UNIVERSIDADE DA CORUÑA

Facultade de Ciencias
Departamento de Ciencias da Navegación e da Terra
Área de Paleobioloxía

Paleoprodutividade inferida por diatomeas en lagos volcánicos das illas Azores durante o Holoceno tardío

Paleoproductividad inferida por diatomeas en lagos volcánicos de las islas Azores durante el Holoceno tardío

Diatom-inferred palaeoproductivity in volcanic lakes from the Azores islands during the late Holocene

Sandra López Romero
Traballo de fin de grao
Data de defensa: 21 de Setembro de 2015

Dirixido polo Dr. Roberto Bao Casal e o Dr. Armand Hernández Hernández

INDEX

Abstract

In this dissertation the paleoproductivity trajectories and organic matter provenance over the last 640 and 800 yr of two volcanic lakes from the Sâo Miguel Island in the Azorean archipelago (Lake Azul, 37° 52' N – 25° 46' W and Lake Santiago 37º 50' N, 25º 46' W) are inferred from the study of diatom accumulation rates in core sediments (DARs), as well as their total organic carbon (TOC) and total nitrogen content (TN). Three paleoproductivity stages could be distinguished in Lake Azul. Stage 1 (c. 1230-1810 cal yr AD), which establishes the onset of the lake after the last volcanic explosive eruption occurred, was characterized by the low productivity conditions characteristic of a lake in the early phases of its ontogeny. An increase in productivity was recorded during Stage 2 (c. 1810-1960 cal yr AD) associated to the rise and decline in green algae and diatoms, respectively, as primary producers, that suggest the prevalence of stratified water column conditions. The recorded increase in productivity is coetaneous with the artificial introduction of non-native planktivorous fishes in the lake, and suggests, according to the Alternative Stable State Theory of Shallow Lakes, that a change from a clear to a turbid state could have taken place. The most recent history of the lake, recorded by Stage 3 (c. 1960-2011 cal yr AD), shows an increase in planktonic productivity coincident with the start of the use of fertilizers and a shift to a more turbulent water column regime, as indicated by the rises and declines of diatoms and green algae, respectively. Compared to Lake Azul, DAR data and TOC content revealed that Lake Santiago was over the entire studied period more eutrophic, and three major productivity stages could also be distinguished in this lake. Stage 1 (c. 1380-1680 cal yr AD) was characterized by a shifting dominance of planktonic vs. benthic productivity and/or origin of organic matter before and after c. 1470 cal yr AD, respectively. During Stage 2 (c. 1680-1985 cal yr AD) productivity shows a net increase until c. 1860 cal yr AD, declining thereafter. These contrasting trends are interpreted as being the product of the intensified delivery of nutrients associated to the deforestation of the basin by the Portuguese colonizers before c. 1860 cal yr AD and, conversely, to the intense afforestation with *Cryptomeria japponica* D. Don that took place after c. 1860 cal yr AD, reducing allochthnous nutrient inputs to the lake. The last decades represented by Stage 3 (c. 1985-2011 cal yr AD) are characterized by a reduction in diatom productivity, and a significant shift from the dominance of centric to pennate planktonic diatoms that could be attributed to the addition of nutrients and/or global warming. Because of the large impact produced by anthropogenic disturbances these lakes are not good candidates to test whether increased primary productivity is the result of natural lake development over time as the classical limnological theory states.

