leavitt and Findlay 1994; Vinebrooke et al. 1998; Pienitz et al. 2000). Organic pigments and their derivate products are biochemical remains of photosynthetic organisms that are relatively stable and uniform through geological time and strongly dependent on environmental conditions at the time of deposition (Leavitt 1993; McGowan 2007). Fossil pigments can therefore be considered as fingerprints of past lake trophic conditions (Guilizzoni et al. 2011) reflecting temporal variations over the drainage area and thus, they serve as an efficient bio-tracer to assess regional paleoenvironmental history.

Laguna Mar Chiquita offers an excellent opportunity to evaluate both magnitude and tempo of natural environmental changes over this climatically sensitive region of subtropical South America (Piovano et al. 2009). To date different approaches have been used to reconstruct lake level variations and their influence on both the aquatic system and sediment composition. They have been interpreted essentially as the result of past hydrological changes across the region (Piovano et al. 2004, 2006; da Silva et al. 2008; Abril et al. 2010; Troin et al. 2010; Stupar et al. 2014). However, many of the proxies previously used in these reconstructions do not allow disentangling the role of climate—from anthropogenic-induced biochemical changes in the lake. Thus, in this contribution we focus on the study of fossil pigments in an attempt to identify changes in biological productivity and their relationship with

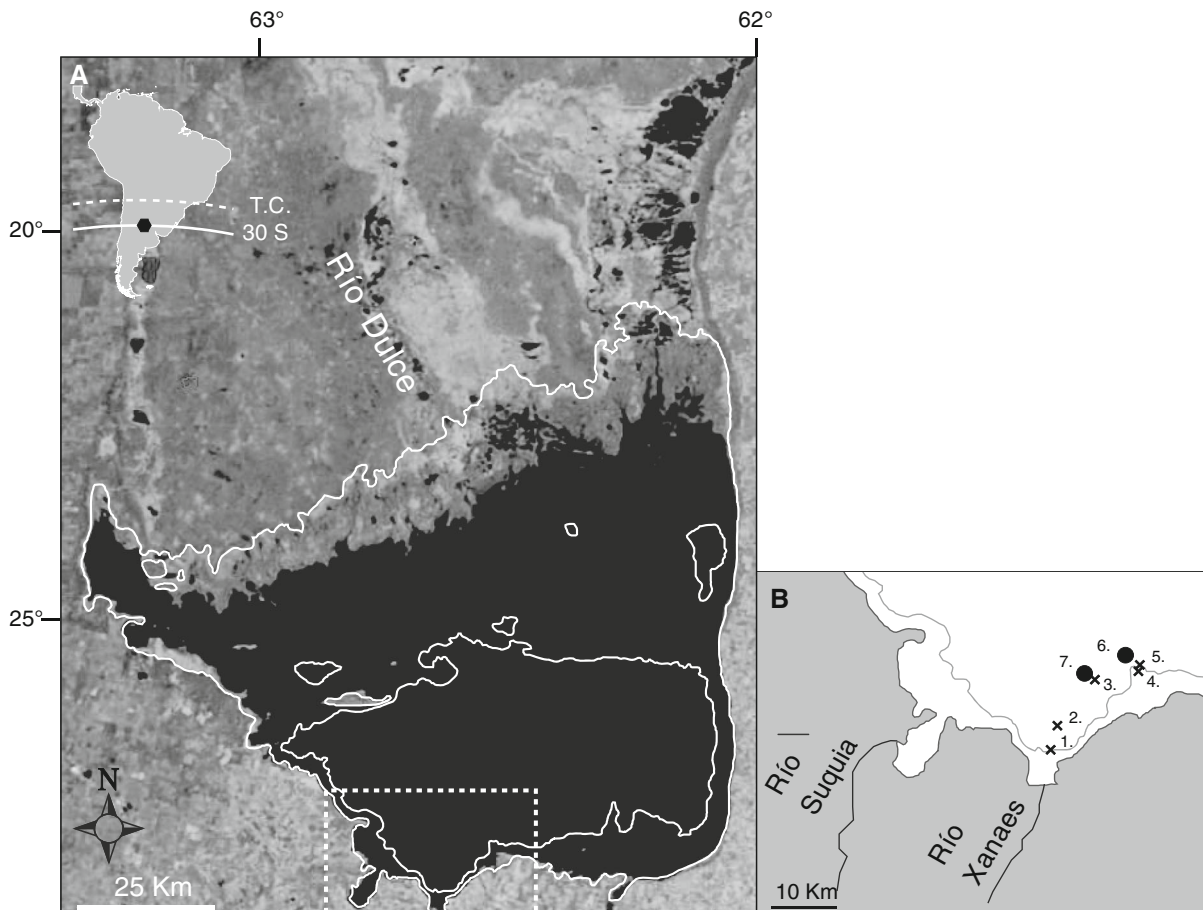
climate triggered salinity changes and human-induced perturbations in the catchment. These results show that this hypersaline lake provides an ideal archive to test the behavior of biological proxies and constrain their use in comparable lacustrine basins.

#### Study site

##### *Climate and limnology*

The lake catchment comprises roughly 127,000 km<sup>2</sup> from 26°S to 32°S and from 62°W to 66°W. The lacustrine system has no surface outlet and the main

water loss is by evaporation, which is favored by the pan-like shape of the basin. Regional climate is mainly defined by the South American Monsoon System that rules the precipitation regime and is one of the major atmospheric features driving seasonal climatic variability in southeastern South America (Garreaud et al. 2009). At present the hydrological budget of the lake is mainly dominated by perennial fluvial systems (ríos Dulce, Suquia and Xanaes; Fig. 1a, b) coupled by groundwater influx balanced by evaporation (Troin et al. 2010). During dry periods such as the earliest 1970s, the lake surface has been reduced to less than 2,000 km<sup>2</sup>, whereas it can reach an area of



**Fig. 1** **a** Map of South America showing the location of Laguna Mar Chiquita in central Argentina. A 2007 satellite image of the lake is overlaid by two different lake shorelines: the largest historical extension of the lake in 2003 AD and the 1972 AD low-stand. The dashed white rectangle indicates the southern part of the lake that was cored in this study, **b** detail of the

southernmost part of the lake displaying the coring sites. The Río Suquia connects the smaller Laguna del Plata to the main water body. Black dots indicate the locations of previously retrieved cores TMC02-02 and TMC-00-1, respectively (Piovano et al. 2002). Number 7 indicates the location of core LMC07-05 analyzed in this paper

approximately 6,000 km<sup>2</sup> during wet periods such as the year 2003 (Fig. 1a). Throughout the twentieth century lake water salinity ranged from a maximum of 360 g l<sup>-1</sup> during lowstands (hypersaline conditions) to a minimum of 28 g l<sup>-1</sup> during high-stands (mesosaline conditions). The lake water is alkaline (pH > 8) due to its chloride-sulfate sodium content. The shallow character of the lake (maximum water depth during high stands is about 10 m) in addition to constant winds results in a well-mixed water column.

The most recent hydroclimatic scenario of the region (Twentieth and twentyfirst centuries) is represented by three contrasting hydrological situations (Piovano et al. 2002, 2009). Long dry intervals characterized the first 70 years of the twentieth century while a wet phase occurred after the 1970s impacting on traditional socio-economic activities in the region (Leroy et al. 2010). After a maximum recorded in 2003 (Fig. 1a) the lake water level started dropping in response to the onset of a less humid phase across the Pampean plains.

