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LITTLE ICE AGE TO PRESENT PALEOENVIRONMENTAL RECONSTRUCTION BASED ON MULTYPROXY ANALYSES FROM NAHUEL HUAPI LAKE (PATAGONIA, ARGENTINA).

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32 Pages – 9 Figures

SERRA ET AL.: 600YR MULTIPROXY RECONSTRUCTION, PATAGONIA.

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Abstract. Lakes are ideal sites to study environmental changes since they preserve climatic, anthropogenic, and volcanic signals in their sediments. Brazo Blest is one of the most important ramifications of lake Nahuel Huapi and it is an interesting site to study climatic variations as it receives direct discharge of heavy suspended sediments loads from Tronador Glacier through River Frías, as a result of the abrasion of the bedrock, and the runoff from the surrounding Valdivian forest. A short sediment core from Brazo Blest was analyzed for chironomids and diatoms assemblages and pigments in order to reconstruct environmental changes during the last 100 years in the basin under study This multiproxy study also included geochemical and physical analysis and reveals changes in the productivity of the lake over time, showing a shift in 1950s AD from autochthonous to allochthonous organic matter. This modification is related to precipitation changes, and the consequent fluvial runoff from two catchments, River Frías and the Blest-Cántaros basin together with the effects of-rising temperatures, which affected Tronador Glacier. Further, it allows us to link volcanic eruptions to a decrease in the species richness and number of chironomid and diatoms, as a consequence of the reduced light intensities and food availability induced by the high content of suspended sediments in the water column,. This study highlights the effectiveness of multiproxy analyses to reconstruct environmental changes.

Key Words: Chironomids. Diatoms. Pigments. Lake sediments. Paleoenvironmental Reconstruction. Patagonia.

Resumen. Los lagos son sitios ideales para estudiar los cambios ambientales, ya que en sus sedimentos se preservan señales climáticas, antropogénicas y volcánicas. Brazo Blest uno de los brazos más importantes del Lago Nahuel Huapi y es un sitio interesante para estudiar variaciones climáticas, ya que recibe la descarga directa de sedimentos en suspensión desde el glaciar Frías, a través del río homónimo. Estos sedimentos se originan a partir de la abrasión glaciaria, y de la erosión fluvial del sustrato en los ambientes de selva valdiviana circundante. Se analizaron los ensambles de quironómidos y diatomeas, así como los pigmentos, de un testigo corto obtenido en el Brazo Blest, para reconstruir los cambios ambientales ocurridos en los últimos 100 años en la cuenca bajo estudio. Este estudio multiproxy también incluyó análisis geoquímicos y físicos, revelando variaciones en la productividad del lago, mostrando un cambio de materia orgánica, de autóctona a alóctona, ocurrido en los 1950s DC. Este cambio se relaciona con las precipitaciones y la escorrentía procedente de la cuenca del río Frías y la cuenca Blest-Cántaros, además del incremento en las temperaturas que afectó a los glaciares del Tronador. Asimismo, esto nos permitió asociar eventos volcánicos con un descenso en la abundancia y riqueza especifica de quironómidos y diatomeas, atribuidos al aporte de sedimentos en suspensión en la columna de agua, produciendo una disminución de intensidad de la luz y reducción de la disponibilidad de alimentos. Este estudio resalta la efectividad de realizar análisis multiproxy para reconstruir cambios ambientales pasados.

Palabras Claves: Chironomidos. Diatomeas. Pigmentos. Sedimentos lacustres. Reconstrucciones Paleoambientales. Patagonia.

LAKE sediments are ideal to study environmental changes, since they represent continuous sequences of climatic and anthropogenic signals that can be reconstructed back in time. They are excellent sensors of environmental change, providing records of change on many time-scales. Multiproxy studies involving physical, chemical, and mineralogical analysis, combined with records of fossil biota preserved in those sediments, are proven to be one of the best and most accurate approaches to infer and reconstruct past environmental conditions, as they allow an overview of natural and non-natural events that can take place in a lake and its catchment area (Briner *et al*., 2006). In the Northern Hemisphere, studies of lake sediments using multiple proxies are increasingly used (Battarbee, 2000; Birks and Birks, 2006). In the Southern Hemisphere, these studies are less common and focus mainly in deciphering multi-millennial climate changes since Lateglacial times. On the other hand, Patagonian lake district of Argentina and Chile, Northern Patagonia, is considered one of the key sites in South America to study environmental changes as it encloses a great variety of forest communities and lacustrine environments, distributed along strong environmental latitudinal and altitudinal gradients, and controlled by regional and local climatic effects (Cusminsky and Whatley, 1996; Markgraf *et al*., 2000; Whitlock *et al*., 2001; Massaferro and Brooks, 2002; Massaferro *et al*., 2005, 2007, 2009, 2013, 2014; Villa Martínez and Moreno, 2007; Gaitán *et al*., 2011; Queimaliños *et al*., 2012).

In addition to its environmental sensitivity, Patagonia is under the influence of several active and potentially active volcanoes from the Southern Volcanic Zone in the Andes (Stern, 2004; Fig. 1). From historical times, tephra from these volcanoes have been carried eastwards by the dominant westerly winds (westerlies) and deposited, affecting large areas of the Andean and extra-Andean Northern Patagonia in Argentina. Two of the most important eruptions in historical times that affected Lago Nahuel Huapi (LNH), especially Brazo Blest, were from Cordón Caulle (Puyehue-Cordón Caulle – Volcanic Complex; 1960 AD) and Calbuco volcanoes (1893 to 1895 AD; Petit-

Breuilh Sepulveda, 1995; Daga *et al*., 2006, 2010; Villarosa *et al*., 2009). Several studies have shown that volcanic eruptions could cause significant impact in the ecosystems (i. e. Hickman and Reasoner, 1994; Eastwood *et al.,* 2002) and changes in the assemblages of organisms that live in the aquatic environments (Araneda *et al*., 2007). Despite the potential of the area for climatic/environmental reconstructions, multiproxy data covering the last millennium remain sparse (Ariztegui *et al*., 1997; Guilizzoni *et al*., 2009). In addition, most of the existing studies in Patagonia focused only on one bioproxy, and only few of these examined the impact of volcanic eruptions on lake biota (Massaferro *et al*., 2005; Araneda et al., 2007; Modenutti *et al*., 2013; Wolinski *et al*., 2013).

Chironomids (Insecta: Diptera) are one of the most abundant and diverse group of benthic aquatic macroinvertebrates of almost all aquatic environments around the world (Smol *et al*., 2001; Williams *et al*., 2012). Due to its chitinous structure, head capsule of chironomid larvae are usually well preserved in lake sediments, allowing their use for environmental reconstructions (evaluation of trophic status of lakes, oxygen levels, water level fluctuations; Brooks, 2000; Brooks and Birks, 2000, 2004; Brooks *et al*., 2001; Larocque, 2001; Little and Smol, 2001; Quinlan and Smol, 2001; Adriaenssens *et al*., 2004; Massaferro, 2009; Massaferro *et al*., 2005, 2007, 2013; Araneda *et al.,* 2007).

Diatoms (Bacillariophyceae) are frequently the dominant algal group in fresh water and marine environments. They have a cosmopolitan distribution, occupy a wide variety of habitats, and can live under extreme conditions, from polar ice to hot springs, from wet to almost dry habitats, and their distribution is related to water chemistry, climate, and geology (Battarbee, 1986; Round *et al*., 1990). Diatoms are one of the most widely used biological proxies because they possess a variety of life strategies, have a distinct ecological preferences, and their short life cycle allow them to respond quickly to environmental changes (Lotter *et al*., 1999; Rühland *et al*., 2003).