Resumen

En este estudio se infiere la trayectoria de la paleoproductividad y el origen de la materia orgánica durante los últimos 640 y 800 años de dos lagos volcánicos de la Ilha de São Miguel en el archipiélago de las Azores (Lago Azul 37° 52' N – 25° 46' W y Lago de Santiago 37º 50' N, 25º 46' W) a través del estudio de las tasas de acumulación de diatomeas (DARs), así como del carbono orgánico total (TOC) y el contenido total de nitrógeno (TN) en sus sedimentos. En el Lago Azul se han podido distinguir tres grandes estadios en relación a su paleoproductividad. El Estadio 1 (c. 1230-1810 cal AD), que coincide con el inicio de formación del lago, se caracteriza por una baja productividad típica de un lago en las fases tempranas de su ontogenia tras su origen después de la última erupción volcánica explosiva que tuvo lugar. Durante el Estadio 2 (c. 1810-1960 cal AD) se registra un aumento de la productividad parejo al incremento y declive de algas verdes y diatomeas como productores primarios, respectivamente, que sugiere una mayor estratificación de la columna de agua. Este aumento es coetáneo a la introducción artificial de peces planctívoros foráneos en el lago y sugiere, de acuerdo a la teoría de Estados Estables Alternativos de los Lagos Someros, que se pudo haber producido un cambio de un estado turbio a uno claro. La historia más reciente del lago, registrada en el Estadio 3 (c. 1960-2011 cal AD), muestra un incremento en la productividad achacable a organismos planctónicos que coincide con el comienzo del uso de fertilizantes y un cambio de la columna de agua a un régimen más turbulento, tal y como reflejan el aumento y declive de las diatomeas y algas verdes, respectivamente. En comparación con el Lago Azul, los datos obtenidos a partir del estudio de DARs y TOC muestran que el Lago de Santiago ha sido más eutrófico durante el período de tiempo estudiado pudiendo distinguirse también tres estadios relacionados con su productividad. El Estadio 1 (c. 1380-1680 cal AD) se

caracteriza por un cambio en la dominancia de la productividad planctónica a bentónica y/o del origen de la materia orgánica antes y después de c. 1470 cal AD, respectivamente. Durante el Estadio 2 (c. 1680 – 1985 cal AD), la productividad muestra un incremento neto hasta c. 1860 cal AD, decayendo después. Estas tendencias contrapuestas se interpretan como el producto de una intensificación en la entrada de nutrientes asociada a la deforestación de la cuenca debido a la colonización portuguesa antes de c. 1860 año AD cal y, recíprocamente, a la intensa repoblación con *Cryptomeria japponica* D. Don que tuvo lugar después de c. 1860 cal AD, que redujo la incorporación de nutrientes al lago. Las últimas décadas, representadas por el Estadio 3 (c. 1985-2011 cal AD) se caracterizan por la reducción de la productividad achacable a diatomeas y un cambio significativo de la dominancia de diatomeas planctónicas centrales a pennales atribuible a la adición de nutrientes y/o al calentamiento global. Debido al gran impacto antropogénico ocasionado, estos lagos no resultan buenos candidatos para comprobar si el incremento de la productividad primaria es el resultado del desarrollo natural del lago a lo largo del tiempo, como se describe en la teoría limnológica clásica.

Resumo

Neste estudo se infire a traxectoria da paleoprodutividade e a orixe da materia orgánica durante os últimos 640 e 800 anos de dous lagos volcánicos da Illa de São Miguel no arquipélago das Azores, (Lago Azul 37° 52' N – 25° 46' W e Lago Santiago 37º 50' N, 25º 46' W) a través do estudo das tasas de acumulación de diatomeas (DARs), así como do carbono orgánico total (TOC) e o contido total de nitróxeno (TN) no sedimento. No Lago Azul poideron distinguirse tres grandes estadíos na súa paleoprodutividade. O estadio 1 (c. 1230-1810 cal AD), que coincide co inicio da formación do lago, caracterízase por unha baixa produtividade típica dun lago nas fases tempranas da súa ontoxenia tra-la súa orixe despois da última erupción volcánica explosiva que tivo lugar. Durante o Estadio 2 (c. 1810-1960 cal AD) rexístrase un aumento da produtividade parello ó incremento e declive de algas verdes e diatomeas como produtores primarios, respectivamente, que suxire unha maior estratificación da columna de auga. Este aumento é coetáneo á introducción artificial de peixes planctívoros foráneos no lago e suxire, de acordo á teoría de Estados Estables Alternativos dos Lagos Someros, que se puido ter producido un cambio dun estado turbio a un claro. A historia máis recente do lago, rexistrada no Estadio 3 (c. 1960-2011 cal AD), mostra un incremento na produtividade achacable a organismos planctónicos que coincide co comezo do uso de fertilizantes e un cambio da columna de auga a un réxime máis turbulento, tal e como reflexan o aumento e declive das diatomeas e algas verdes, respectivamente. En comparación co Lago Azul, os datos obtidos a partir do estudo de DARs e TOC mostran que o Lago Santiago foi máis eutrófico durante o período de tempo estudado poidendo distinguirse tamén tres estadíos relacionados ca súa produtividade. O Estadio 1 (c. 1380-1680 cal AD) caracterízase por un cambio na dominancia da produtividade planctónica a bentónica e/ou da orixe da materia orgánica antes e despois de c. 1470 cal AD, respectivamente. Durante o Estadio 2 (c. 1680 – 1985 cal AD), a produtividade mostra un incremento neto até c. 1860 cal AD, decaendo despois. Estas tendencias contrapostas interprétanse como o produto dunha intensificación na entrada de nutrientes asociada á deforestación da cunca debido á colonización portuguesa antes de c. 1860 año AD cal e, recíprocamente, á intensa repoboación con *Cryptomeria japponica* D. Don que tivo lugar despois de c. 1860 cal AD, que reduciu a incorporación de nutrientes ó lago. As últimas décadas, representadas polo Estadio 3 (c. 1985-2011 cal AD) caracterízanse pola redución da produtividade achacable a diatomeas e un cambio significativo da dominancia de diatomeas planctónicas centrais a pennales atribuible á adición de nutrientes e/ou ó quencemento global. Debido ó grande impacto antropoxénico ocasionado, estos lagos non resultan bos candidatos para comprobar se o incremento da produtividade primaria é o resultado do desenvolvemento natural do lago ó longo do tempo, como se describe na teoría limnolóxica clásica.