Well-dated short cores allowed a calibration of the lake sedimentary, isotope and biological response to the last 100 years of documented lake levels changes (Piovano et al. 2002, 2004). The sedimentological record of low-stand intervals is represented by muds rich in evaporites, such as gypsum, calcite and halite, along with indications of a decrease in primary productivity. Conversely, high-stands are typically represented by dark diatomaceous, organic matter enriched mud partially to well-laminated under radiographic observations (Piovano et al. 2002). The carbon isotope composition of the sedimentary organic matter is the most sensitive indicator to twentieth century changes in the Laguna Mar Chiquita hydrology and salinity (Piovano et al. 2004). The  $\delta^{13}\text{C}$ -organic matter values are related to the isotopic composition of the dissolved inorganic carbon pool and the carbonate equilibrium of the lake water. Relatively low  $\delta^{13}\text{C}$ -organic matter values correspond with high lake levels, low salinity, low alkalinity and high lake productivity. High salinity during lowstands diminishes the amount of primary production and the  $\delta^{13}\text{C}$ -organic matter value is correspondingly high. The significant co-variation between the  $\delta^{13}\text{C}$ -organic matter fluctuations and the instrumental and historical lake-level data allow using this proxy to infer both past lake water salinities and lake water level variations (Piovano et al. 2004). A multi-proxy model

of lake function and a semi-quantitative estimation of paleolake-levels covering the past ca. 13.0 cal Ka can be found in Piovano et al. (2009).

### Biology

Previous investigations of the Mar Chiquita biota have been restricted solely to a few lacustrine taxonomic groups (Reati et al. 1996). It seems that in general, the transition from hypersaline to mesosaline conditions was characterized by an increase in littoral species primarily dominated by the chlorophytes *Caladophora* and *Mougeotia* sp., supplemented by an increase in cover of a macrophyte species belonging to the genus *Ruppia* (Reati et al. 1996). As mesosaline phases exhibit a wide range of taxonomic species, the hypersaline intervals seems to be dominated by *Artemia franciscana* (Cohen 2012). The entire list of species found in Mar Chiquita, as well as a brief description of phreatophytes, helophytes and aquatic vegetation, have been summarized by Menghi (2006). Despite the combined effect of shallow water depths and constant action of wind stress, the sediment/water interface is permanently anoxic. Large amounts of organic matter promote the development of sulfate-reducing conditions due to the presence of *Desulfovibrio* bacteria (Martinez 1995). Regarding water column properties, Bucher et al. (2006) report low transparency in the central parts of the lake and high turbidity in the coastal areas during highstands, probably influencing productivity and the phototrophic properties of the lake water.

### Materials and methods

Five sedimentary cores were retrieved in August 2007 at the southernmost and deepest area of Laguna Mar Chiquita (Fig. 1b) using a sediment core sampler, type Beeker (Eijkelkamp). For further information please refer to <http://en.eijkelkamp.com/products/water-bottom-sampling-equipment/sediment-core-sampler-type-beeker.html>. The cores were kept at 4 °C under dark conditions at the Limnogeology Laboratory of the University of Geneva before opening them for further analysis. The 176-cm-long core LMC07-05 contains the most complete lithological sequence and hence has been the main target for the different analyses.

Petrophysical properties were measured on all cores at the Limnogeology Laboratory of the ETH-

Zürich. Magnetic susceptibility, P-wave velocity and gamma-ray attenuation bulk density were measured using a GeoTek® Multi Sensor Core Logger (MSCL). Calibration of the MSCL was accomplished at the beginning of each analyzed section using a combined aluminum and water standard. These non-destructive measurements provide information about changes in the source and type of sediment including relative amount of lacustrine organic matter (LOM) to the lake. It also gives the opportunity to evaluate the spatial distribution of the different sedimentary components through the basin.

High-resolution photographs, lithological description and sediment sampling were carried out immediately after core opening in order to avoid sediment oxidation.

Bulk organic matter parameters were obtained by Rock–Eval pyrolysis with a Re6® analyzer at the University of Neuchâtel, Switzerland. This method is often used in environmental research to identify the main types and sources of organic matter and in older sediments to further evaluate their oil potential (Ariztegui et al. 2001). It consists of the quantification of the thermal cracking of the organic matter contained in the sediments by measuring the residual products obtained after increasing the sample temperature from 300 to 600 °C. Total Organic Carbon (TOC), Hydrogen Index (HI), Oxygen Index (OI) and Total Inorganic Carbon (TIC) were measured by a pyrolysis step on the bulk sediments followed by the complete oxidation of the residual sample (Steinmann et al. 2003).

Samples for pigment analysis were obtained from core LMC07-05 at 2-cm intervals to a depth down to 60 cm, and at 5-cm intervals from 60 to 176 cm. Pigment preservation is crucial for an accurate interpretation of the data. Leavitt (1993) summarized the best sampling and laboratory conditions to minimize pigment alteration. Pigment extraction was accomplished following the methodology described in Lami et al. (1994). Algal pigments were extracted from approximately 1–2 g wet sediments using 90 % acetone and then centrifuged at 3,000 rpm for 10 min in 15 ml glass centrifuge tubes. Sampling was carried out overnight, at 10 °C, in dark conditions and under a N<sub>2</sub> atmosphere. Chlorophyll derivatives (CD) and total carotenoids (TC) were determined by spectrophotometric analysis following Guilizzoni et al. (1986). Specific pigments were measured as

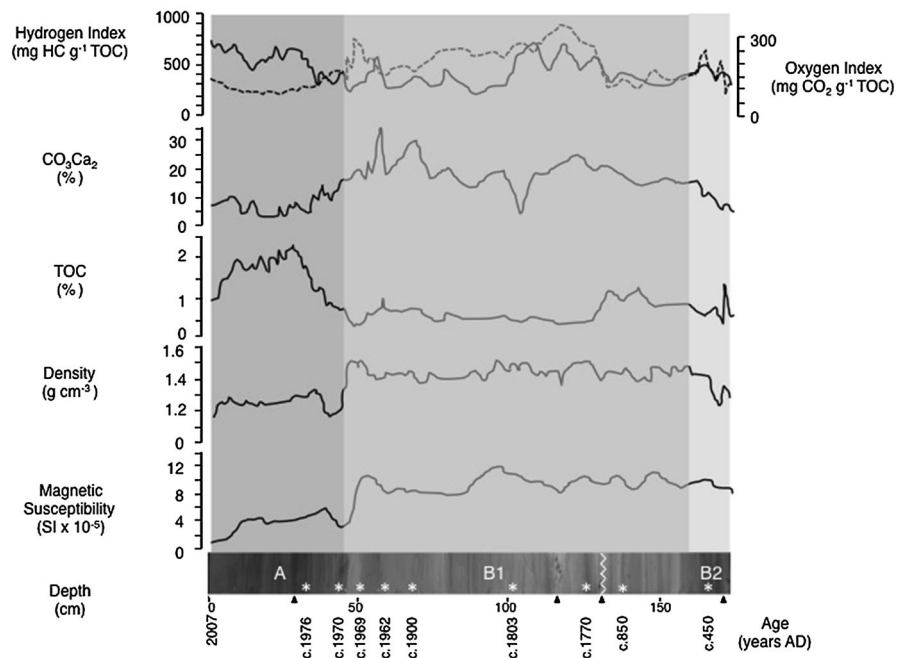
nmol g<sup>-1</sup> of organic matter by ion pairing using reverse-phase HPLC (Mantoura and Llewellyn 1983). Measurements were performed using a gradient pumping system and dual channel variable wavelength UV–Vis detector (set at 460 and 656 nm for carotenoids and chloropigments, respectively). An auto-sampler for sample injection was connected through a pre-column to a reverse-phase C18 in Scolumn (5 µm particle size; 250 × 4.6 mm i.d.). After sample injection (100 µl), a gradient program that ramped from 85 % mobile-phase A (80:20, by vol. methanol: aqueous solution of 0.001 M ion-pairing and 0.001 M propionic acid) to 100 % mobile-phase B (60:40, acetone: methanol) in 30 min with a hold for 20 min provided sufficient resolution for all pigments of interest. Flow rates were calculated from 1 to 2 ml min<sup>-1</sup>. The column was re-equilibrated between samples by linear ramping to 85 % mobile-phase A for 5 min and maintenance for 10 min before sample injection. This procedure allows us to separate zeaxanthin from lutein and β-carotene from pheophytin *a*. Replicates samples analysis yielded a C.V. of 4.5–11.5 %. Identification of pigments isolated from sediments was confirmed by comparison of spectral characteristics and chromatographic mobility of pigments with those obtained from: (1) TLC analysis (Züllig 1982; Guilizzoni et al. 1986); (2) commercial standards (Sigma Chemical Co.); (3) water samples of known phytoplankton composition; and (4) published values on max O.D. (Foppen 1971; Davies 1976; Züllig 1982; Mantoura and Llewellyn 1983). Pigments concentrations were calculated on the basis of molar extinction coefficients at the detection wavelengths. The molar extinction coefficient E<sub>1%</sub><sup>460 nm</sup> and E<sub>1%</sub><sup>656 nm</sup> was applied and is derived from the E<sub>1%</sub><sup>max</sup> reported in Davies (1976) and Wright et al. (1991). All analyses were performed at the CNR-ISE Institute, Verbania-Pallanza, Italy.

