Research paper



# A 700-year record of climate and environmental change from a high Andean lake: Laguna del Maule, central Chile (36°S)

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### Abstract

Central Chile is heavily exploited for mineral and water resources, with agriculture and large urban populations all creating intensive landscape use. Few records of past environmental and climate change are available that afford a broader context. To aid in this assessment, we present a 700-year reconstruction from Laguna del Maule (LdM) in the high Andes of central Chile based on sedimentological, geochemical, diatom and pollen analyses. The age model is based on <sup>210</sup>Pb/<sup>137</sup>Cs and <sup>14</sup>C dating tied into known volcanic eruptions. Sedimentology consists of organic-rich sediments and diatom oozes with several interspersed volcanic-rich facies and two tephra deposits. Sediment geochemistry exhibits increased productivity (high Br/Ti, biosilica) and more dominant oxic conditions (high Fe/Mn) from AD 1300 to 1400 and from AD 1650 to 1850, likely during periods of relatively lower lake levels and better development of littoral environments. However, during this later period, high elevation vegetation was dominant, indicative of regional cooler/ wetter conditions. In contrast, sediments deposited from AD 1850 to 1930 evidence decreased productivity and increased anoxic lake bottom conditions. The 'Little Ice Age' (LIA) in LdM is characterized by significant variations in lake dynamics and hydrology with cooler/wetter conditions (AD 1570–1700), major environmental changes in the 18th century and ending at ca. AD 1850. LdM record documents the impact of the LIA in the southern hemisphere and stresses the global nature of this climate period. Large changes in lake dynamics and diatoms assemblages during the 20th century could be related to anthropogenic impacts, but recent changes in climate patterns cannot be excluded.

### **Keywords**

Chile, diatoms, geochemistry, Late Holocene, 'Little Ice Age', pollen

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# Introduction

Anthropogenic activities have resulted in significant and profound impacts on the Earth's climate, ecosystems and biogeochemical cycles since late 18th century (e.g. Intergovernmental Panel on Climate Change (IPCC), 2007a, 2007b, 2014; Rodhe et al., 1995; Smol, 2008). In the light of increasing greenhouse gas emissions, global warming, human impact and land cover changes, Crutzen and Stoermer (2000) coined the term 'Anthropocene' for this most recent period of the Earth's history. Yet, it is often in the context of long-term regional changes including natural drivers of variability that such impacts can truly be assessed.

Despite significant progress in late Quaternary research across Chile (i.e. Latorre et al., 2007), and recent interannual and multidecadal reconstructions of temperature variations for South America for the past millennium (Neukom et al., 2011), there is less information regarding past climate change and long-term dynamics of central Chile ecosystems. Tree-rings (Christie et al., 2010; Le Quesne et al., 2006) and lake records (Boes and Fagel, 2008; Chambers et al., 2014; De Jong et al., 2013; Fagel et al., 2010; Jenny et al., 2002a, 2002b, 2003; Moreno et al., 2014; Moy et al., 2008; Urrutia et al., 2010; Von Gunten et al., 2009a, 2009c) provided late Holocene reconstructions of climate and human impact. These records have demonstrated significant changes during the last millennium, some synchronous to the 'Little Ice Age' (LIA, that is, AD 1570–1900, see Matthews and Briffa, 2005) and the 'Medieval Climate Anomaly' (MCA; AD 500–1350, Graham et al., 2007), although the regional timing of these fluctuations

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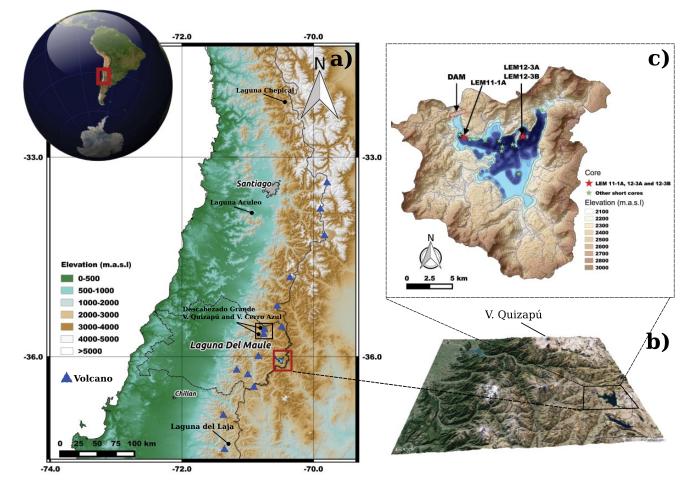
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**Figure 1.** (a) Location of Laguna del Maule (LdM) in central Chile and other sites mentioned in the text. (b) Maule River hydrographic watershed and location of Quizapú volcano. (c) LdM bathymetric map showing core location (2011, 2012 field campaigns) dam location and watershed topography.

often show discrepancies in duration and intensity. Available records demonstrate a significant human impact in mountain ecosystems over the past few centuries. Copper mining and associated land use have had a strong effect through airborne pollutants and eutrophication in central Chile Andean lakes (Von Gunten et al., 2009c). Other high elevation lakes in central Chile (i.e. lakes Chepical and Laja) also exhibit large environmental fluctuations in the 20th century, yet the impact of human activities in explaining such trends has not been evaluated.

To aid in this assessment, a 700-year high-resolution reconstruction of past climate and environmental variability was developed based on limnological variations of Laguna del Maule (LdM), a volcanic lake situated in the high Andes of central Chile (Figure 1a and b). For this, a combination of sedimentological, geochemical and biological proxies was used together with an age model based on multiple dating methods. This multiproxy approach is well suited for addressing the challenges of reconstructing past environmental conditions from lake sequences in the high Andes, as various components of lake systems are mediated by non-climatic factors, such as geomorphology, volcanism, local hydrology, the magnitude of response to climatic forcing for any given lake system may be non-linear (Fritz, 2008). In this paper, the timing of major environmental changes at LdM is established along with how these relate to regional and global climate change (such as the onset and demise of the LIA) and human and climate synergies of 20th century changes in Andean high-altitude lakes.

# Site description

LdM (36°S–70°W, 2160 m a.s.l.) is located in a large caldera in the western (windward) central Chilean Andes. The LdM volcanic field,

located in the Andean Southern Volcanic Zone, extends over 500 km<sup>2</sup> and comprises more than 130 individual vents (Figure 1a and b). Past eruptive history (Hildreth et al., 2010) includes silicic eruptions, generating welded ignimbrites associated with caldera formation, small rhyolitic eruptions, and a culminating ring of 36 post-glacial (<25 ka) rhyodacite and rhyolite coulees and domes that encircle the lake (Feigl et al., 2014). Using satellite radar interferometry, Fournier et al. (2010) measured a deformation field rate of ~180 mm/year between 2007 and 2008, which continues until the present.

LdM is located in the transition zone between the temperate, semi-arid, summer warm (Csb) and the dry-cool high-mountain (E) climate (Koppen-Geiger classification). Median annual temperatures recorded from 2007 to 2013 are as follows: 8.4°C, 9.6°C, 10.3°C, 9.5°C, 8.1°C, 9.1°C and 9.1°C, respectively, whereas for 2014, data were available only until September 23 with 7.6°C. The coldest temperature registered was -8°C (August 2013) (Direccion de Obras Hidraulicas, 2014). Precipitation stemming off cold fronts originates in the mid-latitudes and is most prevalent in autumn (May) to winter months (August; Garreaud, 2009). Occasional summer storms can also occur when favorable conditions aloft allow the advection of moist air masses from the east (Viale and Garreaud, 2014). On interannual to interdecadal timescales, rainfall in subtropical central Chile has been shown to be sensitive to variations in the El Niño-Southern Oscillation (ENSO), the Southern Annular Mode (SAM) and the Pacific Decadal Oscillation (PDO; Garreaud, 2009; Montecinos et al., 2011; Quintana and Aceituno, 2012). Recent decades of global warming (Trenberth and Fasullo, 2013) and projected future changes in the subtropics worldwide (IPCC, 2014) indicate that areas such as central Chile could become drier as winter droughts increase in frequency.