Fossil pigment concentrations in lake sediments are directly related to algal standing stock (Leavitt, 1993), and thus they can be used to reconstruct the evolution of phytoplankton assemblages, and to infer total primary productivity (Züllig, 1982; Guilizzoni *et al*., 1983; Guilizzoni *et al*., 1992). Chlorophyll derivatives (CD) and total carotenoids (TC) are used as proxies for algal biomass. Generally, higher values of CD/TC ratio reflect the inflow of allochthonous material to the basin (Sanger, 1988, according Lami *et al*., 2000) and could also indicate changes in the productivity of a lake (Bianchi *et al*., 1999). In addition, derivatives of chlorophyll and carotenoids have proved to be valuable indicators of characteristics that regulate the transformation of pigments (grazing, anoxia, laminated, light, etc.) in both sediment and water column, and therefore are key indicators of changes in the biotic and physical environment of the lakes. In the same way, plant pigment ratios of absorbance at 430 nm: 410 nm indicates the proportion of degraded chlorophyll and can be used as a measure of pigment quality preservation.

In this study, we propose a multiproxy analysis using chironomids, diatoms, and fossil pigments to reconstruct the history of environmental changes in a short core from Brazo Blest of LNH during the last century. We aim to evaluate and disentangle the occurrence and possible impact of different environmental changes (sediment input, tephra depositions, allochthonous/autochthonous organic matter source), to better understand lake processes related to input from the river and sediments washed out from the basin.

METHODS

Study Site

Lago Nahuel Huapi (LNH) is a glacial lake located in Northern Patagonia Argentina, in the wooded eastern foothills of the Andes (41° 01' 25.66" S - 71° 32' 5.88" W, at 767 masl, with a surface of 557 m^2, maximum depth of 464 m). It has an amoeboid shape with seven branches named Blest, Campanario, Última Esperanza, Huemul, Machete, Rincón, and Tristeza. The lake is fed by melting ice, snow, and rain, and the River Limay lake outlet.

Brazo Blest is one of the most important branches of LNH; it receives discharges from the River Frías, which in turn, carries melting glacial water directly from Mount Tronador´s ice-cap and from a relatively small catchment area, to the northwest of Blest, where arroyo Los Cántaros and arroyo Blest transport sediments into the lake (Fig. 1). The bay of Brazo Blest has 40 m depth and is located within the temperate-cold Valdivian rain forest with a precipitation average of 3000-4000 mm y^{-1} with a marked seasonality, wet winters, with frequent snowfalls and temperature below zero, and dry summers, with temperatures close to 30 °C (Barros *et al*., 1983).

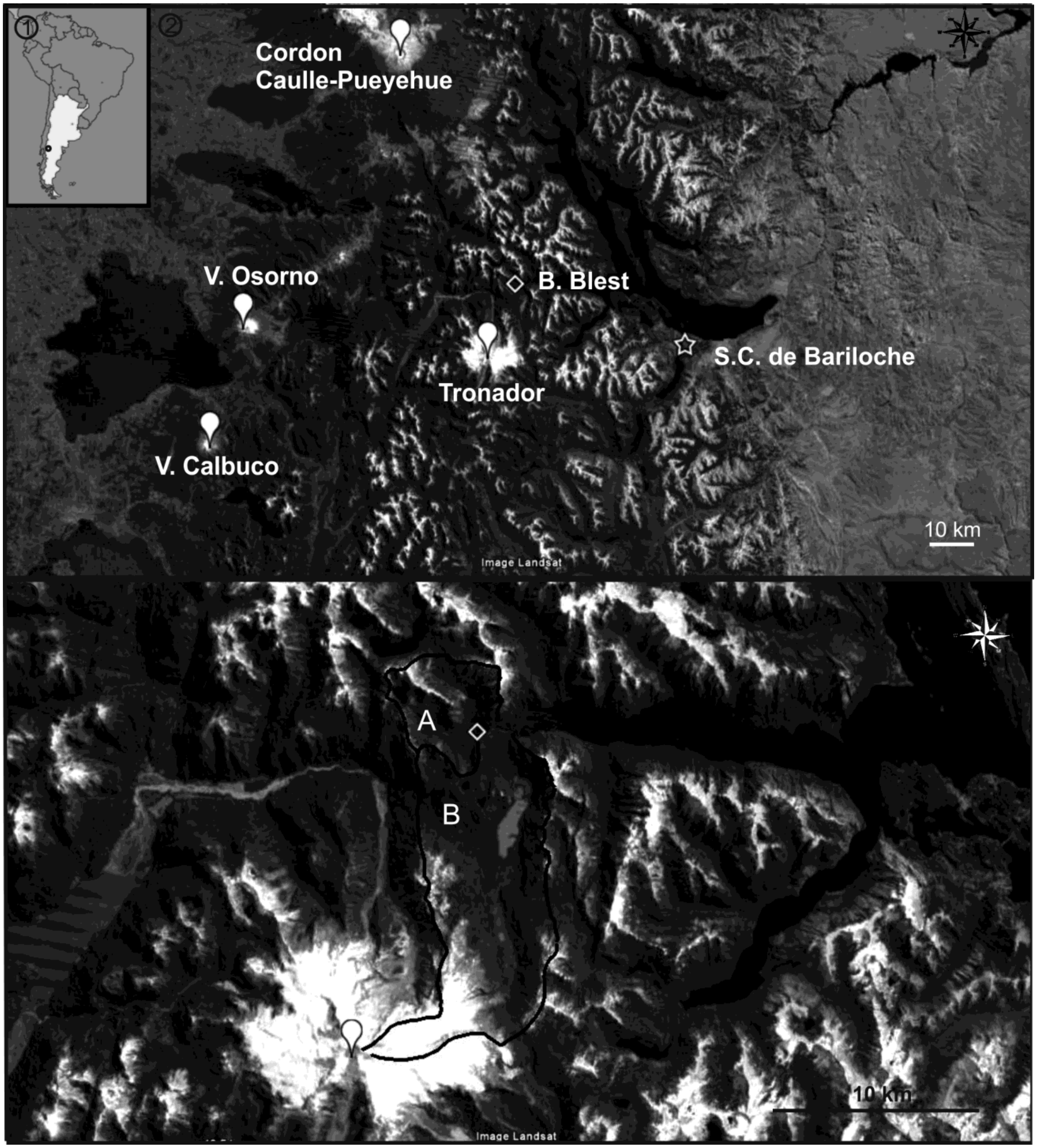

Fig. 1: Image of Google Earth. 1) Argentina, Lago Nahuel Huapi (empty circle) (40° 59´ S – 71° 51´ O). 2) Lago Nahuel Huapi, Brazo Blest (empty rhomb) 41° 01' 25.66" S - 71° 32' 5.88" W, at 767 masl; active volcanoes that affected Lago Nahuel Huapi (white dots). 3) A: Blest-Cantaros catchment area 41° 01' S - 71° 32' W); B: Frías Glacier catchment area.

Core extraction

In July 2011, a short sediment core (35 cm long) named Blest11 was recovered (41° 01' 27.80 "S - 71° 49' 13.86" W, 772 masl), at a depth of 10 m in the bay of Brazo Blest, using a Hammer Corer. The first 20 cm of the core were subsampled every 1 cm, and from 20 cm to the bottom, every 2 cm (27 subsamples). The samples were analyzed for biological, chemical, and physical properties.