## Results

### Lithology and chronology

Two lithological units are defined according to their petrophysical properties and texture (Fig. 2) namely units A and B. The lowermost sedimentary unit (B) is further divided into two sub-units: B1 and B2. Subunit B2 (176–158 cm depth) is characterized by general

**Fig. 2** Petrophysical properties and bulk geochemical parameters of core LMC07-05: Magnetic susceptibility ( $SI \times 10^{-5}$ ), Density ( $g\ cm^{-3}$ ), TOC (%),  $CaCO_3$  (%), HI ( $mg\ HC\ g^{-1}\ TOC$ ) and OI ( $mg\ CO_2\ g^{-1}\ TOC$ ). A, B1 and B2 indicate lithological units (*gray shaded*) and *white asterisks* ages in years AD while *black arrows* indicate evaporitic layers. The chronology has been built by correlation with previously dated sedimentary cores combining  $^{210}Pb$  and  $^{14}C$ -AMS ages (Piovano et al. 2002, 2009). Notice the hiatus between AD 850 and AD 1770. See text for details



dark millimeter-to-centimeter scale laminae intercalated with fine light-gray laminae. A black sedimentary sequence including gypsum layers is present at the bottom of the core (176–170 cm). This sequence is easily recognized by the large amount of evaporites (dispersal in sediments and layers), exhibiting high magnetic susceptibility values (mean value of  $9\ SI \times 10^{-5}$ ) whereas density slightly increases upward from 1.2 to  $1.4\ g\ cm^{-3}$ .

The overlying sequence (B1; between 158 and 47 cm depth) consists of light-gray centimeter scale layers sporadically interbedded with dark-gray lamina with average water content around 50 %. A closer examination of the sediments shows abundant gypsum-rich thin layers at various depths. These evaporite layers are often associated with a relative decrease in both magnetic susceptibility and density, such as at 117 cm depth where magnetic susceptibility and density values reach  $8\ SI \times 10^{-5}$  and  $1.4\ g\ cm^{-3}$ , respectively.

The most recent unit (A; between 47 cm and the top of the core) shows a distinctive black, oily organic-rich layer that characterizes the uppermost sediments of all retrieved cores, and therefore, serves as a prominent stratigraphic marker for core-to-core correlation. Dark, organic rich ooze with a jelly-like consistency occurs in the uppermost 10 cm. Unit A is

clearly distinguishable in comparison to the underlying units displaying a sharp shift in all petrophysical properties. This layer results in synchronous low signals of magnetic susceptibility (maximum of  $6\ SI \times 10^{-5}$ ) and density (average  $1.3\ g\ cm^{-3}$ ).

Previous studies have indicated that the sedimentary records of the Pampean lakes present a significant correlation between sedimentary facies and lake-level changes (Piovano et al. 2002, 2004, 2009; Córdoba 2012). Variations in water salinity during lake-level changes control both the amount of primary producers and the precipitation of authigenic minerals which are recorded as distinctive organic-rich or evaporite-rich/organic-poor facies at highstands and lowstands, respectively. Overall, Pampean paleolimnological records comprise an uppermost carbon-rich mud facies accumulated during the most recent highstands. Therefore, the base of these uppermost organic-rich sediments, present in all retrieved cores, can be defined as a chronostratigraphic marker (T1) with an age of AD 1976–1978. Both Laguna Mar Chiquita (Piovano et al. 2002) and Laguna Melincué  $^{210}Pb$ -based chronology support the general scheme that the uppermost organic-rich facies has accumulated since AD 1976–1978 (Piovano et al. 2002). Hence, based on lithological features, petrophysical properties and TOC content, core LMC07-05 was correlated to

previously retrieved sedimentary cores (TMC-00-1 and TMC-02-2) dated by  $^{210}\text{Pb}$  and 14C-AMS techniques (Piovano et al. 2002, 2009). Details on  $^{210}\text{Pb}$  dating technique can be found in Piovano et al. (2002). Since  $^{210}\text{Pb}$  age models were determined in sedimentary cores retrieved in November 1997 (Piovano et al. 2002) the chronology of core LMC07-05 taken 10 years later (August 2007) was established using the mean sedimentation rate value estimated for highstands conditions in the 1997 core. The derived age-depth profile was validated against the stratigraphic marker T1 (Fig. 2). Analogously, the  $^{210}\text{Pb}$ -age profile was further extrapolated downward to an evaporitic layer that is also a stratigraphic marker (T2) present in all the retrieved cores, with an estimated age of AD  $1775 \pm 5$  years (Piovano et al. 2002). This evaporitic layer indicates the occurrence of an extensive drought that can be further inferred from Jesuitical cartography, which shows reduced and isolated water bodies instead of the today's extended shape of Laguna Mar Chiquita. An abrupt age change from AD 1770 to AD 850 around 130 cm encompasses a hiatus that is interpreted as the result of subaerial lake-floor exposures during pronounced droughts. This hiatus prevented estimating sedimentation rates beyond AD 850 and, thus, radiocarbon ages (AD 850 and 450; Piovano et al. 2009) were not used to develop a continuous age-depth profile.

### Organic proxies

The general trend of the organic matter bulk parameters (TOC, HI and OI) follows the previously described lithological units, reaching maximum values in the youngest unit A (Fig. 2). TOC percentage varies between 0.4 and 2.4 % along the core with highest values towards the top. TOC from the bottom to 130 cm displays a  $\sim 1$  % mean average. Nevertheless several periods with significant organic matter enrichment appear in the lower part of the core at 176 and 172 cm followed by two major peaks at 144 and 133 cm. HI and OI show a slight decrease with values not exceeding  $500 \text{ mg HC g}^{-1} \text{ TOC}$  and  $150 \text{ mg CO}_2 \text{ g}^{-1} \text{ TOC}$  for HI and OI, respectively.

The lowermost subunit B2 is characterized by a marked increase in TIC in correspondence with a decrease of TOC values from the base to the top of the subunit.