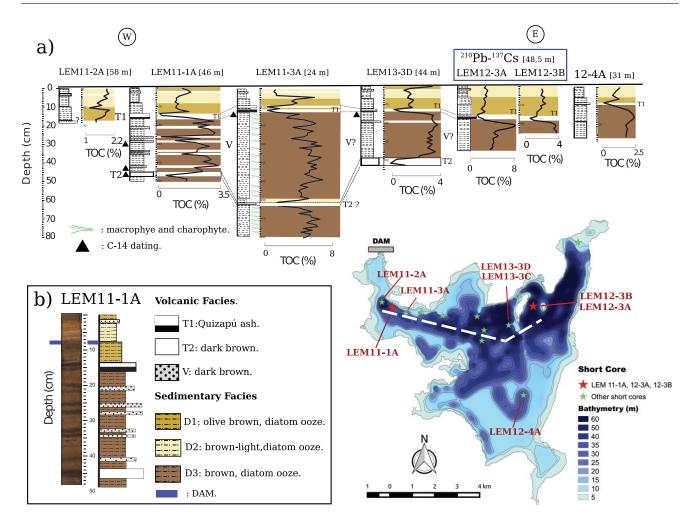


Figure 2. (a) Short sediment core transect in LdM: LEM11-2A, LEM11-1A, LEM11-3A, LEM 12-3A, LEM12-3B and LEM12-4A. Sedimentary facies, TOC, radiocarbon dates and correlation using elemental composition profiles and T1 tephra. The inset shows the bathymetric map with the location of cores used in this manuscript and the dam location. (b) Lithological description of core LEM11-1A. Blue bar (DAM) indicates depositional transition associated to dam construction.

Modern vegetation surrounding LdM is dominated by subshrubs and cushion species and is part of high Andean Shrubland belt (between 2000 and 2500 m.a.s.l.; García Berguecio, 2006; Luebert and Pliscoff, 2006; Teillier et al., 2011). At higher elevations, high Andean Steppe (>2500 m.a.s.l.) is dominated by herbs and cushion species characterized by scattered and/or scarce vegetation. Low Andean Shrublands occur at elevations between 1500 and 2000 m.a.s.l., and Deciduous Forest is found at elevations lower than 1500 m (see Table 2 in Supplemental Files, available online).

LdM is a 54-km<sup>2</sup> lake with a maximum depth of 50 m, part of the Maule river watershed (21,075 km<sup>2</sup>). The lake is irregularly shaped (Figure 1c) and was dammed (construction from 1946 to 1958, Figures 2-6 and 7e-g). The dam is 40 m higher than the former lake level and the maximum potentially flooded area is 56 km<sup>2</sup> (Sandoval Jeria, 2003). As a consequence, the lake volume increased from  $\sim 6 \times 10^8 \text{ m}^3$  to more than  $2 \times 10^9 \text{ m}^3$  (Arias Reyes, 2011). Lake-level fluctuations in recent decades have responded mostly to reservoir management for irrigation and hydroelectric needs. Indeed, the lake level has experienced a severe drop of 27 m in the last 7 years (see Figures 1-3 in Supplemental Files, available online). LdM is fed by winter snow accumulation (minimum of 0.01 m in May, 2010, to a maximum of 3.8 m in September, 2014, see Figure 3 in Supplemental Files, available online) and spring snowmelt. Although limnological data are scarce, depth, local climate and basin geomorphology all possibly indicate that the mixing pattern of LdM corresponds to a dimictic lake. The lake often freezes over in winter at the sectors of Las Nieblas, Potrerillo and La Colorada (Luis Torres, 2014, personal

communication). Water pH ranged from 6.1 to 8.4 (see Table 3 in Supplemental Files, available online).

# Material and methods

## Coring and sampling

A GARMIN GPSmap 178C Sounder was used to reconstruct the bathymetry (Figure 1c) applying a Universal Kriging interpolation method (Bivand et al., 2008). A total of 17 short cores were retrieved along several transects in the LdM basin using a hammer-modified UWITEC gravity corer during three expeditions (2011, 2012 and 2013, Figure 1c, see Table 1 in Supplemental Files, available online). Sediment cores were processed at the IPE-CSIC where they were opened, imaged, described and sampled. The presence of the Quizapú ash layer (AD 1932, T1, 15-17 cm depth, Figure 2a) was used as a stratigraphic marker to correlate across different cores. The core LEM11-1A (0.48 m in length), retrieved at the western sub-basin (43 m depth), was selected for detailed multiproxy analyses (Figure 1c, see Table 1 in Supplemental Files, available online). Sedimentary facies were defined, studied and characterized based on criteria formulated by Schnurrenberger et al. (2003). After employing non-destructive logging techniques (XRF elemental analysis; see below), core LEM11-1A was sampled volumetrically in continuous 1-cm resolution intervals except for diatom samples which were taken at 3-cm resolution (1 cm thickness) and for pollen, at 4-cm resolution (1 cm thickness).

Lab code	Core	Depth (cm)	Sample type	<sup>14</sup> C yr BP	Error (δ)	Cal. yr BC/AD (median)	Error BC/AD (lower)	Error BC/AD (upper)
Poz-59915	LEMI I-3A	14	Macrophyte macrofossil	4820	60	-3559	-3662	-3374
Poz-57545	LEM13-3D	15	Wood	85	25	1891	1704	1945
UCIAMS 133686	LEMI I-IA	30	Bulk sediment	4760	15	-3506	-3632	-3376
UCIAMS 133687	LEMI I-IA	43	Terrestrial plant macros	680	35	1351	1291	1395
D-AMS 001135	LEMI I-IA	47	Bulk sediment	4367	25	-2937	-3021	-2889
Poz-57281	LEM 13-20 m	*	DIC water	2370	30	-397	-515	-257
Poz-60705	LEM 135D	*	Modern macrophytes	2380	30	-403	-537	-265

Table 1. AMS radiocarbon dates from Laguna del Maule.

DIC: dissolved inorganic carbon.

## Chronology

Dating LdM sequence was challenging because the scarcity of terrestrial plant remains and the occurrence of large <sup>14</sup>C reservoir effect. Radiocarbon ages were obtained on five samples from three different cores (LEM11-1A, LEM11-3A and LEM13-3D) including macrophyte and terrestrial remains, wood and bulk sediment (see Table 1 below and Table 1 in Supplemental Files, available online). Ages were determined by AMS <sup>14</sup>C dating at the Poznan (Poland), at the DirectAMS (USA) Accelerator Mass Spectrometry Laboratories and at UC-Irvine (Keck Radiocarbon Facility). Water at 20m depth and living littoral aquatic macrophytes were sampled to assess the modern <sup>14</sup>C reservoir effect (Table 1).

One core, LEM12-3B (Table 1), was sampled in the field every 0.5 cm for <sup>210</sup>Pb/<sup>137</sup>Cs (Figure 4a). The <sup>137</sup>Cs/<sup>210</sup>Pb activities were measured by gamma-ray spectrometry, using a high-resolution, low-energy coaxial HPGe detector coupled to an amplifier at St Croix Watershed Research Station Laboratory, Science Museum of Minnesota. <sup>210</sup>Pb chronology was estimated by applying the constant rate of supply (CRS) model (Appleby, 2001). The core LEM12-3B was correlated with adjacent LEM12-3A and with core LEM11-1A using total organic carbon (TOC) content and the T1 tephra layer horizon (Figure 4a).