Dating and chronology

Core dating was performed using ^{210}Pb technique (My Core Laboratory, Canada). Specific activity profiles were determined by high-resolution gamma ray spectrometry on core Blest11. The Constant Rate of Supply (CRS) model was used for ^{210}Pb dating (Joshi and Shukla, 1991; Robbins and Herche, 1993). Correction of the old date error of the CRS model (Binford, 1990) was implemented by logarithmic extrapolation of the measurements to complement integration to infinite depth. To provide greater reliability to ^{210}Pb dating, a tephrochronologic framework was used for the last millennium (Villarosa *et al*., 2002). Since some of the most important eruptions in the area were those of Calbuco from 1893 to 1895 and Cordón Caulle in 1960 (Petit-Breuilh Sepulveda, 1995; Villarosa *et al*., 2009), the presence of volcanic ash layers in the sedimentary sequence helps to establish absolute dates and corroborate the chronological model. In order to identify the tephras the sediment was washed, sieved and observed under a stereomicroscope. Tephra characteristics were then compared with those of known tephra markers present in the area (Villarosa *et al*., 2002). We also used chronological data from dendrogeomorphological information and historical records (Villalba, 1990).

Magnetic susceptibility (MS)

Magnetic susceptibility indicates the degree of magnetization of a material in response to an applied magnetic field; it is a dimensionless proportionality constant. It is a useful method to identify changes in the sediments, such as tephra layers or changes of minerals abundance and composition. It was measured with a Magnetic Susceptibility Meter Bartington MS2 in the Laboratory of Paleomagnetism at the University of Buenos Aires.

Organic matter content (OM)

Loss on ignition (LOI) is a methodology used to calculate the OM content and carbonates content in sediments (Dean, 1974; Bengtsson and Enell, 1986). In the first reaction the OM is oxidated at 500–550 °C, releasing CO_2 and ash. In the second reaction the carbonates are destructed at 900–1000 °C, releasing CO_2 and producing oxides. We used the first reaction, where the LOI calculates the % OM by comparing the weight of a sample before and after the soil has been ignited, the difference between these weights represents the amount of OM in the sample. Before ignition, the sample contains OM, but after ignition all the remains are the mineral portion of the soil. Dean (1974) shows a strong correlation between LOI (550) and the organic carbon (Total Organic Carbon). Heiri *et al,* (2001) shows that this method is useful to correlate cores.

Organic Matter content was estimated using the LOI method in SACMa laboratory (Geological Department, FCEN – UBA). The method consists of weighting 1 g of sample, placing it in an oven at 60 ° C for 24 hrs, weighting it again, placing it in a muffle furnace at 550 ° C for 4 hrs, and weighing. LOI_{550} = ((weight 60°- weight 550°)/ weight 60°) *100 - %OM = (weight 550°/ weight 60°) *100.

Bioproxies analysis

Chironomids were treated following the standard method described by Brooks *et al*. (2007), which consists of deflocculating the sample with 10 % KOH at 70 °C, then sieving into two fractions (105 µm and 210 µm). The head capsules were picked out of a Bogorov sorting tray using fine forceps under a Lancet stereomicroscope, then were mounted, ventral side up, with Hidromatrix®. Chironomid remains were identified to the lowest possible taxonomic level under a Zeiss binocular microscope and using appropriate literature (Wiederholm, 1983; Armitage *et* *al*., 1995; Rieradevall and Brooks, 2001; Dieffenbacher-Krall *et al*., 2007; Brooks *et al*., 2007; Massaferro *et al*., 2013).

Diatoms analysis was performed following standard techniques for species compositional changes (percent relative abundances) and quantitative study (number of individuals per gram of dry sediment). A fraction of each sample was dried and weighted and then oxidated with H_2O_2 (100 vol) at 80 °C in order to remove all traces of organic matter that would interfere with the correct observation of diagnostic characteristics (Battarbee, 1986). After being neutralized by repeated washes with distilled water, a known volume of a suspension with a known number of microspheres was added in order to calculate the valves concentration (Battarbee and Kneen, 1982). The resulting slurries were permanently mounted with Naphrax®. A test slide was assessed to determine the most appropriate concentration for counting valves and for the correct identification at species level. The identifications were made with a binocular optical microscope Reichert-Jung Polivar equipped with Nomarski interference optics and using 100x oil immersion objective. The taxa which were difficult to identify under the light microscope were observed with a scanning electron microscope Carl Zeiss SUPRA 40 (Centro de Microscopías Avanzadas, UBA) and a Phillips XL 30 (Museo Argentino de Ciencias Naturales "Bernardino Rivadavia", Buenos Aires).

Analysis of fossil pigments were performed in the CNR-ISE (Istituto per lo Studio degli Ecosistemi; Pallanza Verbania, Italy). Algal fossil pigments were extracted from 1 g wet sediment using 90 % acetone and then centrifuged at 3000 rpm for 10 min. Spectrophotometrically-measured total chlorophyll derivatives (CD) and total carotenoids (TC) were obtained with the method described in (Guilizzoni *et al*., 2011). Specific algal carotenoids were obtained by reverse phase HPLC (Dionex Ulitmate) as described in (Lami *et al*., 2000). Once we obtained these values, CD/TC ratio was calculated.

Statistical analysis

Stratigraphic diagrams and statistical analysis (zonation, Broken Stick model) were performed using R package (Bennett, 1996; Birks, 1998; Juggins, 2003).

RESULTS

Dating and chronology

A ^{210}Pb-based estimate of the sedimentation rate was only possible in the upper core section (first 8 cm); below 8 cm no significant radiometric values were obtained. The estimated sedimentation rate varied from 17 to 14 g $m^{-2}y^{-1}$ in the first 4 cm (0.1284 cm yr^{-1}) of the core and 5 g $m^{-2}y^{-1}$ at the 8 cm deep level (0.0263 cm yr^{-1}) (Fig. 2). According to the ^{210}Pb, the date of the 5–6 cm depth corresponds to the period 1960 AD; at that time two important volcanic events occurred in the area 1960 Cordón Caulle and 1961 Calbuco eruptions (Petit-Breuilh Sepúlveda, 2004, Global Volcanism Program). This was confirmed with stereomicroscope examination of 1-cm interval samples after sieving and cleaning of the sediment. Tephra from the 4–5 and 5–6 intervals show mixture of vitric and crystal components (fragments size between 250 μm–125 μm), mostly angular brownish vitric pyroclasts that are the result of broken vesicle walls of larger fragments, only a few are pumice with elongated vesicles parallel to the long axis of the pyroclast. According to the distribution patterns of tephras from historic eruptions and considering the characteristics of the glass fragments, this maphic glass corresponds to the 1961 Calbuco eruption. However, the presence of silicic glass may be attributed to the 1960 Cordón Caulle eruption, which may have deposited a thin layer of fine ash as this area might have been marginally reached by the plume. Both were moderate to large eruptions (Volcanic Explosivity Index, VEI 3). A second tephra was found at 9–10 cm, identified by a peak of MS and a decrease of LOI (Fig. 3), and confirmed by petrographic analysis,,that could correspond to a historic eruption from volcán Calbuco. Historic records confirm a significant eruption that lasted almost a year, from 1893 to 1894 (VEI 4) and affected Brazo Blest (Petit- Breuilh Sepulveda, 1995; Global Volcanism Program). Deeper than 10–11 cm, continuity of the sedimentation rate cannot be assumed due to the strong changes in sedimentation density. Assuming sedimentation rates are similar to the last dated centimeters (7–8 and 8–9 cm), where sedimentation rates become constant at 0.059 - 0.048 cm/yr $^{-1}$ (Tab. 1), and based on the chronology curve using absolute dating from tephra (1893 AD) as the age for the 9–10 cm depth, we calculated an age for the base of the core ranging between 13511452 AD.