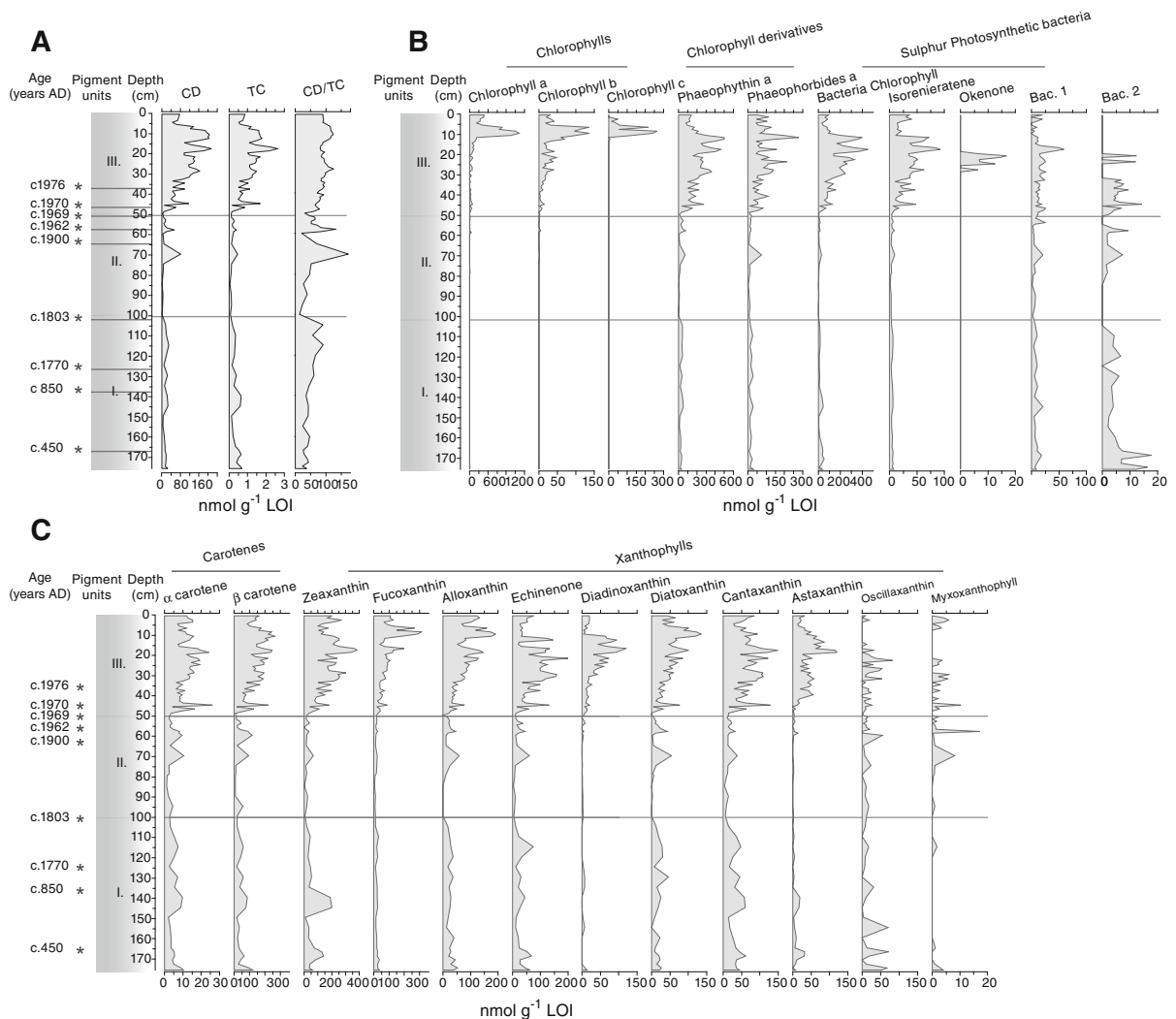
The overlying unit B1 begins with a decline in TOC from 1.25 to 0.5 % initiating a long time interval of

low organic matter content. Two minor pulses of increasing OM at 79 and 58 cm depth interrupt this low TOC phase, respectively. HI throughout this unit exhibits a distinctive switch that is recognizable in all cores. High values appear at 129, 119 and 110 with average values rising from  $220$  to  $270 \text{ mg HC g}^{-1} \text{ TOC}$ . Three other peaks are present at 79, 70 and 58 cm depth. The OI reaches the highest values between 133 and 64 cm and an average value of  $250 \text{ mg CO}_2 \text{ g}^{-1} \text{ TOC}$  for the entire (B1) unit. Total carbonate content displays a constant increasing profile with values enhancing from 5 to 30 % until 58 cm. A significant drop at 102 cm depth interrupts this increasing trend.

Unit A encompasses the top uppermost 47 cm displaying distinctive changes in all measured parameters. After a major decrease of TOC values in the top of subunit B1, Unit A shows a noticeable shift towards the highest organic matter content of the core. HI and OI values display a mirroring behavior but in opposite phase to those observed in the most recent sediments. While OI increases up to  $300 \text{ mg CO}_2 \text{ g}^{-1} \text{ TOC}$ , HI decreases to  $200 \text{ mg HC g}^{-1} \text{ TOC}$ . From the base of Unit A onwards a sharp and continuous increase in TOC is noticeable reaching a maximum of 2.4 % at 30 cm depth. The most recent 10 cm of core LMC07-05 shows an important drop in TOC down to 0.9 % at the top. A significant decreasing trend in carbonate content starts at the base of Unit A, while it shows a reversal trend to higher values parallel to the drop in TOC values. Unit A is also distinguished by a decrease in the values of MS and density as a result of higher overall percentages of LOM in the unit.

### Pigment preservation and stratigraphy

Chlorophyll derivatives and TC profiles show a similar distribution throughout the core although with quite different concentrations in  $\text{nmol g}^{-1} \text{ LOI}$  (Fig. 3a). Their ratio can be used as a good indicator of the degree of pigments preservation (Guilizzoni and Lami 2002). Variations in pigment concentration allow the identification of three different units with very good correspondence with those identified using petrophysical and sedimentary data. From the oldest to the youngest sediments the following units were identified: Unit I (176–100 cm), Unit II (100–47 cm) and Unit III (47–0 cm). Note the increase in all pigments in the uppermost part of the sedimentary core



**Fig. 3** Laguna Mar Chiquita pigment results expressed in  $\text{nmol g}^{-1}$  LOI. **a** Chlorophyll derivatives (CD) and total carotenoids (TC) show similar distribution throughout depth. Note the increase in all pigment concentrations in the uppermost part of the sedimentary core corresponding to the last quarter of the twentieth century (unit III), **b** carotenes and xanthophylls pigment distribution. The most abundant are zeaxanthin,

fucoxanthin and  $\beta$ -carotene pigments (notice different scales), and **c** chlorophylls and sulfur photosynthetic pigments profiles with depth. The most abundant are chlorophyll *a* and its derivative product phaeophytin *a*. Bacteria chlorophyll is the most abundant along with two new unknown pigments (Bac. 1 and Bac. 2) that have been discovered in Laguna Mar Chiquita

corresponding to the record of the last lake level increase and salinity drop during the last quarter of the twentieth century (Unit A).