### Geochemistry

An AVAATECH x-ray Fluorescence II core scanner at the University of Barcelona was applied to core LEM11-1A at 4 mm measuring resolution using an Rh x-ray tube. Although the output includes a large number of elements (Figure 3b), Br, Al, Ti, Ca and Sr were selected to describe the changes in sediment composition. A total of 12 samples were analyzed using inductively coupled plasmaoptical emission spectrometry at the CEBAS-CSIC laboratory and used to validate semi-quantitative XRF data (counts/s).

Elemental geochemical analyses were performed on continuous 1-cm sample intervals for total carbon (TC), total inorganic carbon (TIC) and total sulfur (TS) measured in a LECO SC 144 DR furnace and for total nitrogen (TN) in a VARIO MAX CN elemental analyzer. For TOC/TN<sub>atom</sub>, standard procedures were followed (Meyers and Teranes, 2001).

Biosilica (BSi) analyses were performed according to Hansen and Grasshoff (1983) and Mortlock and Froelich (1989) using a continuous flow AutoAnalyser Technicon II. Standard procedures for precision of the biosilica quantification were done following Bernárdez et al. (2005).

## Diatoms

Approximately 0.15 g of dry sediment from each 13 samples, from core LEM11-1A, were processed following the Queen's University methods (http://post.queensu.ca/~pearl/diatoms.htm; Ruhland K et al., 1999). Clastic sediments were removed using a sodium poly-tungstate treatment. Microspheres were added for calculating

diatom concentration (Battarbee and Kneen, 1982), and permanent slides were prepared using Naphrax® (Battarbee et al., 2001). Diatoms were identified and quantified under a trinocular Carl Zeiss microscope, AxioLab A1, with an oil immersion objective (1000×). Quantitative analyses were done by calculating relative abundances by counting approximately 400 valves (up to 600 valves were counted in some levels down to 300 when diatoms were scarce), in random fields per slide. Diatoms were classified to species or variety level (Rivera, 1970, 1974; Rivera et al., 1973, 1982; Round et al., 1990). Standard floras were used for references (Dunck Oliveira et al., 2012; Hustedt, 1961-1966; Karthick et al., 2012; Krammer, 2000, 2002, 2003, 2009; Krammer and Lange-Bertalot, 1991a, 1991b, 1997a, 1997b; Lange-Bertalot, 1999, 2001; Levkov, 2009; Patrick and Reimer, 1966, 1975; Rumrich and Lange-Bertalot, 2000; Spaulding et al., 1997; Van de Vijver et al., 2010; Watanabe et al., 2012). Scanning electron microscopy (SEM LEO 1420VP in the SEM Laboratory of the Physics Department of the Pontificia Universidad Católica de Chile (http://servicios.fis.puc.cl/ sem)) was employed to recognize valve ultrastructural features and diagnostic characteristics. Optical microscopy images (1000×) were taken using a digital SLR camera (Canon EOS Rebel) attached to microscope. The nomenclature status of species or variety was verified using the Catalogue of Diatom Names (California Academy of Sciences, http://researcharchive.calacademy.org/research/diatoms/ names/index.asp; Fourtanier and Kociolek, 2011). Diatoms were grouped according to life forms and ecological characteristics (http://westerndiatoms.colorado.edu/and Spaulding et al. (2010) and references therein: see Aulacoseira alpigena ecology in http:// westerndiatoms.colorado.edu/taxa/species/Aulacoseira alpigena). Figure 5 was plotted using the Tilia software (version 2.0.19).

## Pollen

A total of 11 pollen samples (1 cm<sup>3</sup> sediment volume) were obtained from core LEM11-1A and processed following Faegri and Iversen (1989) methods to extract pollen grains. Lycopodium tablets were added for calculating pollen concentration (grains/ cm<sup>3</sup>; Stockmarr, 1971) and accumulation rates (grains/cm<sup>2</sup>/year). Pollen grains were mounted on glass slides and identified and quantified under an Axiostar Carl Zeiss microscope (400× and 1000×) using published pollen atlas (Heusser, 1971; Markgraf and D'Antoni, 1978) and the reference pollen collection of the Paleoecology Laboratory at Centro de Estudios Avanzados en Zonas Áridas (CEAZA). Pollen counts include 300 terrestrial pollen grains excluding paludal taxa. Relative abundances (%) are presented and discussed using selected taxa which were grouped according to their distribution within the vegetation belts described by Luebert and Pliscoff (2006). Pollen interpretations are based on the main vegetation belts present (composition and dominant species) and their elevation, according to the literature (Luebert and Pliscoff, 2006; Teillier et al., 2011; see Table 2 in Supplemental Files, available online). Data were analyzed and plotted using Tilia software (version 1.7.16).

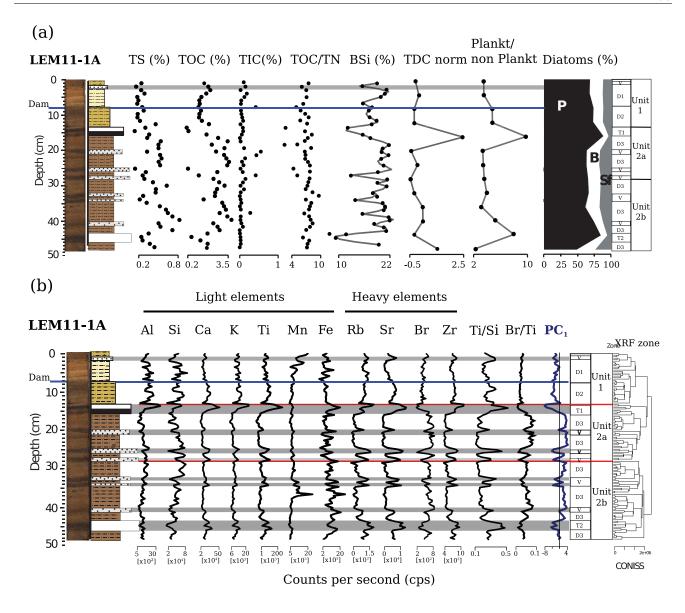


Figure 3. (a) Sedimentological, compositional, geochemical and diatom data and facies and stratigraphic units for core LEMII-IA. (b) Core LEMII-IA XRF data (cps). PCI and a CONISS analysis (plotted to the right; see text for explanation). Dam construction (AD 1946–1958) is also indicated (blue line).

TS: total sulfur;TOC: total organic carbon;TIC: total inorganic carbon;TOC/TN<sub>atom</sub>: total organic carbon/total nitrogen ratio; BSi: biosilica;TDC: total diatom concentration; plank/non plank: planktonic/non-planktonic ratio; P: % of planktonic diatoms; B: % of benthic diatoms; Sf: % of small fragilarioid; XRF: x-ray fluorescence; PC1: score plot of the first component (70% of total variance) for PCA of XRF data.

## Data analyses

Analyses and charts were performed on the Open Sources software Quantum GIS and in the R Programming Language (R Development Core Team, 2013). Statistical treatment of data was carried out following Riani et al. (2009) and Grimm (1987).