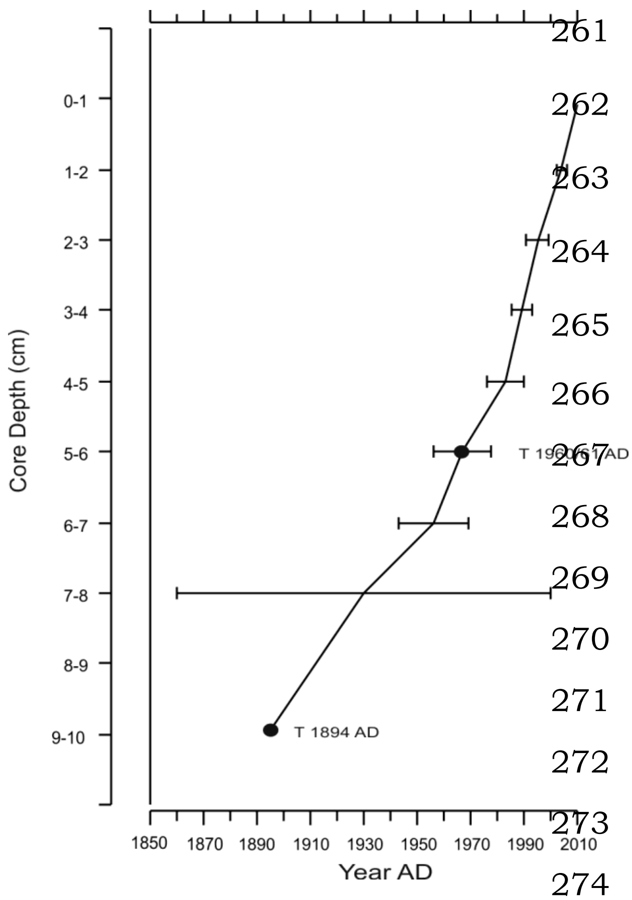

Fig. 2: Calibration Curve. Calibrate Years estimated from ^{210}Pb of the first 9 cm of the core. Dots show tephra.

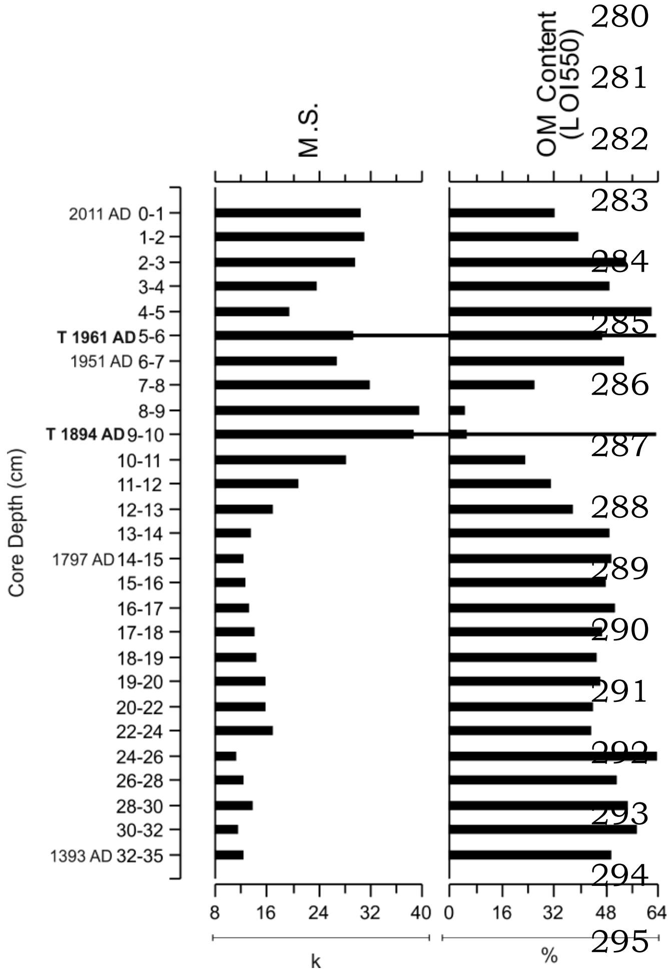

Fig. 3: M.S.: Magnetic Susceptibility (k, dimensionless proportionality constant); O.M.: Organic Matter Content (% LOI550).

Table 1: Chronology. ^{210}Pb dates and extrapolated dates.

Section of the Core (cm)	210 Pb age	STD in date (years)	Modeled Age Max	Modeled Age Min	Modeled Age Calc Rate
0	2011	0			
1	2004	2			
2	1994	4			
3	1988	4			
4	1982	7			
5	1964	11			
6	1951	13			
7	1932	70			
8	1912				
9	1894				
10			1872	1876	1874
11			1851	1859	1855
12			1831	1842	1835
13			1810	1825	1816
14			1789	1808	1797
15			1768	1791	1777
16			1747	1774	1758
17			1726	1757	1739
18			1706	1740	1720
19			1685	1724	1701
20			1664	1707	1681
21			1643	1690	1662
22			1622	1673	1643
23			1601	1656	1624
24			1581	1639	1605
25			1560	1622	1585
26			1539	1605	1566
27			1518	1588	1547
28			1497	1571	1528
29			1476	1554	1508
30			1456	1537	1489
31			1435	1520	1470
32			1414	1503	1451
33			1393	1486	1431
34			1372	1469	1412
35			1351	1452	1393

Bioproxies

A total of 27 chironomid morphotypes were found along Blest11 sediment sequence. The most abundant taxa were *Limnophyes* Eaton, *Riethia* Kieffer, and *Cricotopus* van der Wulp (from 16 to 12 % of relative abundance) (Fig 4; taxa with relative abundances higher than 5 %), whereas *Apsectrotanypus* Fittkau, *Acricotopus* Jean-Jacques Kieffer, *Chaetocladius* Kieffer, *Corynoneura* Johannes Winnertz, *Macropelopia* Thienemann, *Paralimnophyes* Brundin, *Podonominae*

Thienemann, *Smittia* Holmgren, and *Symbiocladius* Kieffer were the less abundant taxa (1 % of relative abundance). Total chironomids head capsules showed a maximum peak at 22–24 cm, then the number gradually decreased until 11 cm to finally increase (to 7 %) in the 0–1 cm interval. Littoral taxa such as *Cricotopus* and *Limnophyes* were the most important taxa, followed by profundal taxa such as *Parochlus* and *Riethia*, and finally semiterrestrial/terrestrial taxa such as *Harrisius* and *Stictocladius* (Fig. 4).