Figure 3 summarizes the phytoplankton evolution of Laguna Mar Chiquita at highly variable water salinities through time. Figure 3b shows that although sedimentary pigments vary greatly through the core, most pigments display a synchronous increase towards the youngest sediments. Higher concentrations of

fossil pigments occur in the oldest Unit I (sedimentary subunit B2 + part of Subunit B1) and youngest sediments of Unit III (sedimentary subunit A) with other peaks in several pigments within Unit II (part of sedimentary subunit B1) as well. The dominant pigment assemblage along the entire sedimentary sequence is mainly zeaxanthin (maximum  $400 \text{ nmol g}^{-1}$  LOI at 26 cm) and fucoxanthin (maximum  $300 \text{ nmol g}^{-1}$  LOI at 8 cm). Significant



contributions of phaeophythin *a* and phaeophorbides *a* pigments (chlorophyll *a* degradation products) are also distributed through the entire sediment core. Nevertheless, a short shift in the phototrophic community appears in the uppermost sediment (4–10 cm) with the dominance of fucoxanthin, alloxanthin and diatohxanthin pigments.

The carotenoids group comprising carotene and xanthophylls are hydrocarbons and oxygenated derivatives more stable than chlorophylls. Therefore, they are preferentially preserved in the sedimentary record. The carotene group illustrates similar upward trends, with a greater concentration of  $\beta$ -carotene (Fig. 3b). This pigment, which is present in all algal taxa, has been recognized as a biological tracer for total phototrophic quantification and thus, providing a reliable indicator of paleoproductivity (Hurley and Armstrong 1990; Leavitt 1993; Romero-Viana et al. 2010).

The xanthophylls group includes ten pigments that mostly follow the common distribution pattern described above. Zeaxanthin has been identified in cyanobacteria but is also common in other eukaryote species. Furthermore, its presence has been interpreted as a protection against excessive exposure to light and oxygen and to prevent possible damage (Demmig et al. 1987). Several pigments belong to specific taxonomic groups as fucoxanthin and diadinoxanthin that characterize Chrysophyta and diatoms, respectively. Echinone and cataxanthin are used as marker pigments for cyanobacteria, whereas alloxanthin is a specific xanthophyll chosen as a proxy for cryptophyta identification. Variations in a phototrophic community composition have been previously used as a reliable proxy to monitor paleolake level changes (Züllig 1982; Pienitz et al. 1992; Leavitt and Findlay 1994; Guilizzoni et al. 2009). As shown by Vinebrooke et al. (1998), diatoms-dominated (diatoxanthin), lutein and zeaxanthin carotenoids are discriminant pigments reflecting warm and saline lake waters conditions, whereas fucoxanthin is a discriminant marker for fresh water systems. Alloxanthin and myxoxanthophyl are more common in low  $\text{Ca}^{2+}$  and high dissolved organic carbon (DOC) lake content. Laguna Mar Chiquita sediments contain further pigments taxa such as astaxanthin, which may indicate removal of grazers by planktonic fauna (Kamenik et al. 2000). On the other hand, several other pigments such as oscillaxanthin (characteristic

for *Oscillatoria rubescens* = *Plankthotrix rubescens*), myxoxanthophyl (Cyanophyta) and two unknown sulfur photosynthetic bacteria pigments (Bac 1 and Bac 2) display different distributions through depth (Fig. 3).

Chlorophylls are sparse and concentrated in the youngest sediments. Chlorophyll *a* is found in all photosynthetic aquatic organisms and is highly concentrated reaching more than  $1,600 \text{ nmol g}^{-1}$  LOI in the uppermost 10 cm coinciding with a shift in pigments indicative of the phototrophic community (see above). Notice that traces of chlorophyll *a* are present in small quantities in the oldest sediments. Phaeophorbides *a* has been used as a marker pigment associated with the grazing activity of zooplankton. This chlorophyll *a* derived product is mostly abundant in the youngest sediments. Moreover, in the uppermost part of the core there is a high concentration of pigments indicative of sulfur photosynthetic bacteria such as okenone (only between 28 and 18 cm), isorenieratene and bacteria chlorophyll. These carotenoids proliferate under strictly anoxic conditions of the hypolimnion or at the water/sediment interface in the presence of  $\text{H}_2\text{S}$  (Brown et al. 1984; Ryves et al. 1996). Thus, these groups of taxa are reliable indicators of redox conditions of a water body. Previous investigations have shown that Laguna Mar Chiquita bottom waters are undersaturated in oxygen confirming this interpretation. The presence of sulfate-reducing bacteria in the bottom sediments triggers the development of oxygen undersaturation at the sediment/water interface (Martinez 1995).

## Discussion

### Pigments as paleoenvironmental indicators in saline lakes

Pigments represent the phototrophic community as they are produced by algae and other photosynthesizing organisms (bacteria) and are specific to particular groups. They are often preserved in sediments of saline lakes and offer evidence of past algal abundance and community composition (Sanger 1988; Pienitz et al. 1992, 2000). In comparison to other organic material, pigments are labile compounds and their individual stability varies (Leavitt 1993). In aquatic environments they can be degraded by chemical,

photochemical and biological processes (Guilizzoni and Lami 2002). However, it has been demonstrated that total sedimentary CD and carotenoids undergo little diagenetic modifications once they are deposited and buried beneath the oxidized layer at the sediment–water interface (Sanger 1988). The elevated concentrations, especially in the interval corresponding to Unit III, of the labile chlorophylls and fucoxanthin (Fig. 3b, c) suggest generally good preservation conditions. Carotenoids are inherently more stable than chlorophylls. Unlike chlorophylls they are often broken down to colorless compounds, by destruction of the long chain of alternating double bonds that cannot be detected by regular pigment analysis methods (Leavitt and Hodgson 2001).

The ratio of total CD to TC (Fig. 3a) provides some indication of changing lake trophic status and also some evidence for the relative contribution of allochthonous versus autochthonous sedimentary organic matter (Sanger and Gorham 1972; Swain 1985). This is because the two types of compounds degrade at different rates. Many studies showed that carotenoids degrade faster than chlorophylls under oxidizing conditions in terrestrial soil and humus layers. Because the reducing conditions found in many lake sediments preserve both chlorophyll and carotenoids at levels near those at production, the ratio CD/TC is lower in lake sediments than in soils. If the low TC values found in terrestrial systems are the result of oxidizing conditions, then oligotrophic lake sediments should yield higher CD/TC values than eutrophic lakes. Degradation of pigments should be greater in oligotrophic lakes because of the relatively thicker oxidized microzone and slower burial rate. However, the interpretation of this ratio is often uncertain because other mechanisms are involved in producing the CD/TC values such as differential proportion of allochthonous/autochthonous organics, and/or changes in the phytoplankton composition or macrophytes.

Good preservation conditions for LOM in shallow lakes preventing the removal of the most labile components (Molongoski and Klug 1980) occurs in Mar Chiquita due to the presence of an anaerobic hypolimnion layer (Martinez 1995). The pigment record from Laguna Mar Chiquita confirms the latter since the 430/410 nm index is indicative of good preservation (Guilizzoni et al. 1992, 1993). On the other hand, TOC values vary concomitantly with most of the identified pigments and the best preservation

conditions are observed in the upper and lower parts of the core (Fig. 3a). Comparatively less dissolution of diatoms and chrysophytes was also observed in smear slides in these two sections reinforcing this argument and pointing towards better preservation conditions. Good preservation of sensitive siliceous fossils has been previously interpreted in other saline lacustrine systems as an indication of meromixis that can enhance both Si and LOM preservation in these environments (Hurley and Armstrong 1990; Ryves et al. 2006).