# Results

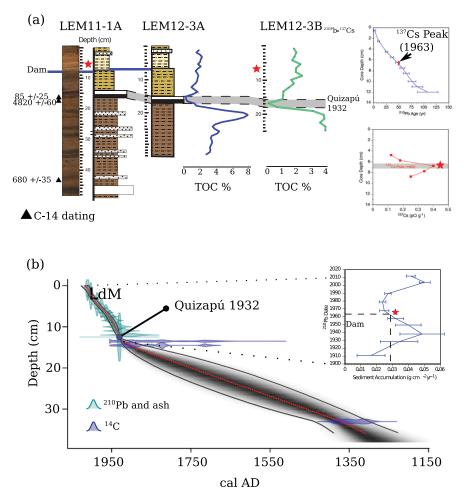
## Sedimentary facies

The LdM short cores are composed of massive to banded, brown, diatom and organic-matter-rich silts (facies D) with interspersed volcanic-rich facies (T and V; Figures 2 and 7g). In the lacustrine silts, the organic content ranges between 1% and 8% TOC and BSi between 9% and 22% (Figure 3a). Mineral fraction is mostly composed of plagioclase (60–80%), quartz (<5%), cristobalite (10–20%) minerals and glass particles (up to 20%). According to texture and composition, three main lacustrine facies have been identified. Finer facies (D1 and D2) are relatively less organic-rich (TOC: 1–2%; TS: 0.1–0.3%) and with a variable diatom content (BSi: 15–22%; Figure 3a). D1 is finer and with higher organic and diatom content than D2

(Figures 2 and 3a). Facies D3 are banded, coarser organic-rich silts (Figures 2 and 3a), with relatively higher organic matter content (TOC up to 3.5%; TS up to 0.8%) and more abundant terrestrial and littoral macrophyte remains. Layering in facies D3, defined by small changes in abundance of organic matter, coarser grain size and the abundance of macrophytes remains suggest a more littoral depositional setting for facies D3 compared with D1 and D2 (Figures 2 and 3a). Macrophyte-rich facies are also more common in littoral cores (e.g. LEM 11-3A, 24m water depth (Figure 2a)).

Two main sedimentological units are defined based on facies occurrence. Basal Unit 2 (50-14 cm) is composed of facies D3, whereas the top Unit 1 (0-14 cm) is made of finer facies D1 and D2. Increasing TOC values (from 1.4% to 3.5%) define subunit 2B (50-30 cm), whereas relatively constant TOC values occur in 2A (30-15 cm). Low and relatively TOC and TS values characterized Unit 1 (Figure 3a).

Up to eight volcanic-rich layers occur as centimeter-thick, massive, gray and dark, brownish layers (Figures 2 and 7g). They are composed mostly of volcanic glass, quartz and plagioclase, with elevated but variable amounts of diatoms and organic



**Figure 4.** LdM age model with dates from cores LEM11-1A, LEM12-3A and LEM12-3B. (a) Correlation between sediment cores LEM12-3A and LEM12-3B using TOC profiles and the Quizapú ash fall tephra. Right inset: <sup>137</sup>Cs-<sup>210</sup>Pb dating using the CRS model (Appleby and Oldfield, 1978; core LEM12-3B, <sup>137</sup>Cs peak at 7 cm). Stars indicate the location of radiocarbon dates and <sup>137</sup>Cs peak. (b) A Bayesian age–depth model (Blaauw and Christen, 2011) based on three AMS <sup>14</sup>C from cores LEM11-1A (terrestrial plants), LEM11-3A (aquatic macrophytes, with a calculated reservoir effect of 4700 years) and LEM13-3D (wood sample), <sup>137</sup>Cs-<sup>210</sup>Pb dating from core LEM12-3B and the Quizapú ash layer (1932). See text for details. Dam construction (AD 1946–1958) is indicated by the blue line.

remains. Based on textural characteristics and composition, two main types of volcanic facies were identified: T and V (Figures 2 and 7g). Facies V are dark brown, with gradational boundaries and include more biogenic components (organic remains, diatoms) than T, but are not present in all cores. Facies V are interpreted as reworked volcanoclastic deposits, associated with increased alluvial transport in the basin of volcanic material from the watershed. Facies T (T1 and T2 layers) have distinctive sharp basal and upper boundaries, internal texture, dominant volcanic composition and have been identified in cores throughout the lake basin. They have been interpreted as ash fall deposits from recent volcanic activity. T1 is a distinctive 2-2.5-cm-thick tephra with sharp basal and upper boundaries, and composed of a black, coarser basal layer grading into finer gray layers, and it has been associated with the last eruption of the Quizapú volcano in 1932 (Hildreth and Drake, 1992; Ruprecht et al., 2012; Figures 2 and 7g).

#### Chronology and age model

We had to use more than one analytical method (<sup>14</sup>C, <sup>210</sup>Pb/<sup>137</sup>Cs and tephrochronology) and several cores to obtain enough material for dating (Figure 4, Table 1). Hence, the age model includes <sup>137</sup>Cs/<sup>210</sup>Pb dating from the core LEM12-3B, two AMS <sup>14</sup>C dates from wood and terrestrial plant samples from cores LEM13-3D and LEM11-1A (Table 1, Figure 4b). Three <sup>14</sup>C dates (on bulk organics and plant macrofossils) were obtained from core LEM11-1A, but

only one (plant macrofossil) was used in our age model as the other two clearly had a large reservoir effect. A reservoir effect is common in Andean volcanic lakes and is likely caused by a large contribution of volcanic CO<sub>2</sub> (Geyh et al., 1999; Valero-Garcés et al., 1999). We used two approaches to determine this variable <sup>14</sup>C reservoir effect: (1) dating the water-dissolved inorganic carbon (DIC) at the mixolimnion (~20 m) and modern macrophytes (Table 1) and (2) by comparing the calibrated ages of  ${}^{14}C$  dates to samples (14C-dated or otherwise) with no reservoir effect from the same stratigraphic interval (i.e. wood, the Quizapú volcano eruption of AD 1932, see Table 1, Figure 4a). Fortunately, the correlation across all of our short cores was enabled by the similar TOC profiles and validated indirectly by the key presence of the Quizapú eruption ash layer (Figure 2a). The DIC-based reservoir effect was similar to living macrophyte (~ca. 2400 years) but considerably lower than the macrophyte-based estimate based on the comparison of samples from the same stratigraphic level (~ca. 4700 years). This variable range of the reservoir effect underlines the complexity of the carbon cycle in high-altitude volcanic lakes and also suggests that biological effects on the littoral realm may be significant.

We used a Bayesian age–depth model (Blaauw and Christen, 2011) to establish the deposition rates along the core; tephra layers have been removed for the calculation since they are assumed as instantaneous deposition. The final age-depth model uses Bayesian statistics and includes the <sup>210</sup>Pb/<sup>137</sup>Cs dates, Quizapú eruption (at 13 cm) and three AMS dates, two

without reservoir effect (wood and terrestrial plant sample from LEM13-3D (15 cm) and LEM11-1A (43 cm), respectively) and one with corrected values (macrophyte macrofossil sample from LEM11-3A at 14 cm; Figure 4b). The AD 1963<sup>137</sup>Cs peak centered at 6.5–7 cm (Figure 4a) fits the <sup>210</sup>Pb chronology well, thus adding considerable confidence to the <sup>210</sup>Pb dating. The Pb/Cs ages estimated a sedimentation rate mean of 1.2 mm/year for the upper Unit 1. The resulting model indicates that the core LEM11-1A spans the last 700 years (Figure 4b).