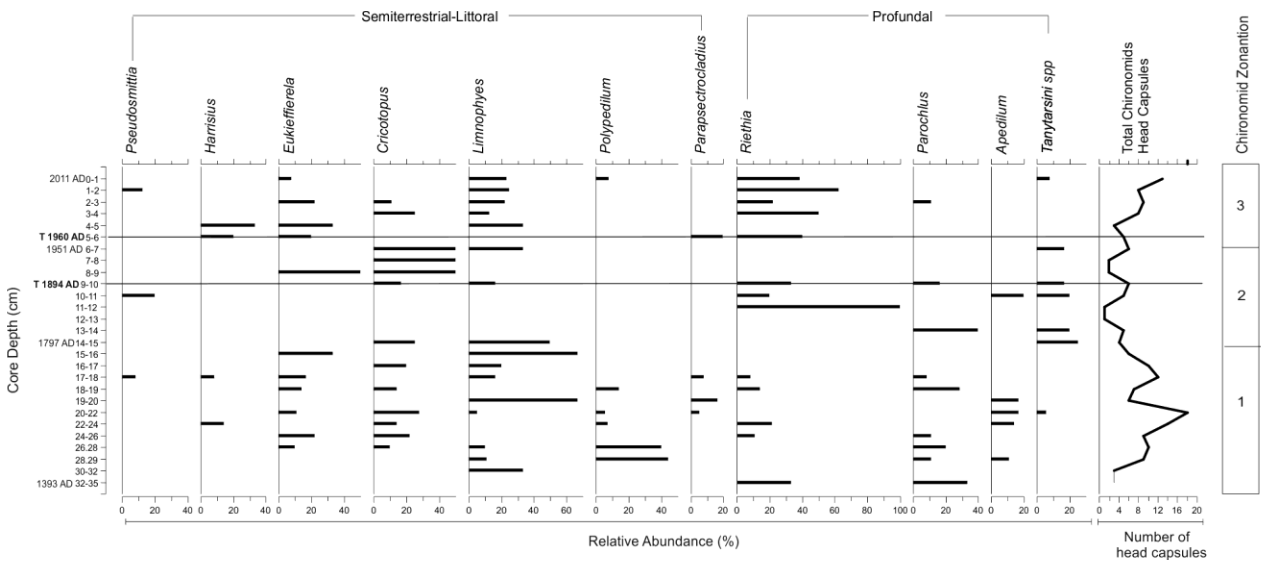

Fig. 4: Chironomids abundances along the studied sequence. Only taxa with more than 5 % of relative abundances are shown. Plain lines indicated tephras. On the right side chironimid zonation.

Diatoms were well preserved in the studied core. They were abundant in almost all the samples except in the intervals from 4 to 9 cm depth, where they were almost absent. A noticeable bottom-top decrease in diatom abundance was observed, ranging between 1.8 to 440 million of valves per gr of dry sediment. The diatom assemblage was composed of 47 genera and 121 infrageneric taxa. Despite the high number of species, only 11 taxa appeared with more than 3 % of relative abundance in any given sedimentary interval (Fig. 5). Only four taxa are strictly planktonic: *Aulacoseira distans* (Ehrenberg) Simonsen, *Discostella* spp *(D.stelligera* (Cleve & Grunow) Houk & Klee, *D. glomerata* (H.Bachmann) Houk & Klee), and *Urosolenia eriensis* (H.L.Smith)

Round & R.M.Crawford in Round, Crawford & Mann; and five taxa are periphytic: *Eunotia implicata* Nörpel Lange-Bertalot & Alles, *Achnanthidium* spp *(A.minutissimun* (Kützing) Czarnecki, *A.subatomoides* (Hustedt) Monnier, Lange-Bertalot & Ector), *Sellaphora pupula* (Kützing) Mereschkovsky, and *Gomphonema gracile* Ehrenberg. Due to the difficulties to recognize them under light microscope, several small sized fragilarioides taxa (*Staurosira construens* var. *venter* (Ehrenberg) Hamilton, *Staurosirella pinnata* (Ehrenberg) Williams & Round, *S*. *leptostauron* (Ehrenberg) Williams & Round, and an unidentified *Punctastriata* Williams & Round species) were counted together. Both *Discostella* spp and "fragilarioides" were grouped because they show similar trends along the studied core. Two planktonic *Fragilaria* spp (*F. bicapitata* A. Mayer and *F. capucina* Desmazières) were also found but they never reached 3% in relative abundance. *Aulacoseira granulata* (Ehrenberg) Simonsen is tychoplanktonic and *Tabellaria flocculosa* (Roth) Kützing, is commonly periphytic, but it can also be found living forming chains in the plankton (tychoplanktonic).The relative frequency of stricktly planktonic taxa decreases towards the upper part of the core. In particular, *Urosolenia eriensis*, with high abundance from the bottom of the core up to 7–8 cm deep, where decreases and remains in low proportions up with the top of the core. Simultaneously, the planktonic *U*. *eriensis* is replaced by the tychoplanktonic *Aulacoseira granulata* and the periphytic/tychoplanktonic *Tabellaria flocculosa* (Fig. 5).

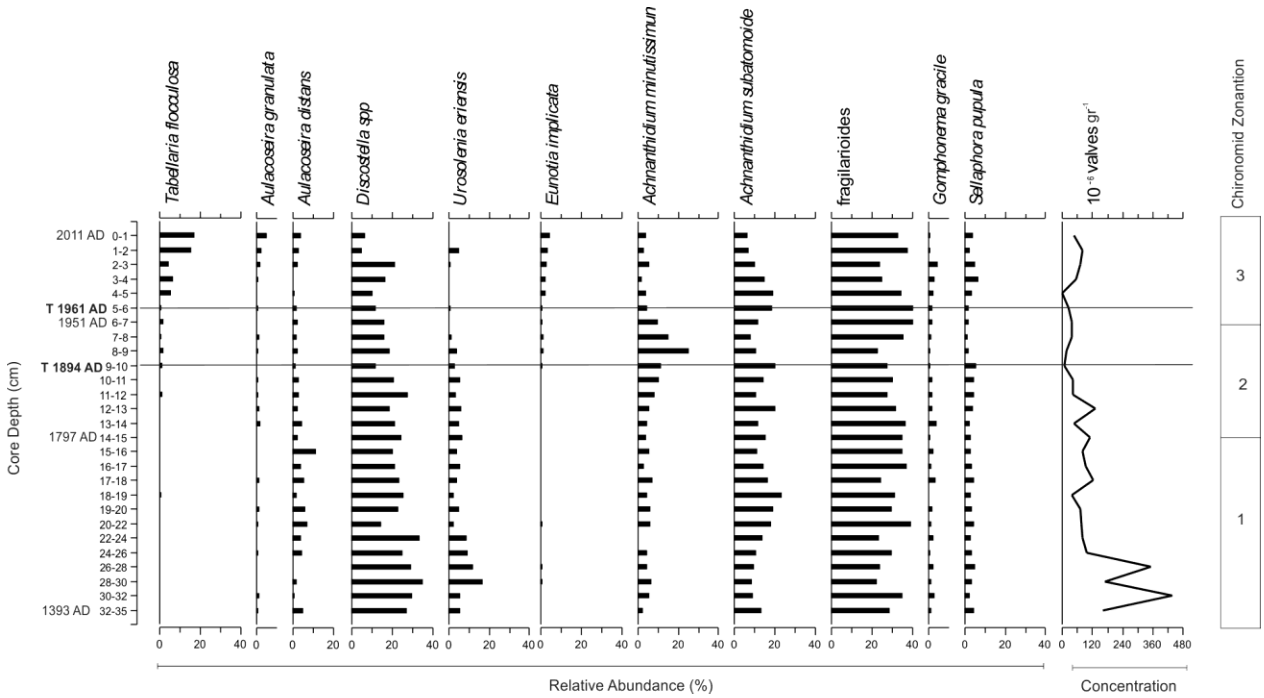

Fig. 5: Diatom abundances along the studied sequence. Only taxa with more than 3 % of relative abundances are shown. Plain lines indicated tephras. On the right side chironimid zonation.