Salinity has been recognized as a major factor controlling bioproductivity in saline lakes. Piovano et al. (2009) described the strong correlation between precipitation/evaporation (P/E) ratio and organic matter content in Laguna Mar Chiquita sediments. Instrumental salinity data (Troin et al. 2010) along with geochemical analyses and paleosalinity reconstructions (Piovano et al. 2004) demonstrate that salinity had experienced strong variability driven by hydrological changes. Lake waters are alkaline chloride–sulfate sodium type, supersaturated in calcite and gypsum during lowstands and supersaturated in calcite and occasionally in gypsum during highstands (Martinez 1995). Consequently, high lake-levels and therefore low salinities have been associated with a large enrichment of organic matter in the sediments as a result of increasing primary productivity. Laguna Mar Chiquita sediments show a preferential preservation of total organic matter and pigments indicative of autochthonous taxa during high lake levels. Conversely, during low lake levels and high salinities (up to  $311 \text{ g l}^{-1}$ ) lake productivity is lower (Piovano et al. 2002) and the contribution of catchment derived organic matter is more significant (da Silva et al. 2008).

The presence of pigments indicative of phototrophic organisms is almost steady throughout the entire sequence that is dominated by cyanobacteria and diatoms as primary producers. However, their abundance as with all pigments presented in this study, has undergone major variations. Moreover, it appears that independent of lake-water level the phototrophic signature of the lake is mostly dominated by a benthic signal. The amount of LOM is preferentially more abundant in the deepest part of Laguna Mar Chiquita, while the shallower zones are mostly depleted as noted in other saline lakes by Hammer (1990). The latter might be the result of sediment focusing since even though the greatest species richness and biomass may occur in near shore environments, sediments and

biological remains can be transported by currents to the deeper parts further enhancing the amount of LOM in those areas (Spears et al. 2010).

The Laguna Mar Chiquita fossil pigment stratigraphy allows us to identify changes in the composition of the phototrophic communities and their relative abundance. Since these changes can be related to changing lake trophic conditions, fossil pigments can serve as accurate indicators for hydroclimatic oscillations over its watershed during approximately the past two millennia. Using organic carbon and fossil pigment content the Laguna Mar Chiquita record can be divided into three distinctive Intervals (Fig. 3): Interval I (corresponding to the period from ca. AD 450 to 1770); Interval II (covering between AD 1770 until 1970); and Interval III (spanning from the 1970s until present). From these three intervals, both the oldest and the youngest show the highest organic production and preservation, especially the interval covering the most recent sediments.

#### *Interval I (>AD 450–1770)*

This interval is characterized by moderate organic matter deposition (Fig. 2). Pigment analyses indicate relatively little but regular accumulation of LOM during this interval in comparison with the twentieth century record.  $\beta$ -carotene concentration, that covers the entire sequence, displays uniform but minor lake productivity indicating greater concentration of the algal biomass as further corroborated by geochemical data in the oldest sediments. The lake was characterized by the presence of Cyanobacteria and partially dissolved benthic diatoms, which indicate the predominance of benthic communities during this period (Sylvestre, pers. communication). Moreover, distinctive pigment signals such as phaeophorbides and alloxanthin (zooplanktonic and planktonic markers, respectively) are relatively low but their presence is generally indicative of deeper open waters. A water–sediment interface predominantly depleted in oxygen is further indicated by the presence of isorenieratene and bacterial chlorophyll pigments. These diagnostic pigments have been investigated in many similar lacustrine environments as markers of strict photic anoxic conditions in the lake water or at the water–sediment interface (Züllig 1985; Ariztegui et al. 2001). Consequently, oxygen-depleted bottom water conditions in Laguna Mar Chiquita highlights periods of

moderate to high lake stands as previously shown by Piovano et al. (2009). Three high lake levels stages in Mar Chiquita were reconstructed between 372/612 AD and 920/960 AD indicating wet conditions. Hence, the organic signal initially interpreted from the  $\beta$ -carotene and TOC content may not necessarily stand for increase productivity, but rather may account for reworking and flooding episodes from the near shore environment as proposed by Anderson et al. (1958) and McGowan et al. (2011).

Based on the calibrated AMS  $^{14}\text{C}$  dating (Piovano et al. 2009), the uppermost part of the Interval I sediments was deposited during the climate period known as the Medieval Climatic Anomaly (MCA; Ninth–fourteenth centuries AD) (Hughes and Diaz 1994; Keigwin 1996). The results of pollen and tree-ring studies in central Argentina indicate increased precipitation and/or mean temperatures during this time (Villalba 1994). This humid and warm phase may have been responsible for increased river discharge that in turn triggered three pulses of increasing water levels in Laguna Mar Chiquita. However, this wet phase was not uniform and included important and long dry intervals as indicated by the isotopic composition of the TOC ( $\delta^{13}\text{C}$ ) (Piovano et al. 2009) as well as by the occurrence of hiatuses as shown by the development of evaporite layers (halite, gypsum and calcite) within the sediments of Interval I. Wet conditions during this interval resulted in an increasing nutrient load changing the organic matter sources promoting primary productivity as regional temperature increased (Villalba et al. 2009). However, highly variable lake level conditions from highstands during MCA to lowstands with subaerial lake-floor exposures during pronounced droughts (after AD 850 and prior to AD 1770 in Fig. 3a) ascribed to the Little Ice Age (LIA; Piovano et al. 2009) allow to estimate that the LMC07-05 core site was located both in the pelagic area as well as close to the shore during periods of lake surface reduction leading to erosion and intensive reworking of the lake floor. Such a scenario points towards highly variable hydroclimatic conditions during Interval I, in which lake-level fluctuated significantly.

#### *Interval II (AD 1770–1970)*

Paleolimnological reconstructions indicate that Interval II matches a period of mainly low lake-water level,

mostly corresponding to the LIA, interrupted by short-lived humid events. High salinities and lowstands dominated from the LIA until the early 1970s when the shift to hyper humid conditions took place in central Argentina (Piovano et al. 2009). Several well-documented records in this region have identified the LIA as a cold and arid episode occasionally interrupted by more humid events (Villalba 1994; Piovano et al. 2009). The entire section contains predominantly allochthonous organic matter as indicated by the low HI and relatively high OI (Fig. 2). This dominantly terrestrial trend shows occasionally increasing algal contribution, probably associated with short-lived wetter conditions occurring both at the beginning of this period and during the last part of the nineteenth century. Sporadic short pulses of lake-level rise, both in the first and last phases of Interval II, are recorded as an increase in geochemical (TOC, HI and OI) and biological (CD/TC and isorenieratene pigment) indicators. During the late stages of the LIA record (around 70 cm core-depth in Fig. 3), most pigment concentrations show strong fluctuations reflecting higher organic deposition as a consequence of enhanced primary productivity of the lake. Historical records register an extraordinarily wet period starting in 1824, which induced channel shifts along the northern fluvial belt in the lake catchment (Mon and Gutiérrez 2009). Moreover, the waters delivered into Laguna Mar Chiquita by the Río Dulce were highly enriched in dissolved salts as the flooded areas upstream included the Ambargasta salt-pans (Zanor et al. 2012). Dissolution of gypsum from the Salina de Ambargasta may have liberated sulfate along with other nutrients to the lake waters further promoting algal growth and bacterial productivity, which is recorded as very thinly laminated sediments formed by fine-grained calcite laminae alternating with organic matter-rich layers (Piovano et al. 2002). According to Villalba et al. (2009) warm conditions within the LIA occurred in this region during this time interval. We therefore postulate that comparatively warmer and wetter conditions within the dry phase may have enhanced the aquatic productivity in Laguna Mar Chiquita accounting for pulses of autochthonous LOM.

The contemporaneous decrease in all pigment concentrations through the middle section of this interval—some of them barely detectable—appears to be associated with a major drought during the LIA in

agreement with a previous lake water-level reconstruction (Piovano et al. 2004). The CD/TC ratio of Laguna Mar Chiquita sediments (Fig. 3a) indicates a shift in the lake phototrophic productivity recorded as extremely low values, which could be attributed as well to possible sub-aerial exposure of the lake sediments during periods of excessive dryness. This is further corroborated by the high  $\text{CaCO}_3$  content (Fig. 2) indicating prolonged intervals of low water level promoting the precipitation of evaporitic layers (calcite, gypsum and halite) and sedimentary hiatuses.