1. Introduction

Primary productivity is at the base of the production that takes place in aquatic ecosystems. It can be defined as the yield of new photosynthesizer's growth during a specified time period (Margalef, 1983). According to this definition, a clear distinction should be made between productivity and production. Whereas productivity is a time dependent process (it is a rate with dimensions of mass per unit area/volume per time), production is a quantity, with dimensions of mass (Dokulil & Kaiblinger, 2009).

Primary productivity is affected by multiple factors such as turbulence, circulation and nutritional conditions, vertical organization in the water column transparency and depth of eutrophic zone, amount of solar energy reaching the substratum, and redox conditions (O'Sullivan & Reynolds, 2004). According to classical limnological theory (Deevey, 1955; Hutchinson, 1973), natural lake development involves an enrichment in nutrients, leading to increased primary productivity. Although this is still the prevailing view among many limnologists, Quaternary paleoecologists have provided evidence that many temperate-region lakes follow the opposite trend and become more dilute and unproductive over time (e.g. Engstrom *et al.*, 2000). This is because natural development of lakes is influenced by several environmental factors, acting and interacting within lakes and catchments. Besides this, lakes in densely populated areas may receive high amounts of anthropogenic nutrients, making them susceptible to consequent changes in nutrient concentration and primary productivity. Depending on which factors, natural and anthropogenic, have the determining influence, lakes may develop in different productivity and trophic state trajectories (Digerfeldt & Håkansson, 1993). However, studies of lake palaeoproductivity are scarce, in spite that the knowledge of past primary productivity is important for understanding lacustrine biogeochemical cycles (Ishiwatari *et al.*, 2009)

Sediments provide the most complete, continuous and reliable record of past environmental change in lacustrine systems (Smol, 2008). Analyzing sediments with different environmental proxy data allow to reconstruct changes in paleoproductivity. Among these, total organic carbon (TOC) and total nitrogen (TN), as well as diatom accumulation rates (DARs) have been widely used for this purpose (Battarbee *et al.*, 2001; Meyers & Teranes, 2001).

TOC represents the fraction of organic matter that escaped remineralization during sedimentation, and it integrates the different origins of organic matter, delivery routes, depositional processes and amount of preservation (Meyers & Tenares, 2001, Meyers, 2003). TN in the sediments is usually used to derive TOC/TN ratios which are a useful tool for distinguishing long-term transitions between terrestrial to algal-input derived organic matter (Meyers & Lallier-Vergès, 1999; Meyers & Teranes, 2001; Meyers, 2003).