Chironomids and diatoms have their minimum values of total number of individuals were associated to the tephra levels, at 4 and 8 cm, right after ashes deposition. However, chironomid abundances do not seem to decrease as diatoms do, which almost disappear after every tephra. Nevertheless, chironomids appear to have a faster recovery on their abundance, while diatoms show a gradual increase.

Photosynthetic pigments were present along the whole core and, as shown by the 430:410 ratio and the ever presence of chlorophyll *b*, its preservation was quite constant along the core (Fig. 6). CD, TC and single pigments have a similar trend showing peaks at 0–6, 6–10, 16–20 cm, and at 27 cm. Along the profile, the section at 8–10 cm appear to be particularly rich in carotenoids from diatoms (fucoxanthin, diatoxanthin), cryptophytes (alloxanthin), and cyanobacteria (cantaxanthin). In contrast, chlorophyll *a* and *b* remain constant.

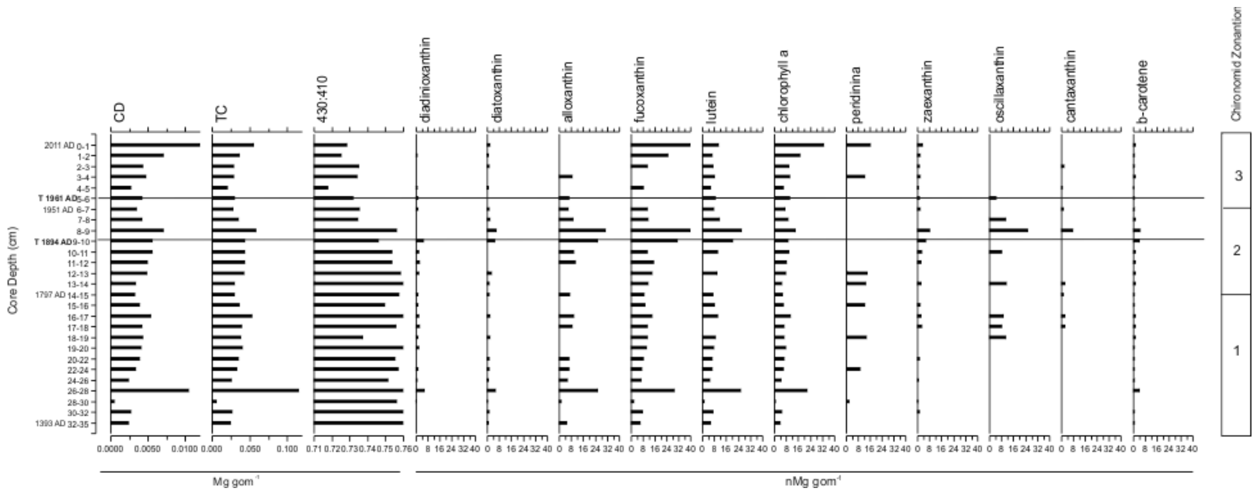

Fig. 6: Total and specific algal pigment isolated from the core Blest11. It also shows chlorophyll derivatives (CD), total carotenoids (TC) and the ratio 430nm:410nm. Plain lines indicated tephras. On the right side chironimid zonation.

Zonation

To facilitate the description of the bioproxies along the stratigraphical sequence, optimal partitioning and Broken Stick model were applied to identify significant zones along the biota composition. Based on chironomid composition, three significant zones were recognized, (Fig. 7). This results are also coincident to major changes in CD/TC, 430;410, MS and OM. The Broken Stick made with diatoms gives many and unreliable areas (e.g. areas of 1 cm). Pigments were not used for this analysis because many of them have a terrestrial origin and could bias the results (Fig. 7).

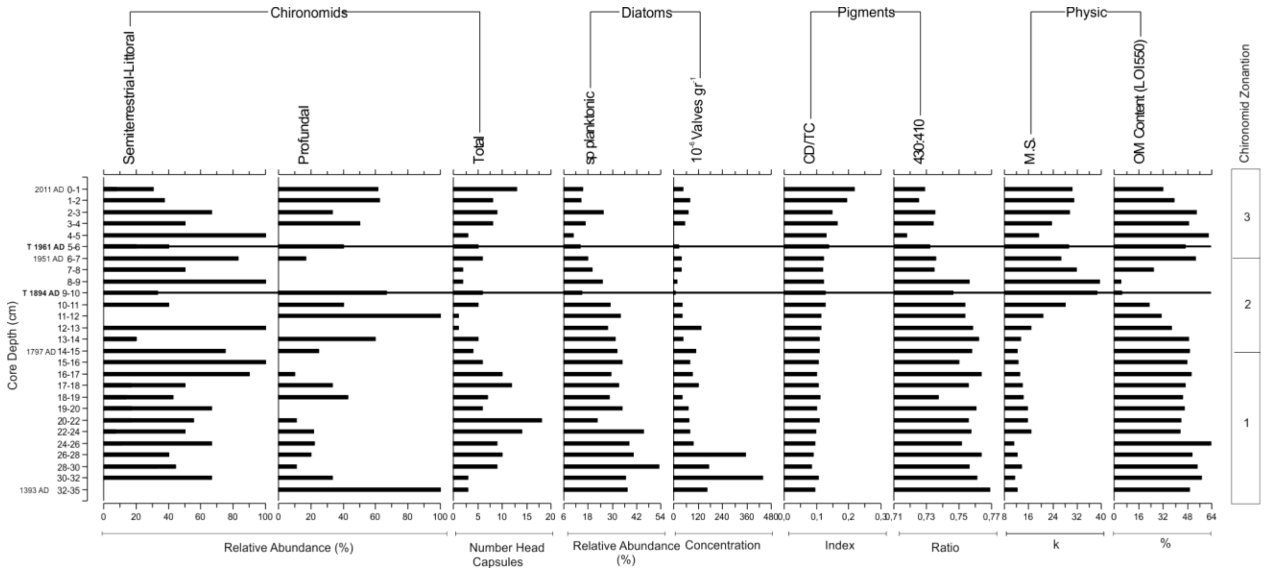

Fig. 7: Bioproxies, physicochemical characteristics, and environmental measures in the sediments. Chlorophyll Derivatives/Total Carotenoids Index (CD/TC); Photosynthetic pigments ratio (430:410); Magnetic Susceptibility (M.S.); Dimensionless proportionality constant (k); Loss On Ignition (LOI). Plain lines indicated tephra layer, whereas dotted lines indicates chironomid zonation. On the right side chironimid zonation.

Zone 1 (from the bottom of the core up to 14 cm; ca. 1393 to 1797 AD): the highest number of chironomids was recorded in this zone, with elevated percentages of semiterrestrial/littoral taxa (*Cricotopus*, *Limnophyes*, and *Polypedilum*). Diatom concentrations are high up to 26–28 cm and then decreases to the top of the zone. Planktonic species such as *Discostella* spp and *Urosolenia eriensis* have high relative abundances all along this zone, with a gradual decrease up to the top. Pigments such as alloxanthin, carotene, β-carotene, chlorophyll *a*, diatoxanthin, diadinoxanthin, fucoxanthin, and lutein, show a peak at 26–28 cm. Oscillaxanthin and cantaxanthin appear at 18–19 cm. CD/TC ratio has constant values, with a slight increase up to the top of the zone, with values ranging from 95.61 to 106.71. The 430:410 index presents constant values (between 0.737 nm and 0.768 nm) with a decrease and quickly recovery at 18 cm. MS show minimum values at 24 cm (11), with a slight increase at 22 cm (16.67). In addition, a high OM content is observed throughout the zone (Fig. 7).