## Geochemistry

The first two components of a PCA of the XRF core scanner dataset explain ~80% of the variance (see Figure 5 and Table 4 in Supplemental files, available online). The eigenvector associated with the higher eigenvalue (7.58) define two main groups of loadings: (1) Rb (0.34), Zr (0.34), Zn (0.34), Ti (0.32), K (0.29), Y (0.29), Sr (0.30) and Ca (0.27) that are interpreted as the volcanic input, and (2) Br (-0.30), S (-0.16), P(-0.19), Si (-0.05) and Fe (-0.04) which are related to the amount of organic matter in the sediment. The formation of iron sulfides when anoxic conditions are more dominant explains the relationship between TOC and Fe. In addition, a significant correlation occurs between TOC values and Br (R2=0.79). As shown for other lake sequences (Gilfedder et al., 2011), Br content is associated with the amount of organic matter in the sediment, in turn a function of productivity, allochthonous input and preservation. Since most organic matter in the LdM sequence is of lacustrine origin (macrophytes and algae), in this study, the ratio Br/Ti is used as an indicator of organic matter content and as a reflection of bioproductivity and preservation. TOC and BSi also show good correlation (R2=0.48, p<0.001).

The Fe/Mn ratio is interpreted as indicator of changes in anoxic bottom conditions (Davison, 1993; Tipping et al., 1981; Wersin et al., 1991). Pronounced Mn enrichment at the top 5 cm (facies D1) and in some levels in facies D3 (35–40 cm depth) are suggestive of diagenetic Mn precipitation (Froelich et al., 1979; Kasten et al., 2003; Figures 3b and 7f) during relatively more frequent anoxic conditions. TOC, TS and Br/Ti ratio values are higher in Unit 2 than Unit 1 reflecting an enhanced primary production and incomplete decomposition of organic matter at the lake bottom because of more frequent anoxic conditions.

#### Diatoms and biogenic silica

A total of 233 different diatom taxa were identified from the analyses of thirteen samples, although only 10 species reached a 2% in at least one level (Figure 5). Most taxa are planktonic (75.4%) and only 18.5% are benthic. The LdM diatom flora is dominated by two planktonic species Discostella stelligera (mean: 55.1%) and Aulacoseira alpigena (mean: 18.6%) as well as by a group of small fragilarioid benthic taxa (mean: 15.6%) consisting of Staurosira construens (dominant), Staurosirella pinnata, Staurosira brevistriata, Fragilaria pseudoconstruens, Pseudostaurosira brevistriata, Staurosira construens var binodis, Staurosirella dubia, Fragilaria martyi, Fragilaria leptostauron var leptostauron and Fragilaria (possibly a new species). Epiphytic taxa reach a mean relative abundance of 0.5%. Five additional taxa exhibit relative abundances of at least 3% in at least one sample, that is, Aulacoseira distans, Cyclotella meneghiniana, A. lirata, epiphytic Rhoicosphenia curvata and Cocconeis placentula as well as benthic Nitzschia amphibia (Figures 3a and 5).

Results are summarized into groups of taxa according to their life forms (benthic, epiphytic, planktonic and tychoplanktonic). The mean percentage ratio of planktonic to non-planktonic (P/NP) taxa fluctuates ~4.7 with the lowest values at the base (61.7% of planktonic taxa, ratio 1.8) and two peaks with higher values at 44–45 cm (83.3% of planktonic taxa; mainly *Cyclotella* taxa,

ratio: 11.8) and 16–17 cm (87.7% of planktonic taxa, mainly *Cyclotella* and *Aulacoseira* taxa, P/NP ratio: 11.3, Figures 3a and 5). Total diatom concentration (TDC) shows little variation (mean  $\sim 10E^6$  valves g<sup>-1</sup>) with only two peaks at the base at 49 cm and at 17 cm (Figure 3a). BSi values show a similar pattern with higher values in Unit 2 and lower values in Unit 1. Three main zones are identified based on diatom assemblages.

Basal ZoneD3 (45–50 cm): the more abundant diatoms are *Discostella stelligera* (54%) and *Staurosira construens* (24.1%; Figures 3a and 5). Planktonic diatoms show their lowest value (61.7%; Figure 3a).

ZoneD2 (17–45 cm) shows the highest abundance of *Discostella stelligera* (59.5–78.1%), followed by *Staurosira construens* (4.9–14.8%) and *Staurosirella pinnata* (10.4%; Figure 5). The upper part of ZoneD2 shows decreasing values of *Discostella stelligera* (66.7%) and *Staurosira construens* (16%; Figure 5).

Diatom assemblages in ZoneD1 (0–17 cm) are characterized by a co-dominance of *Discostella stelligera* (29.5–57%), *Aulacoseira alpigena* (13.3–35.7%) and *Aulacoseira distans* (32.5%; Figure 5).

## Pollen

A total of 47 pollen taxa were identified, 25 reached at least 2% in at least one level. Pollen compositions (Figure 6) are dominated by Poaceae throughout the record, but three distinct zones are definable based on associated pollen taxa.

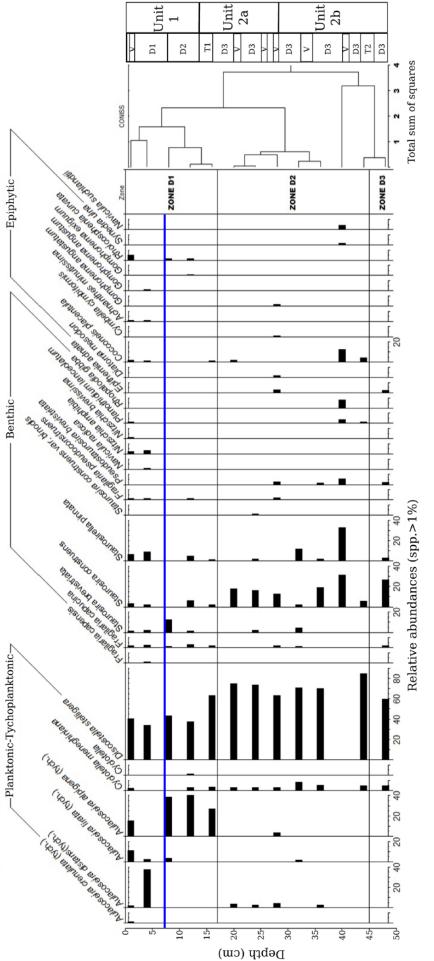
ZoneLEM-1 (29–48 cm depth) is dominated by Poaceae (60– 51%) accompanied by mostly high Andean Low Shrubland taxa such as *Ephedra* (8.7–5.5%). ZoneLEM-2 (18–30 cm depth) shows the highest percentages of Poaceae (61–56%) associated with increases in High Andean Steppe taxa and a decrease in pollen types associated with Low Andean Shrubland. ZoneLEM-3 (0–18 cm) shows the most prominent change over the entire record. Poaceae % drop to 29, whereas Low Andean Shrubland and Forest taxa % increase. Exotic taxa (an indicator of human perturbations) appear and paludal taxa increase at the top.