Diatoms are unicellular and eukaryotic photosynthezisers that make up an important part of the phytoplankton and periphyton. They probably contribute more to primary productivity than any other photoautotrophic group (Theriot, 2001) and can therefore be used for the reconstruction of paleoproductivity in both oceans and lake systems when they are preserved in the sediments. Inferring past changes in diatom productivity and lake trophic status from sediment diatom assemblages has however been undertaken using a variety of methods (Battarbee *et al.*, 2001). Some of these approaches rely on the use of transfer functions (Birks *et al.*, 2012) or indicator species (Hall & Smol, 2010). However, only local transfer functions should be used when inferring paleoenvironmental variables for a region (Birks *et al.*, 2012), and the use of indicator species is usually restricted to the few diatom taxa for which autoecologies are well known. Alternatively, DARs can be used to indicate changes in lake productivity (Anderson, 1990). Given the diatom concentration (valves g^{-1}), sedimentation rate (cm yr^{-1}), and sediment density (g cm^{-3}), DARs (valves cm^{-2} yr^{-1}) can be easily calculated (Battarbee *et al.*, 2001). This measurement is a rate with dimensions of mass per unit area per time, as those used in productivity estimates (see above) and, thus, reflects the flux of diatoms to the sediments in a given time.

In this dissertation TOC, TN and DARs data are used to infer the main changes in past productivity conditions in two volcanic lakes from the Azores Archipelago, Lakes Azul and Santiago, over the approximately past 785 and 640 yr, respectively, and interpret the most likely causes driving those changes.

2. Objectives

1. To reconstruct the major changes in TOC, TN and DARs in lakes Azul and Santiago
2. To interpret the main causes explaining the observed trajectories in paleoproductivity in both lakes
3. To compare the results obtained in an anthropogenic highly impacted lake (Azul) with a less disturbed one (Santiago)

3. Study site

3.1 Geographical and geological setting

3.1.1. Azores archipelago. São Miguel Island

The Azores archipelago (Portugal, 36° 55' - 39° 45' N and 25° 00' - 31° 15' W) consists of a group of islands and several islets located in the Atlantic Ocean. According to their dispersion, three groups are distinguished: the Eastern group, formed by the São Miguel and Santa María islands; the Central group, consisting of the islands of Terceira, Graciosa, São Jorge, Pico and Faial; and the Western group, formed by the Flores and Corvo islands (Fig. 1).

This archipelago is located in the contact of the Eurasian, North American and African tectonic plates. The islands have a volcanic origin related to the great seismic and volcanic activity of the area. The morphology of each of the islands is mainly related to the type of volcanic eruptions from they were originated (Constância *et al.*, 2001).

São Miguel island (37° 30' - 38° 00' N and 25° 35' - 26° 00' W), is the largest island within the Azores Archipelago (Fig. 1). It covers about 747 km^2, and Pico da Vara (1,103 m), Pico da Barrosa (947 m), and Pico das Éguas (873 m) are its highest elevations. The island presents a general East-West orientation with three volcanic strata formed by the subsidence calderas of Furnas, Fogo, and Sete Cidades, considered the most important active volcanos of the archipelago.

The lakes in São Miguel cover about 8.2 km^2. Approximately 58% of the water masses are located in Caldeira de Sete Cidades and Serra Devassa. According to its 45 km^2 of surface, the greatest lake in the island is Sete Cidades, which includes two water masses, Lake Azul and Lake Verde. (Constância *et al.*, 2001). Close to this lacustrine system is Lake Santiago.

Figure 1: Location map of São Miguel Island (Azores archipelago) showing Lake Azul and Lake Santiago

3.1.2 Lake Azul

Lake Azul (Figs. 1 and 2A) is a monomictic lake located in the municipality of Ponta Delgada, in the district of Sete Cidades, 259 m above the sea level. More than 70 water courses flow into Lake Azul, which occupies the crater of a still active volcano. It has a maximum length of 4,225 m and a maximum width of 2,030 m, covering an area of 4.35 km^2. It contains about 3.98 x 10^7 m^3 of water, showing maximum and average depths of 33 m and 11 m, respectively. The residence time was established in 2.02 yr (Gonçalves, 2008). Temperature and pH show average values of 17.1ºC and 8.2, respectively.