The dominantly allochthonous imprint of the LOM through this entire interval most probably reflects the combination of grazing processes by microorganisms (as shown by phaeophorbides concentration) and the possible contribution of detritic oxygen-enriched organic compounds that potentially indicate a change in the type of native vegetation. Lutein, the main pigment accounting for the contribution of Chlorophyta and aquatic vascular plants, is however absent in the record. The latter may be associated with a long residence time that may have prevented the preservation of these labile compounds. Terrestrial remains may have also been rapidly dissolved in the lake water, which would explain the low occurrence of distinctive pigments throughout the record. Alternatively, these compounds may have been microbially degraded since there are bacterial pigments through the record (Fig. 3c). As the lake productivity decreased, the main primary producer seems to remain present even though only the less labile components were preserved. Moreover, we postulate that as a consequence of diminishing water input to the lake and associated low stand conditions, turbidity would have been reduced. This in turn may have promoted a decrease in photosynthetic organisms in the lake waters (zeaxanthin). The contemporaneous change in the hydrological balance of the lake catchment has affected the surrounding vegetation structure, modifying both source and concentration of allochthonous organic matter delivered into the lake.

#### *Interval III (ca. AD 1970–2007)*

This interval corresponds to the sedimentary record of the highest historically documented and instrumentally recorded lake level of Laguna Mar Chiquita (Unit A in Fig. 2). A largely positive hydrological balance characterized a vast region of subtropical southeastern

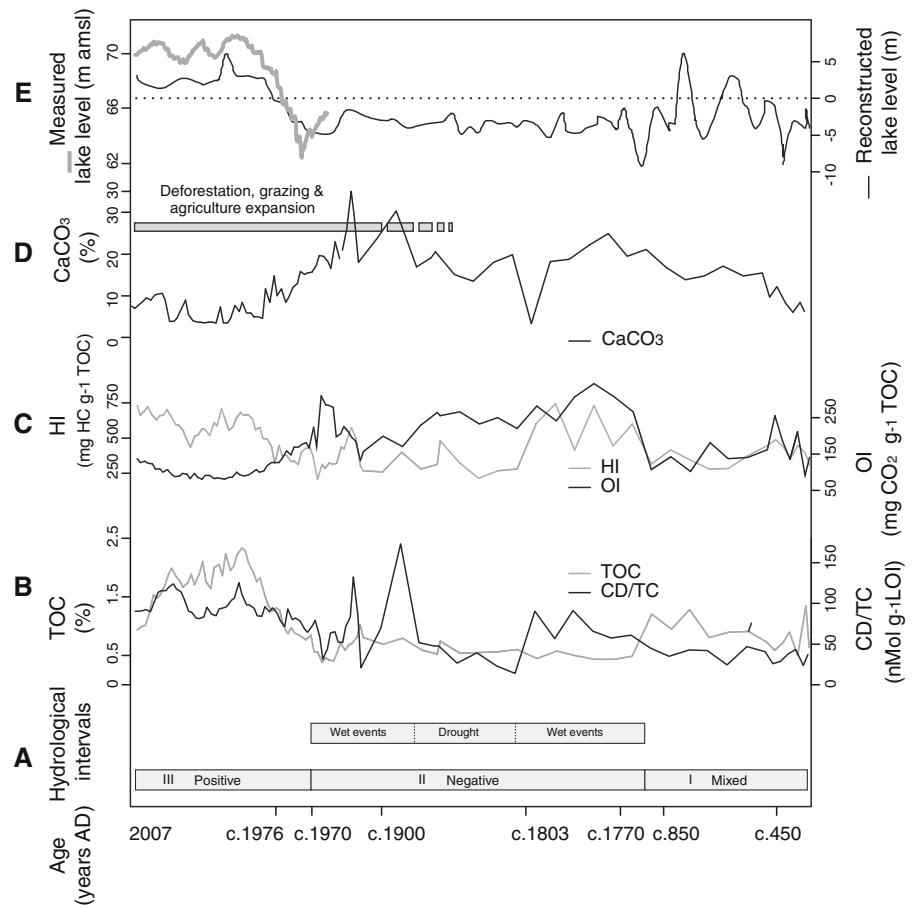
South America towards the end of the twentieth century (Pasquini et al. 2006; Troin et al. 2012). This humid phase due to the increasing moisture transported from the Amazon basin into central Argentina triggered the expansion of Laguna Mar Chiquita from the 1970s until AD 2003, when a water level drop started (Troin et al. 2010). The highest LOM values of the entire sedimentary record are recorded from AD 1970 to present suggesting both high primary production and large exchange between the lake and its catchment area. The uppermost decrease in TOC values (Fig. 2a) could be the response to the most recent lake level drop and salinity increase after 2003. Pigment stratigraphy along with the increasing amount of LOM suggest that the record of the humid phase during the last part of the twentieth century contains the largest amount of pigments indicative of high primary productivity. From November 1967 to May 2003 the lake volume expansion triggered a salinity change from approximately 270 to around 30 g l<sup>-1</sup>, respectively. A summary of lake water total dissolved solids (TDS) and chloride concentrations during the 1926–2005 period can be found in Troin et al. (2010). Biogeochemical markers registered in the sedimentary record of this time interval point towards an anoxic organic-rich environment dominated by autochthonous organic matter in agreement with previous results (da Silva et al. 2008). The organic matter-rich black laminae that characterize this interval (sedimentary Unit A in Fig. 2) represent near-bottom oxygen reduction contemporaneous with the well-documented hydroclimatic change to hyper humid conditions that occurred after the 1970s. These anaerobic conditions further promoted good LOM preservation as supported by the chlorophyll *a*/pheophytin *a* index and by the presence of chlorophyll *b* pigment in the sedimentary record. Chlorophyll *b* could be interpreted as aquatic macrophyte deposition but it is also characteristic of allochthonous matter (Godwin 1958), such as *Ruppia* (Seckt 1945). Labile pigments are usually abundant when algal remains are rapidly buried in an anoxic environment (Leavitt et al. 1989). Nevertheless, a sudden change in the community composition of primary producers is characterized by the dominance of fucoxanthin, alloxanthin and diatoxanthin indicating an increasing planktonic contribution to the LOM. This could account for a change in the transparency of the lake waters as a result of a more lentic condition.

### Anthropogenic influence

The impact of increased cultural eutrophication on saline lakes is still largely unknown. This is particularly true in the Southern Hemisphere where there is a clear need for long term combined limnological/limnogeological studies on changes in nutrient levels and algal biota. Thus, the magnitude of the anthropogenic influence on the LOM is still an open question since anthropogenic eutrophication has clearly increased over the last century (Vernet and Favarger 1982). Indeed, human activity surrounding lakes and their catchments has dramatic consequences for limnological processes that are recorded in the sediments. The current study on Laguna Mar Chiquita sediments allowed us to improve our knowledge about the impact of environmental changes on the primary productivity of this lacustrine system where the anthropic effect is combined with the effect of drastic water salinity changes associated with hydrological variability. Nevertheless, whether the most recent observed changes in LOM are purely climatically driven remain uncertain.