# Discussion

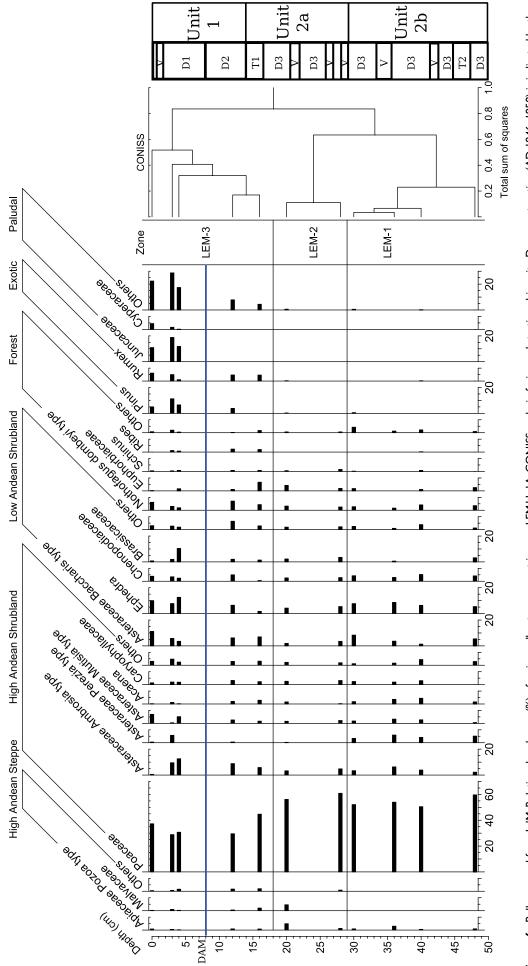
#### LdM basin processes since AD 1300

Sediment delivery. Similar K, Ca and Ti profiles likely reflect the same depositional processes governing the distribution of these elements in lacustrine facies, that is, mainly minerogenic sediment input from the surrounding watershed. Fe, Rb, Sr and Zr all follow the same overall pattern of K, Ti and Ca in Unit 1 (Figure 3b). Because of the relatively immobile characteristics of Ti, this element has been used as an indicator for clastic input (Demory et al., 2005; Haberzettl et al., 2005, 2007a, 2007b; Haug et al., 2003). Ca follows a similar pattern to Ti because of the presence of Ca-bearing volcanic rocks in the catchment (plagioclase), although elevated values of Al and Si (a mixed signal of allochthonous clastic input and autochthonous production of biogenic silica) show a high-frequency pattern in facies D1 and D2. Al values are lower in Unit 2, whereas Ti/Si fluctuates, with relatively high values suggesting a higher diatom component (indicated by TDC and BSi values, Figure 3a). Fluctuations in sediment delivery to the lake are associated with runoff variability which in turn is related to variations in the amount and seasonality of precipitation (summer vs winter) and the duration of winter snowfall and thus are reflected in the high-frequency Ti fluctuations throughout Units 1 and 2 (Figure 3b). Periods of prolonged snow cover in the catchment area reduce the annual duration of fluvial activity and potentially diminish the lake clastic input. In addition, longer periods with lake water stratification under snow winter accumulation and prolonged anoxic conditions at the sediment/water interface, lower organic matter oxidation. Additionally in winter, the snow accumulation in the lake











and period of water stratification may lead to anoxic conditions at the sediment/water interface, consequently lowering in organic matter oxidation. This leads to higher organic matter preservation and increased TOC values. Extended snow cover, however, can also extend the time of snow accumulation in the catchment, leading to greater runoff during snowmelt. This would result in an enhanced minerogenic flux to the lake sediments. The duration of the periods of snow accumulation is likely controlled by the timing of snow accumulation and melting and by winter minimum temperatures, which controls the thickness of the snow layer (Livingstone, 2005). Although some minor fluctuations occurred within Unit 2, the most significant change in LdM sequence is the relatively higher values of minerogenic input in Unit 1 compared with Unit 2.

**Diatoms.** Subfossil lake diatoms records are scarce for central Chile, the multiproxy studies from Laguna Aculeo are an exception (Jenny et al., 2002a, 2002b) as well as a recent record from Lago Laja (Urrutia et al., 2010). Although the resolution of diatoms in LdM record is lower than geochemical proxies, it captures the centennial-scale variability and characterizes the main changes within the different units.

High percentages of benthic fragilarioid taxa have been linked to cold conditions (Fey et al., 2009; Stoermer, 1993 and references therein) in many lakes (Rühland et al., 2008); in LdM, a high-altitude Andean lake, this relation is also seen (Figures 3a and 5). The presence of small fragilarioid (4.1–30.4%) taxa throughout the entire record might also be indicating shallow waters in coastal areas of circumneutral to alkaline and oligotrophic to mesotrophic conditions of deeper lakes (Douglas and Smol, 2010; Fernández et al., 2013; Figures 3a and 5). *Staurosira construens* and *Staurosirella pinnata* are the most abundant benthic diatoms.

Discostella stelligera has been observed to bloom in lakes during the 20th century in relation to physical properties, i.e. thermal stratification (Harris et al., 2006) and warmer conditions (Hyatt et al., 2011; Rühland et al., 2003, 2010; Rühland and Smol, 2005). The abundance of Discostella stelligera in LdM after ~AD 1900 (post-LIA) decreases to almost half (ZoneD1). Concordantly, LdM record shows large diatom assemblage shifts over the past 100 years, similar to those recorded in many lakes of the northern hemisphere (Hyatt et al., 2011; Rühland et al., 2003, 2010), although species involved are different. The shift in abundance between Discostella and Aulacoseira is highly characteristic of the upper 15 cm of LdM core and is opposite to patterns described for Arctic lakes during the past centuries (Rühland et al., 2008) and some Andean records (Micheluttie et al., 2015). These last century changes are also prevalent in other diatom records from central Chile. At Lago Laja (37.3°S), this shift is observed between Discostella stelligera, Discostella aff. glomerata and Aulacoseira distans which has been interpreted as a combination of increases in nutrient concentrations coupled with large drops in lake level during recent decades (Urrutia et al., 2010). At Laguna Aculeo (33.8°S), this shift involves maximum abundance of Melosira pseudogranulata and Aulacoseira granulata and minimum of Cyclotella operculata, which has been interpreted as increased eutrophication (Cabrera and Montecino, 1982; Jenny et al., 2002a, 2002b). Furthermore, the co-dominant species in LdM record (AD 1900-2011) is Aulacoseira alpigena (3-35.7%) and, although its ecology is not well known, has been considered as a low-nutrient indicator. This species has also been found at other high Andean lakes such as Laguna Negra and Laguna el Ocho (Alvial et al., 2008) as well as in southern Patagonia (Fernández et al., 2012). Frequent re-suspension (enhanced mixing, Kilham et al., 1996; Köster and Pienitz, 2006; Rühland et al., 2008) and consequently high turbidity and low light also seem to favor this species.

The late 19th century is a period of significant climate changes at a regional scale (end of the LIA, Jenny et al., 2002a), and it could have been a dominant forcing in LdM environmental change. For example, an increase in the intensity of local winds could have contributed to create turbulence in the water column, allowing Aulacoseira taxa (heavy silicified) to remain in the photic zone. An increased turbidity may have reduced the photic zone, leading to conditions under which better flotation and higher surface to volume exposure afforded Aulacoseira a greater competitive advantage (Vilaclara et al., 2010). The location of the coring site, which is relatively close to the lake margin, could also have favored more turbid conditions because of enhanced sediment delivery or re-mobilization. Although the rapid increase in Aulacoseira taxa occurred ~50 years prior to dam construction, early anthropogenic impacts (fishing and other early recreational uses) cannot be ruled out as an explanation for this change in diatom assemblages. In addition, damming since AD 1946 and water level management policies can affect lake hydrological properties, possibly increasing turbidity and decreasing light availability, with subsequent changes to water column mixing and stability (Rühland et al., 2010; Saros and Anderson, 2014). The presence of Aulacoseira distans, a typical wetland species, could also be because of recent conductivity changes in the lake (Camburn and Charles, 2000). In summary, the rapid changes in diatom assemblages at the top of the core are likely responding to a combination of all these factors.

At the bottom of the core (ZoneD3) planktonic diatoms were at their lowest abundance which is indicative of lower water levels. Increases in epiphytic taxa (Figures 3a and 5, ZoneD1) possibly point to stronger wind and wave transport of epiphytic diatoms from littoral macrophyte habitats toward the coring site where they were re-deposited together with planktonic diatoms.