3.1.3 Lake Santiago

Lake Santiago (Fig. 1 and 2B) is also a monomictic lake from the municipality of Ponta Delgada, in the district of Sete Cidades, that occupies an elongated crater in a North – South direction 355 m above the sea level. It contains 3.38 x 10^6 m^3 of water in a maximum length of 700 m and a maximum width of 475 m. Residence time was estimated in 2.30 yr (Gonçalves, 2008). The lake covers an area of 0.24 km^2 showing an average depth of 13.3 m, and maximum of 29 m. Average values for temperature and pH are 15.2°C and 7.5, respectively. In the last years some volcanic eruptions have taken place, causing the dispersion of the materials throughout the Sete Cidades district.

3.2 Climate

The Azores archipelago is characterized by a temperate oceanic weather and mild temperatures. The mean temperature of Ponta Delgada is around 17ºC, with strong winds and cloudy skies. The Azores archipelago is usually under the direct influence of the semi-permanent, high-pressure Azores Anticyclone. During most of the year (September to March), if this high-pressure center is dissipated or displaced, the Azores region is frequently crossed by the North Atlantic storm-track, the main path of rain-producing weather systems. Conversely, during late spring and summer, the Azores climate is mainly dominated by the Azores anticyclone (Agostinho, 1948; Santos *et al.* 2004; Azevedo, 2006). Thus, the precipitation record from Ponta Delgada displays a strong seasonal cycle and large inter-annual variability (Marques *et al.*, 2008). The precipitation increases with the altitude, being around 958 mm yr^{-1} near the coast and around 2,500 mm yr^{-1} over 600 m above the sea level (Constância *et al.*, 2001).

4. Materials and methods

4.1 Core sampling

In September, 2011, one sediment core from Lake Azul (core AZ11-02, 96 cm long; 25 m depth), and 2 sediment cores from Lake Santiago (cores SA11-02A and B, up to 136 cm long; 32 m depth) were recovered with an UWITEC$^®$ piston corer installed in a platform raft, for the case of Lake Azul (Fig. 2C), and from a boat for the case of Lake Santiago. Cores were split longitudinally, described according to the composition of their sediments, and imaged using an AVAATECH XRF II core scanner at the Department of Stratigraphy, Paleontology and Marine Geosciences of the University of Barcelona (Sáez, pers. comm). For the case of Lake Santiago a composite core recording the maximum sedimentary infill (144 cm) of the offshore zone was constructed from the detailed description and correlation of the two obtained cores. From here on, all core depths are referred to this composite core (core SA11-02). Samples from core AZ11-02 were taken every 1 cm between the top of the core and 32 cm depth, every 2 cm from 32 to 62 cm depth, and every 4 cm from 62 cm to the bottom of the core. Samples from core SA11-02 were taken every 2 cm between the top of the core and 62 cm depth and every 4 cm from 62 cm to the bottom of the core.

Figure 2: A) Lake Azul, B) Lake Santiago, C) UWITEC platform at Lake Azul during the 2011 coring campaign

4.2 Chronology

The preliminary chronological model for Lake Azul is based on 5 accelerator mass spectrometry (AMS) ^{14}C datings (Björck & Wohlfarth, 2001) (Table 1) performed on terrestrial plant macroremains and pollen concentrates at the Poznan Radiocabon Laboratory (Poland) and BETA Analytic Inc. (USA). The chronological model for Lake Santiago was constructed from ^{210}Pb and ^{137}Cs analyses (Appleby, 2001) performed at the Environmental Radioactivity Laboratory from the Institute of Environmental Science and Technology (Universitat Autònoma de Barcelona, Spain) (Giralt, pers. comm), as well as from 9 AMS ^{14}C datings performed at the Poznan Radiocabon Laboratory (Poland) and BETA Analytic Inc. (USA) (Table 1). Obtained radiocarbon dates were calibrated with the 2IntCal09 data set (Reimer *et al*., 2009) implemented in the CALIB 7.1 software package. From all radioisotope ages, an age-depth model was constructed by simple linear interpolation for Lake Azul, whereas the software described in Heegaard *et al*. (2005) was employed to construct a reliable age-depth model for Lake Santiago, furnishing a final corrected age for each calibrated date, assuming the year of sampling (2011 AD) for the core top age (Giralt, pers. comm.). All post-bomb ^{14}C dates (Björck & Wohlfarth, 2001) from Lake Santiago, which are incongruent with the ^{210}Pb dates, and a reversal ^{14}C date from Lake Azul were disregarded for the construction of the age models.