Several studies have mentioned the likely role of human settlements and agricultural activities in the vicinity of the lake (Cabido and Zak 1999; Bucher et al. 2006) for the time period spanning the enrichment of organic content occurring during Interval III. However, Piovano et al. (2002) highlighted the dominant linkage between the increased LOM in Laguna Mar Chiquita since the earliest 1970s with changes in water salinity due to the onset of the lake volume expansion caused by the hyper-humid phase. Historical records indicate that substantial modern human activity in the Argentinean Pampas is punctuated by a two-steps increase occurring at the end of both the nineteenth and the twentieth centuries (Bucher et al. 2006). Intensive deforestation followed by agricultural activities and grazing at the end of the nineteenth century irreversibly started affecting the pristine environmental conditions of this region (Bucher et al. 2006; Fig. 4d). In addition, increasing precipitation recorded in the area promoted a second pulse of agriculture expansion starting in the 1980s (Menghi 2006). The use of chemical agents such as fertilizers in Argentina after the Second World War (Lamer 1957) has certainly impacted the lake productivity as recorded in the sediments. An additional factor has been the high input of soluble nutrients that

**Fig. 4** A Distinctive intervals in the hydrological balance of Laguna Mar Chiquita, B, C and D correlation between TOC, pigment ratio CD/TC, bulk geochemical parameters (HI and OI), and total carbonate content for the uppermost 100 cm of core LMC07-05. All parameters have been measured in the same samples; and E Instrumental and historically reconstructed lake level fluctuations (*gray line*) and paleohydrological reconstruction (*black line*) from Piovano et al. (2002, 2009). A hiatus is marked at around 130 cm depth. Notice the good correlation between parameters and the historically and instrumentally documented lake level changes



were delivered to the lake by surface runoff and in particular, streams passing through agricultural and/or populated areas (Miglioranza et al. 2004; Matzinger et al. 2007). Although anthropic influences may have amplified the most recent changes in lake productivity, it is important to notice that the observed extreme changes in water salinity (i.e.,  $270 \text{ g l}^{-1}$  in 1970 and  $29 \text{ g l}^{-1}$  in 1986) highlight that the “salinity factor” is the main forcing controlling lake productivity.

Recent investigations show that the sedimentary records of the Pampean lakes present a significant correlation between sedimentary facies and lake-level changes (Piovano et al. 2004; da Silva et al. 2008; Córdoba et al. 2012). As mentioned, variations in water salinity during lake-level changes control both the amount of primary producers and the precipitation of authigenic minerals and this is recorded as distinctive organic-rich or evaporite-rich/organic-poor lacustrine facies at highstands and lowstands, respectively. Even more, this common feature overall the Pampean lakes—

an uppermost carbon-rich sediments—constitutes a stratigraphic marker for correlating lake sediments accumulated during the most recent highstands (Córdoba 2012). These anthropogenic changes, however, do not mask the natural trend resulting from changes in the E/P ratio. Analogously, the LOM and pigment record of Laguna Mar Chiquita show no distinctive signs which may indicate increase of anthropogenic influence in the region except for a short temporal phototrophic change of the dominance of fucoxanthin, alloxanthin and diatoxanthin pigments appearing in the youngest sediments (Fig. 3). This combined evidence appear to indicate no direct linkage between lake productivity and the beginning of human activity in the late nineteenth century and further agriculture expansion by the end of the twentieth century. Ongoing diatom analysis may give information on both changing salinity and potentially an eutrophication signal.

Figure 4 summarizes the analyzed proxies and the hydroclimatic variability represented by the lake level

curve. Three distinctive hydrological intervals can be linked with changes in the organic production and preservation. There is a good correlation between LOM, bulk geochemical parameters (TOC, HI and OI) and total carbonate content for the uppermost 100 cm of core LMC07-05 (Fig. 4b–d, respectively). There is also a noticeable good correlation among parameters and with the historically and instrumentally documented lake level changes (Fig. 4e).

## Summary and conclusions

Bulk organic matter and pigment investigations covering the last ~1,500 years of Laguna Mar Chiquita sediments allow the identification of the main environmental factors governing organic accumulation throughout this lacustrine basin. Evidence inferred from multiproxy analyses including preserved sedimentary pigments enables the reconstruction of lake paleoproductivity and its separation into three distinctive intervals as follows: Interval I (from ca. AD 450 to 1770); Interval II (between ~AD 1770 until 1970); and Interval III (spanning the second half of the twentieth century and the beginning of the twentyfirst century). They encompass different trophic states of the lake, which are the result of lake water-level changes and associated variations in water salinity triggered by large-scale hydroclimatic variability (MCA, LIA, twentieth century) in South Eastern South America. Intervals I and III contain high LOM whereas Interval II is characterized by lower organic matter content. The Laguna Mar Chiquita LOM record confirms previous studies using independent proxies indicating that this lacustrine basin is highly sensitive to changes in the hydrological balance over its entire catchment area. High pigment concentrations contemporaneous with a decrease in carbonate and other evaporites are related to increase productivity, lower salinity and higher water levels that have been correlated with an instrumentally recorded warmer and more humid climate (MCA, last part of the twentieth century). Yet, a decrease in primary productivity is probably reflecting low lake levels and hypersaline conditions associated with cooler and mostly drier intervals (LIA and the first part of the twentieth century).

The sedimentary pigment composition of the studied core highlights the predominantly autochthonous

character of the LOM during high-stands. It also relates maximum organic matter accumulation with the development of possibly permanent anoxic conditions at the sediment–water interface. Conversely, greater relative content of allochthonous organic material is registered during low stands and decreasing river discharge as inferred by sedimentary pigments, which is possibly due to reduced grazing pressure. It also appears that the structure of the phototrophic community is predominantly composed of benthic microorganisms independent of the lake water level surviving a large range of salinity. Species richness and total biomass seem to be climatically driven as changes in water salinity is the main factor governing their habitat. Furthermore, the multiproxy data suggest that increasing water temperature and sunlight intensity are more important than lake nutrient availability in limiting pigment and carotenoids distribution. In this highly turbid lake, the benthic signal can be attributed to in situ growing organisms as shown by the typical jelly-like consistency of the uppermost 10 cm of the lake sediments that may play a role protecting the lake bottom.

The high LOM content and fossil pigment record occurring during the Laguna Mar Chiquita main highstand intervals (AD 450 and after 1970s) show no major compositional changes in the lake primary productivity. Therefore, the latter would indicate a limited or insignificant anthropogenic impact on the most recent LOM. Conversely, our results indicate that Laguna Mar Chiquita has been naturally productive, even prior to the impact caused by major European migration to the region and the associated agriculture development and urbanism.

Finally, this study has further shown the importance of comprehensive paleolimnological research in saline lakes to clarify the effect of increase cultural eutrophication in their catchments on LOM production and preservation. It provides the grounds for further understanding the effects of changing salinity and nutrient concentration on lake productivity and structure of the biological communities.

**Acknowledgments** This research has profited from the invaluable help from the scientific staff of both the Istituto per lo Studio degli Ecosistemi (Verbania-Pallanza, Italy) and the CICTERRA (Universidad de Córdoba/CONICET, Argentina). A. Gilli from the Limnogeology Laboratory at the ETH-Zurich, Switzerland, is gratefully thanked for helping with petrophysical measurements and useful discussions. We also thank T. Adatte

from the University of Lausanne, Switzerland, for Rock–Eval analyses. This work was partially funded by CONICET (PIP-11220110100759), SECYT-UNC (2012–2013), PID-2008 (Ministerio de Ciencia y Tecnología de la Provincia de Córdoba), European Community's Seventh Framework Programme (FP7/2007–2013) under Grant Agreement No 212492: CLARIS LPB, "A Europe-South America Network for Climate Change Assessment and Impact Studies in La Plata Basin". The authors kindly acknowledge the thoughtful comments of two anonymous reviewers as well as Associated Editor S. Metcalfe and Chief Editor T. J. Whitmore.

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