The presence of *Cyclotella meneghiniana* (ZonesD1, 2 and 3) is typical of halobous to oligohalobous, alkalibiont and littoral environments (Gutiérrez Téllez, 1996). The appearance of *Nitzschia amphibia* (ZoneD1), although in very low abundances, could be a response to local development of more eutrophic environments (Bennion, 1994; Chávez-Lara et al., 2012; Hassan, 2013; Whitmore, 1989).

In the northern hemisphere, large 20th-century changes in diatom assemblages are related to climate-induced changes in the thermal regime, resulting in enhanced periods of stratification and increasing productivity associated with extended growing seasons and warmer conditions (Interlandi and Kilham, 2003; Rühland and Smol, 2005; Saros and Anderson, 2014; Saros et al., 2012, 2013). In the LdM record, the large change in diatom assemblages in the upper zone is coincident with the end of the LIA (after AD 1850) and occurs after a period of higher productivity (indicated by BSi, TDC and geochemical indicators; Figures 3 and 7e). The recent trends indicative of decreased productivity over the last decades at LdM could be associated with warming or other anthropogenic impacts and limnological perturbations. Warming temperatures and relatively higher levels after the dam construction in the 1950s would have increased the stability of the water column and might be contributing in reduced upwelling of deep-water nutrients to surface waters, thereby significantly decreasing overall lake production, although this does not explain the abundance of Aulacoseira. To the contrary, these taxa would decrease in abundance if the lake became more stratified after ~AD 1900. At Laguna Chica de San Pedro, Urrutia et al. (2000) provide evidence that macrophyte beds might be storing nutrients that then become unavailable for the phytoplankton. In LdM LEM11-1A record, macrophyte remains are more abundant in facies D3 (Figure 3a), before the past century, but not in more recent facies. The recent expansion of littoral macrophyte beds, however, suggested by the increased abundance of the epiphytic diatom Rhoicosphenia curvata (Figure 5) could also influence biogeochemical processes, but their impact on the diatom

community will need to be assessed by more specific research. Additionally, macrophyte-rich facies are highly abundant throughout the more littoral core LEM 11-3A (Figure 2a).

**Organic bioproductivity.** The TOC/TN<sub>atom</sub> fluctuates around a mean of 7 (Figure 3a) and suggests a predominantly algal origin of the organic matter (between 4 and 10, Meyers and Teranes, 2001). The TOC/TN<sub>atom</sub> variability reflects different amounts of macrophyte debris admixed with algal organic matter, (Figure 3a). As TOC, TS, TDC and BSi display a rather similar pattern at LdM (Figure 3a), they are likely related to the same controlling factors. These are primary productivity, dilution by minerogenic input and organic matter preservation (Meyers, 2003). Silica sources are diatoms, phytoliths, chrysophytes and sponge spicules and minerogenic materials. Elevated Ti/Si ratios could possibly reflect higher input of Si from biosilica, an interpretation which is further supported by the TDC and BSi record (Figure 3a). Hence, for the LdM record, the Ti/Si ratio appears to be a reliable proxy for diatom productivity.

Changes in productivity are also controlled either by a varying influx of nutrients through fluvial and/or aeolian input or the duration of open water which enables photosynthesis, and so controls the length of the growing season for algae and macrophytes.

Ti/Si, Br/Ti and BSi profiles and PC1 (Figure 3b) show coherent patterns over the last 700 years interpreted as productivity (both algae and macrophyte) indicators. The record presents two century-scale peaks from AD 1300 to 1400 and AD 1650 to 1850 (Figure 7e). Low values occur from AD 1400 to 1650 as well as during most of the late 19th and 20th centuries. A small increase in the last decades is marked by increases in TOC, TS, BSi, Ti/Si and Br/Ti (Figure 3a and b). Endogenic carbonates are absent, although there is a level with relatively high TIC (up to 1%) at between 19 and 20 cm (~AD 1800–1850; Figure 3b) that suggests a short period of carbonate formation in the lake, possibly associated with increased organic productivity.

Vegetation changes. The highest percentages of Poaceae and High Andean Steppe taxa are suggestive of a displacement toward lower elevations of the high-altitude vegetation belts during zone LEM-2, compared with zone LEM-1. Although these results suggest a shift toward more humid and/or cooler environmental conditions, we should be cautious because of the low resolution of this sampling interval and the lack of local pollen rain transects. Low pollen accumulation rates of shrubland taxa suggest decreased pollen deposition, possibly associated with scarce plant cover (more typical of high-altitude vegetation assemblages). Moreover, low pollen accumulation rates are also recorded before and after LEM-2, but within the zones, the values are minimal (see Figure 4 in Supplemental Files). Pollen assemblages in zone LEM-3 show an increase in taxa more typical of vegetation belts from lower elevations (Low Andean Shrublands and Forest taxa) suggesting of a precipitation decrease and/or temperature increase. Furthermore, the increase in both exotic and paludal taxa at the top of the sequence indicates anthropogenic perturbation and seasonal variation of water level in the lake related to dam activities.

Existing records from Lago Laja (Torres et al., 2008) and Laguna de Matanzas (Villa-Martínez, 2002) indicate overall drier conditions before AD 650 and from AD 1560 to 1890. This contrasts with the relatively colder and moisture conditions interpreted from the pollen assemblages in the LdM record (Pollen Zone LEM-2).

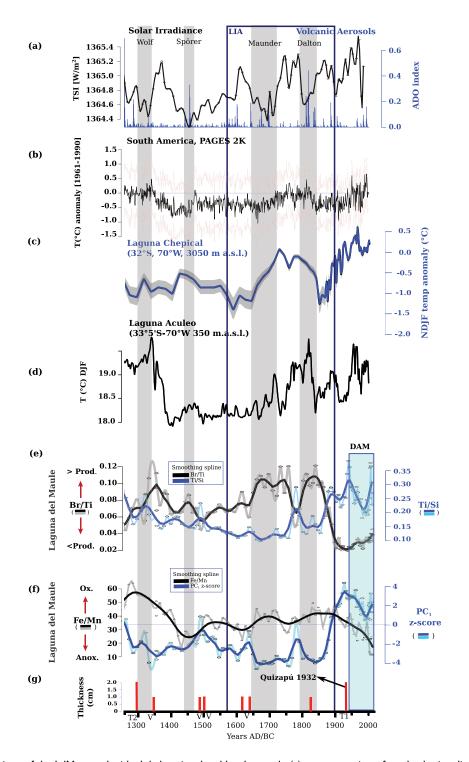
# The LIA and recent global changes in the high Andes of central Chile

The LdM record provides a high-resolution reconstruction of past environmental and climate variations during the last 700 years in the high Andes of central Chile and can lead to further assessment of the regional importance of the LIA, as well as major environmental changes that occurred during the 20th century. Two periods of paleoenvironmental change can be inferred across all of the proxies in the LdM record. Diatom assemblages, sedimentological properties and geochemical indicators (TOC, TS and Br/ Ti) show a change at ca. ~AD 1300, when lower organic bioproductivity and more frequent anoxic conditions occurred. The second but more significant limnological change occurred at the late 19th century, when a large drop in productivity (Figure 7e) and the rapid increase in *Aulacoseira* mark the end of the LIA (Figure 5). Changes in the diatom assemblages could possibly be because of early anthropogenic impacts or climate factors as increased winds that would create the turbulence needed for *Aulacoseira* to remain in the photic zone and dominate the phytoplankton (clearly competing with *Cyclotella* taxa, typical of thermally stratified environments).