4.3 Diatom samples preparation

Samples for diatom analyses were processed using standard techniques (Renberg, 1990). Measured aliquots of the cleaned subsamples were dried onto coverslips and mounted with Naphrax® high refractive medium (R. I. = 1.74). Between 300 - 550 valves were counted per sampled interval. All counts were made at X1000 under oil immersion with a Nikon Eclipse 600 microscope with Nomarski differential interference contrast optics.

Absolute diatom abundances (valves g^{-1} dry sediment) were estimated using *Lycopodium* spores

Laboratory code	Sample	Depth (cm)	Conventional AMS ^{14}C age	Calibrated Age (2S cal yr AD)	Calibrated Age AD (median probability)
Poz-67992	SA11/02B-26	29	108.2±0.3 pMC	1995.6 - 1998.1	---
Poz-67987	SA11/02A-46	52	128.8±0.4 pMC	1993.0 - 1995.1	---
Beta-331414	SA11/02B-50	53	114.7±0.4 pMC	1995.5 - 1996.9	---
Poz-67988	SA11/02A-53	59	129.9±0.4 pMC	1992.9 - 1995.1	---
Poz-67989	SA11/02A-73	79	350 ± 30 BP	1537 - 1635	1554
Poz-67991	SA11/02A-97	103	325 ± 30 BP	1481 - 1644	1561
Beta-331415	SA11/02B-103	111	330 ± 30 BP	1478 - 1642	1561
Beta-321655	SA11/02B-124	132	590 ± 30 BP	1299 - 1370	1346
Poz-67994	SA11/02B-130	138	415 ± 30 BP	1429 - 1518	1463
Beta-316594	AZ11/02- 5.5	5.5	154.4±0.4 pMC	1989.8-1992.0	1991
Beta-316595	AZ11/02- 46	46	200 ±30 BP	1770±40	---
Beta-331408	AZ11/02- 61	61	410±30 BP	1475±45	---
Beta-331409	AZ11/02- 86	86	690±30 BP	1290±20	---
Beta-316596	AZ11/02- 114	114	380±30 BP	1610±30	---

^{210}Pb dates: It is possible to establish a constant sedimentation rate with a CF:CS model (Appleby, 2001) for the uppermost 25 cm (60 years; 0.42± 0.02 cm/yr).

Table 1: Radiocarbon and calibrated calendar ages for cores AZ11-02 and SA11-02. Shaded lines correspond to data not included in the construction of age models (see text)

following the procedure described in Kaland & Stabell (1981) to avoid the effects of non-random distribution of diatoms over the cover slides (Battarbee & Kneen, 1982). Diatom accumulation rates (DAR; valves cm^{-2} yr^{-1}) were calculated multiplying the obtained absolute diatom abundances (valves g^{-1}), by the dry bulk density of the sediment (g cm^{-3}), and the sedimentation rates (cm yr^{-1}) estimated on the basis of the chronological models. No attempt was made to identify diatoms to the species or genus level, so results reflect total diatom fluxes to the sediments.

4.4 Geochemical analyses

Powdered sediment samples were treated with diluted (1:4) HCl to eiliminate minor amounts of carbonates, and total organic carbon (TOC), and total nitrogen (TN) measured directly with a Carlo Erba 1108 elemental analyser in the Centres Científic i Tecnològics from the University of Barcelona. TOC/TN data are expressed in the form of atomic ratios (Meyers & Teranes, 2001).