Zone 2 (from 14 to 6 cm; ca. 1797 to 1951 AD): there is a general decrease in the total number of chironomid head capsules which are almost all profundal taxa with *Riethia* as the dominant taxa followed by *Limnophyes* and *Cricotopus*. In this zone it is possible to distinguish two subzones (Z2a and Z2b), due to a change in the number of chironomids, diatoms, MS, and OM. In Z2a (14 to 10 cm; 1797 to 1874 AD) there is high relative abundances to profundal chironomids taxa and diatoms, high values of 430:410 and OM content, and low values of MS (which increases to the top). Z2b (10 to 6 cm; 1874 to 1951 AD) show high relative abundances of semiterrestrial/littoral chironomid taxa and low planktonic diatoms, as well as lower values of 430:410 and OM content and higher values of MS. At 8–9 cm there are high relative abundances of *Eukieffierela* and *Cricotopus*. Diatom concentrations have their minimum values at 9–10 cm (tephra layer), with a markedly decrease of planktonic diatoms, while some periphytic taxa show their maximum abundances (Fig. 6). Planktonic species like *Discostella* spp decrease from the bottom to the top of the zone. While *Urosolenia eriensis* relative abundance continues decreasing up to 6–7 cm where virtually disappears, *Tabellaria floculosa* and *Eunotia imlicata* appear and have their lowest values along the core. Other periphytic species such as *Achnanthidium subatomoides* and *A. minutissimum* have peaks of high relative abundance. Fragilarioids relative abundance has a slight decrease up to 7–8 cm where starts increasing. Most of the pigments as well as CD/TC ratio show a peak at 8–9 cm; in contrast, concentrations of other pigments such as β-carotene and chlorophyll *a* as well as the 430:410 index drops at that level following the same decreasing pattern as diatom concentrations. The MS record shows a strong increase at 9–10 cm, accompanied by the consequent sharp decrease in OM content (Fig. 7).

Zone 3 (from 6 cm to the top; ca. 1951 to 2012 AD): there is a clear increase of total chironomids towards the top of the core with a turnover from semiterrestrial-littoral to profundal taxa at 3–4 cm. The dominant taxa within this zone are *Limnophyes* and *Riethia* followed by

Harrisius, *Cricotopus*, *Pseudosmittia*, and *Gymnomectrionemus*, as well as *Parochlus* and *Tanytarsini*. Diatoms keep on decreasing, having their lowest values at 4–5 cm, above the second tephra layer, after what it slight increase their values. *Discostella* spp have a peak at 2–3 cm and decrease to the top of the core, *Urosolenia eriensis* disappears and *Tabellaria floculosa* and *Eunotia imlicata* have their highest relative abundances. *Achnanthidium* spp decrease their relative abundance to the top of the core while the fragilarioid group keeps its high numbers. *Aulacoseira granulata* was present in very low relative abundance along the whole core, but on this zone it shows its highest relative abundance values (Fig. 6). MS shows a similar trend than the bioproxies, with lower values at the tephra at 5–6 cm than those recorded in the tephra layer at 9–10 cm, and its lowest values of the zone at 4–5 cm, followed by an increase up to the top. OM content increase to its average values (47.9 %) reaching values of 61.7 % at 4–5 cm. CD/TC ratio has a very marked increase from 6 cm deep to the top (from 122.73 to 218.60). Also chlorophyll *a* shows an increase at 2–3 cm. 430:410 index values range between 0.718 and 0.736, which are the lowest values along the core, showing a bottom-top decrease, as opposed to CD/TC ratio, which gradually increases from bottom to top and has its highest values in this zone (Fig. 7).

DISCUSSION

Multiproxy data from Brazo Blest show paleolimnological changes that track the history of the basin back to ca. 800 yrs BP.

Between 35 and 14 cm (Zone 1; ca. 1393–1797 AD) the high percentages of semiterrestrial-littoral chironomids taxa and planktonic diatoms, along with the high abundance of pigments from cryptophytes, could be associated to periods of strong precipitation and increasing runoff from the area. In fact, Brazo Blest is located marginal to the Valdivian rain forest, receiving an average annual precipitation of 3000 mm, deriving in continuous fluvial transport of sediments from the catchment area to the lake. The dominance of *Discostella* spp in this zone could indicate clear and calm waters. Michelutti *et. al* (2015) found that the presence of *D. stelligera* throughout the sediment core indicates lake stratification or, at least, that the lake stratifies long enough for this planktonic taxon to dominate the assemblage. At 18–19 cm (ca. 1720 AD) the appearance of myxoxanthin and oscillaxanthin, typical pigments of bluegreen algae, could indicate an increase of the lake trophic status, as bluegreen algae are strongly correlated to total algal biomass, with high values when there is high productivity of algal biomass (Canfield Jr. *et al*., 1989). In addition, high values of 430:410 index and low values of CD/TC indicate high pigment preservation and autochthonous organic matter production. Low values of MS also indicate low input of clastic sediments and organic matter from the catchment area.

Zone 2 (between 14 and 6 cm; 1797–1951 AD) is characterized by the decrease of total chironomids and diatoms, as well as the decrease of planktonic diatoms, LOI, and 430:410 ratio. Changes in the bioproxies, from semiterrestrial/litoral chironomd taxa to profundal taxa, a decrease of planktonic species and concentration of diatoms, decrease of 430:410 index and OM content, as well as an increase of MS, indicate high climatic variability during this interval, allowed to recognize two subzones (Z2a and Z2b). In the lower portion of this zone (Z2a, 14–10 cm, 1839–1855 AD), the significant decrease of semiterrestrial-littoral chironomids and planktonic diatoms, together with the presence of profundal chironomids and the increase of periphytic diatoms, indicate a drop in the precipitation. This agrees with Villalba (1990) who described a dry and warm interval from 1839 to 1899 AD that resulted in a retreat of the Frías Glacier, the northernmost tongue in the Argentina portion of Mount Tronador. Increasing proportion of mineral fractions (LOI depletion) is interpreted as the result of high input of glacial meltwaters to Brazo Blest carrying abundant suspended fine sediment load. At 9–10 cm high values of MS and low values of LOI indicate the presence of a tephra layer associated with the 1893–1894 AD Calbuco eruption. This tephra impacted the biotic community producing significant reduction of the number of chironomids and diatoms, due to the input of suspended sediment to the water column. In Z2b (10–6 cm, 1874–1951 AD), the increase of semiterrestrial-littoral chironomid taxa, with the presence of *Eukiefferiella* littoral chironomid genus, the decrease of profundal taxa, the peak of *A. minnutissimum*, with the presence of *Tabellaria flocculosa* and *Eunotia implicata* in low numbers, and a peak of lutein, dominant pigment in detritus of terrestrial origin (Frey, 1974), indicate an input of eroded soil material to the lake, associated with the increased in rainfall. This agrees with Villalba (1990) who reported a cold-moist interval between 1900 and 1910 that triggered the readvance of Frías Glacier. This condition increased the runoff of sediments from the Blest-Cántaros catchment area including an important amount of volcanic material. It is possible that by this time, diatoms were replaced by other algae, more tolerant to low light intensities (i.e. cyanobacteria, cryptophytes). During this period the tephra added a large amount of suspended sediments to the water column already turbid by the runoff of fine material from the catchment areas, reflected in an increment in sedimentation rates. Moreover, the decrease of chironomids and diatoms total number, particularly at 9–10 cm interval, was produced by large amounts of clastic material, diluting the concentrations of the bioproxies, and reducing of food availability and decreasing autochthonous OM production. High values of 430:410 index and low values of CD/TC ratio indicated a low degradation rate of pigments due to a low productivity of the system and autochthonous organic matter, which could be related with the high precipitation, water turbidity and low temperatures mentioned by Villalba (1990) (Fig. 8).