The large environmental changes seen in the LdM record are for the most part coeval with other regional records in central Chile and predate the onset of colder temperatures in the northern hemisphere during the LIA (Matthews and Briffa, 2005). Regional records from Central Chile (De Jong et al., 2013; Urrutia et al., 2010; Von Gunten et al., 2009c) show that climate was characterized by relatively colder conditions, particularly cooler summers and relatively wetter conditions since AD 1350, although summer temperatures during the 18th century were significantly higher than the previous interval (De Jong et al., 2013; Figure 7c). A reflectance record from Laguna Aculeo indicates summer temperatures even higher than those at present from AD 1100 to 1350 (Von Gunten et al., 2009c), at the end of the MCA (sensu Graham et al., 2007) and prior to the onset of the LIA. This was followed by a decrease in summer temperatures of ~1°C from AD 1350 to 1700 before the onset of the LIA (Von Gunten et al., 2009c). Pollen records from Lago Laja and Laguna de Matanzas, as well as evidence from glacial geomorphology and dendrochronology, also suggest cooler and wetter conditions between AD 1350 and 1700 and at ~AD 1800 (Araneda et al., 2009; Espizua, 2005; Espizua and Pitte, 2009; Jenny et al., 2002b; Le Quesne et al., 2009; Neukom et al., 2010, 2011; Urrutia et al., 2010; Villa-Martínez et al., 2004; Von Gunten et al., 2009b). Further evidence for a cold episode during the LIA comes from a record of glacial advance between AD 1550 and 1720 from the same region as the LdM (Espizua, 2005; Espizua and Pitte, 2009). The LIA, thus, stands out as a time of significant and complex hydrological, environmental and climate change in central Chile.

In contrast, dendrochronological records taken along the western Andean slope between 32 and 38°S show that the last 100 years are also some of the driest of the last few centuries (Christie et al., 2010; Le Quesne et al., 2006, 2009). Geochemical proxies at LdM indicate that a large decrease in productivity occurred toward the end of the 19th century, although dominant anoxic conditions appeared to have remained at the lake bottom. Pollen assemblages (Low Andean Shrublands and Forest taxa) suggest a precipitation decrease and/or temperature increase in the 20th century. An increase also in exotic and paludal taxa may indicate seasonal variations of the water level in the lake related to dam management.

Over the last decades, the LdM record evidences a dominance of *Aulacoseira* in the diatom communities, a possible increase in the development of littoral macrophyte meadows and a slight recovery of bioproductivity (relatively higher TOC, Br/Ti, BSi and Ti/Si). The increase in the trophic state of the lake could be related to an increase in actual nutrient loading as a consequence of sport fishing and outdoor human activities. The development of macrophyte meadows suggested by the recent appearance of the epiphytic diatom *Rhoicosphenia curvata* (Figure 5) is coherent with an increase in the extent of shallow lake environments as shown in other lake systems (Balls et al., 1989). This could be related to the extensive flooding of



**Figure 7.** A comparison of the LdM record with global, regional and local records: (a) reconstruction of total solar irradiance (TSI; after Delaygue and Bard, 2010) and volcanic aerosols (AOD) based on Antarctic sulfate records (Crowley et al., 2008); (b) reconstruction of South America temperature anomalies from the PAGES 2 K initiative (after Ahmed et al., 2013); (c) a temperature reconstruction from the Andes of central Chile (L. Chepical 32°S, 3000 m, after De Jong et al., 2013); (d) a temperature reconstruction from the central valley of Chile (L. Aculeo, 34°S, 350 m, after Von Gunten et al., 2009c); (e) the Laguna del Maule record including proxies for productivity (Br/Ti and Ti/Si); (f) redox conditions (Fe/Mn) and organic versus clastic influence (PC1, from XRF data related to the organic matter and minerogenic input in the sediment (see Supplementary Files Figure 5 and Table 4, available online)); (g) thickness of volcanic facies of LdM. LIA: Little Ice Age' (after Matthews and Briffa, 2005); PAGES: past global changes; DAM: time since dam construction.

shallow areas after the dam construction in the 1950s and the water management regime for irrigation and hydropower generation. Lower values of TDC for recent decades (Figure 3a), however, suggest that the planktonic (mainly *Cyclotella* and *Aulacoseira* taxa) productivity has decreased although littoral productivity (macrophytes) may have increased (Figure 7e). Macrophytes could act sequestering nutrients, with consequent lowering of phytoplankton productivity, but this hypothesis requires further confirmation, pointing to a complex pattern of productivity changes in LdM.

Another factor to consider is the higher temperatures recorded for the recent decades of global warming in the high Andes of continental Chile (Falvey and Garreaud, 2009). In central and northern Chile (17–37°S), *in situ* temperature observations confirm the strong contrast between cooling off the coast  $(0.2^{\circ}C/decade)$  and warming in the central valley and western Andes  $(+0.25^{\circ}C/decade)$ , only 100-200 km further inland (and 500-2500 m higher in elevation). The warming rate along the western slope of the Andes is similar to that observed on the eastern (continental) slopes.

Warmer temperatures in the high Andes are related to a shorter duration of the snowpack of the LdM in recent decades and are conducive to an early melting of the snow cover, increased runoff and meltwater discharge into the lake during spring and early summer, and more turbulent conditions in coastal areas. This scenario could be evidenced by the presence of *Aulacoseira* taxa, although it could also be indicating windier conditions and/or higher water levels (Fernández et al., 2012).

What drives the centennial-scale environmental changes visible in the Laguna del Maule record? Although many features of the LdM record are in accordance with global variations in climate (i.e. colder climates at the onset of LIA, recent 20th-century warming) others appear to be clearly regional and not global in extent (onset of colder, anoxic conditions and decreased productivity during the early 15th century, and increased temperatures, oxic conditions and productivity during the 18th century). In Patagonia, changes in the location and intensity of the Westerlies have been considered as the main forcing for dry/wet phases during the LIA (Moreno et al., 2014; Moy et al., 2008) associated with reduced Hadley circulation during period of reduced solar activity (Chambers et al., 2014). In LdM region, moisture changes during the last centuries should be related to winter precipitation variability, mostly controlled by the intensity and location of the South Pacific High and changes in ENSO dynamics (Garreaud, 2009). The possible link with solar irradiance and ENSO dynamics of the internal LIA variability shown in LdM record needs to be explored with high-resolution records from the Andes and other areas where human impact was minimal until the mid-20th century.

# Conclusion

The history of Laguna del Maule over the past 700 years has been reconstructed based on sedimentological, geochemical and biological indicators. Geochemical proxies (Fe/Mn and S/Ti) show more frequent oxic bottom conditions prior to AD 1400 followed by a general trend to increased anoxic conditions, punctuated by a phase of higher oxygenation between AD 1650 and 1850. In LdM record, periods of increased productivity indicated by Br/Ti and Ti/Si (AD 1300-1400 and AD 1650-1850) correspond with phases of decreased anoxia, likely associated with lower lake levels and occurred during periods of climate transition to and from colder states that signified prominent changes in summer temperature throughout central Chile and southern South America. Past variations in lake limnology and hydrology coincide in part with the LIA (with cooler/wetter conditions from AD 1570 to 1700 and a final phase ending ca. AD 1850) but also indicate major environmental change in the 18th century, seen in other records across central Chile and northern Patagonia. Both anthropogenic and climate factors are likely responsible for recent changes in LdM basin. Introduction of new species mainly because of fishing activities, increased turbulence of the water column and changes in the thermal stratification caused by the damming and warmer conditions could all contribute to the changes seen in diatom assemblages in the 20th century. These recent changes have no previous analog in the past 700 years and indicate a possible environmental shift in the lake toward an unprecedented state.

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