Zone 3 (6–0 cm) dated from ca.1951 to 2011 AD, shows changes on chironomid and diatom assemblages together with an increase of terrestrial pigments, β-carotene and lutein, suggesting an increase of organic-rich sediments transport into the lake. The presence of semiterrestrial/littoral taxa, such as *Limnophyes* and *Cricotopus*, simultaneously with a low number of diatom valves and the increase of *Aulacoseira granulata*, indicates the transport of sediments dragging sediment and semiterrestrial-littoral taxa with them. *Aulacoseira granulata* has been reported in rivers (O'Farrell *et al*., 2001), being typical of relatively warm and nutrient-rich water (Risberg *et al*., 1999), and it can tolerate low light conditions, which is also agreeing with the increase on the turbidity on the water column, originated by fluvial soil erosion (OM). By that time, water from the melting of Frías Glacier reached Brazo Blest through River Frías carrying heavy loads of fine suspended sediments (clay-silt) produced by glacial abrasion of the bedrock (Ariztegui *et al*., 2007). These suspended sediments produced a significant increase in turbidity of the water column limiting light penetration that causes a direct impact on planktonic diatom populations, decreasing their abundance. The turbidity in the water column was the trigger for the decrease of planktonic diatoms, which was clearly shown by the decrease of *Discotella* spp and *Urosolenia eriensis*. Light availability is broadly implicated in niche partitioning of phytoplankton, and the *Discostella* species are no exception to that. There is evidence that suggests that vertical distribution patterns of this group of species are partly a function of its physiological requirements for light and not simply size-based sinking losses (Saros and Anderson, 2014). Input of suspended sediments can also be confirmed by the presence of pigments related to low light intensities such as cryptophytes (alloxanthin) and cyanobacteria (oscillaxanthin), the increase of terrestrial pigments such as β-carotene and lutein, the presence of *Aulacoseira granulata*, and the decrease of planktonic species. Moreover, the increase of *Tabellaria flocculosa* could be related with higher temperatures, as observed by Michelutti *et al*. (2015). This interpretation is coincident with data from Masiokas *et al*. (2008) who reported an increase in temperature during the warm season (October–March; 0.056 °C per decade) and a decrease in precipitation during the cold season (April–September; 4.89 % per decade) in the last century (from 1912 to 2002 AD). This increase of temperature could be the cause of the melting of Frias Glacier. The low values of 430:410 index and high values of CD/TC ratio are related to the shift from autochthonous to allochthonous OM input. At 5–6 cm a sharp decrease in both chironomid and diatom abundances took place. This decrease is directly related to the 1961 AD volcanic eruption of Calbuco volcano and possibly to the 1960 eruption of Cordón Caulle, which probably caused habitat disruption for communities and deposited ash on the lake floor and adding suspended sediment to the water column. After this tephra the number of chironomids increases to the top, with high percentages of profundal taxa. Diatoms have a slight increase and remain constant. CD/TC reaches its highest values, contrary to 430:410 ratio that has its lowest values at the top of the core, supporting the allochthonous OM (Fig. 8).

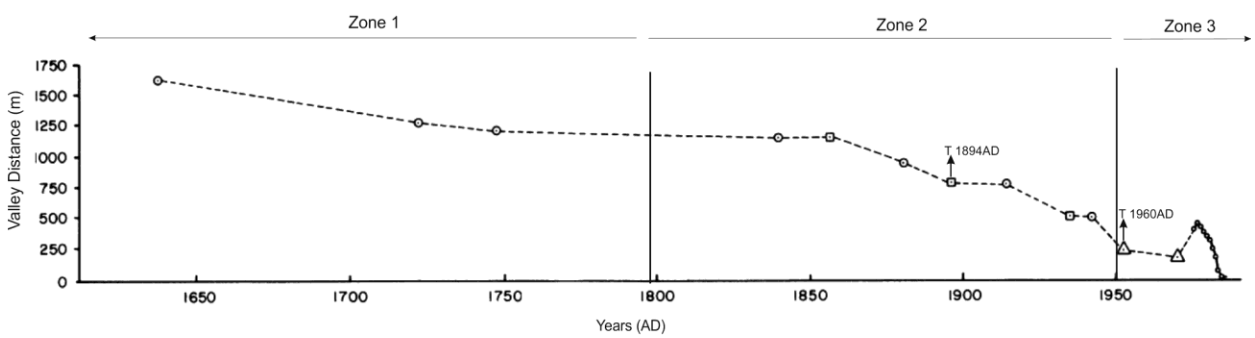

Fig. 8: Zonation for Brazo Blest based on chironomids and chronology of Frías Glacier fluctuations from Villalba (1990), which supported climatic variations. Circules: dated moraine; Square: historical record; Triangle: air photographs; Dark Circle: measured period; Vertical Lines: chironomid zonation with deep of the core in centimeters; Arrows: tephra layers (T1: Calbuco volcano1893 AD; T2: Caulle volcano 1960 AD).

CONCLUSIONS

This study provides evidence of environmental changes in Brazo Blest. Bioproxies indicates changes in the glacial catchment area from River Frías (input of glacial sediments), as well as of Blest-Cántaros catchment area (OM and mineral input). Volcanic eruptions impacted the biotic communities reducing light penetration, food availability, and decreasing abundances and diversity, producing a change in the trophic status of the lake.

Zone 1 represents the last portion of the Little Ice Age (LIA). Even though no clear shifts in the bioproxies related to temperature were detected, the high autochthonous OM content, together with the presence of semiterrestrial/littoral chironomids taxa from fluvial runoff, the planktonic diatoms indicating clear and calm waters, and the pigments from cryptophytes, are interpreted as indication of a wet period with low glacial sediment input in to lake due to low melting by cold climate. This interpretation matches the humid and cold conditions inferred for the LIA (Villalba, 1990; Masiokas *et al*., 2008). Zone 2 represents the transition between the environmental conditions from the end of the LIA to the modern-day climatic conditions, showing high variability in temperature and precipitation. The first half of this zone showed low precipitation and warm temperatures, resulting in the Frias Glacier melting; and the second half showed OM input and low productivity of the system. Zone 3 is similar to present climatic conditions, with higher temperatures and high transport of sediments from the catchment area with allocthonous OM content.

From zone 2 to 3, shifts from autochthonous to allochthonous OM are reflected in changes in the relative abundance and composition of bioproxies. Allochthonous OM is interpreted as the result of fluvial input of organic rich sediments derived from soil erosion during warm climate and rainy conditions, combined with a relative depletion of the glacial sediment load from River Frías, due to the already reduced dimensions of the glacier (Masiokas *et al*., 2008). Pigments also provided important information about past phytoplankton communities' changes, showing variations in the light penetration of the water column (turbidity) related with the suspended sediments.

Volcanic eruptions in the area affected the bioproxy communities, modifying the chironomid and diatom abundance and biodiversity, inflected by the abrupt input of ashes to the system, adding suspended sediment to the water column and covering the bottom of the lake. However, their impact is no long-term impact as evidenced by the rapid recovery of the bioproxies.

This work shows that multiproxy analysis from lakes sediments is an excellent tool to reconstruct historical climatic conditions, record environmental events and acquire information about the dynamic and functioning of aquatic ecosystems in order to understand future environmental scenarios.

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