5. Results

5.1 Facies description and main lithological units

5.1.1 Lake Azul sedimentary facies

Four sedimentary facies could be distinguished in the sedimentary record of this lake (Fig. 3A):

Facies A (deep plain silt massive deposits). This facies is composed by brown massive sandy fine-medium silt 2 to 5 cm in thickness. The mineralogical composition is dominated by quartz, with sanidine, plagioclases and anfibol grains (derived from felsic volcanic rocks) as secondary minerals, and residual quantities of zeolite, illite, smectite and chlorite (clay minerals produced by the alteration of mafic rocks). Diatoms are abundant and dominated by euplanktonic (*Aulacoseira* spp. forming colonies) and tychoplanktonic genera (*Tabellaria* spp. and *Fragilaria* s. l.). Organic matter is present in a scattered amorphous form with very low composition of pythoclasts. Facies A prevails in the upper part of the lake sequence. This facies would be interpreted as deposited by decantation of fine suspended sediments transported by runoff generated during regular precipitation in the lake area.

Facies B (deep plain, greenish deposits). Facies B is made up by brown greenish laminated fine to coarse silts deposited in layers 2 to 7 cm-thick. They contain a higher content of periphytic diatoms (*Fragilaria* s. l., *Navicula* s. l. and *Nitzschia* spp.) than facies A and show dark golden rod

- green phytoclasts. This facies is recorded in the middle of the sequence in offshore zones. It represents the decantation of the fine sediments transported by suspension in a way similar to those generating deposits of facies A. By contrast, Facies B was created during regular precipitations in the lake area without the intense anthropogenic activity that characterize the facies A deposits.

Facies C (Dark plant-rich deep plain flood event deposits). Facies C corresponds to dark brown fine sand and silty deposits recorded as layers ranging 0.2 to 4 cm in thickness. This facies shows very few diatoms and a high concentration in macro and micro terrestrial plant remains, including charcoal particles. Smear slides showed a high content of micro phytoclasts in this facies (transparent tissues and opaque particles). Facies C corresponds to lobe bodies deposited in the offshore zone of the lake. The lobes were likely deposited from flood events that occurred during major precipitation episodes and/or a more regular precipitation regime that removed sediments enriched in terrestrial vegetation remains. The deposition likely occurred due to increased human activity in the catchment (i.e. cropping, deforestation, and fires).

Facies V (basal volcanic deposits). The sedimentary record lays on a volcanic substratum composed by grey to light-brown tephra. These materials correspond to explosive eruptions that emitted big amounts of lapilli and piroclastic material.

These volcanic, lacustrine and alluvial facies have a stratigraphic distribution that allowed to define 3 lithological units. Unit 1 (133 – 89 cm) is composed by Facies V and corresponds to volcaniclastic deposits including some lacustrine sediments which were deposited during short volcanic episodes in a transition from a high volcanic activity period to a continuous lacustrine sedimentation. Unit 2 (89 - 57 cm) has a thickness of around 32 cm and is mainly dominated by facies B, and in lesser extent by facies C. Unit 3 (57 - 0 cm) is dominated by facies A interbedding layers of facies C.

5.1.2 Lake Santiago sedimentary facies

Lake Santiago sedimentary record is made up by a single lithological unit (Unit 1). This unit is composed by four sedimentary facies (Fig. 3B):

Facies A (Deep plain diatom oozes). It is made up by green and yellow-banded organic rich muds. Bands show variable thicknesses ranging mm to cm. Diatoms are very abundant, with *Aulacoseira granulata* (Ehrenberg) as the main taxon. Organic matter is less abundant than diatom skeletons and it shows a low content of phytoclasts. Facies A is prevalent across the whole sedimentary sequence, indicating a deep and stable lacustrine depositional environment.

Facies B (Deep plain orange mud). It is composed by orange bands of organic-rich mud. Facies B has the same composition of Facies A, but shows different color. Color differences could be attributed to changes in organic matter composition. Depositional conditions can be considered the same that produced Facies A.

Facies C (Dark-brown deep plain flood event deposits). Facies C corresponds to dark brown silty and sandy deposits present as layers ranging 0.5 to 5 cm in thickness. This facies has few diatoms and shows a high concentration in terrestrial macro- and micro-plant remains, including charcoal particles. Facies C corresponds to lobe bodies deposited in the offshore zone of the lake. The lobes were likely originated from flood events that occurred during major precipitation episodes and/or regular precipitations that removed sediments enriched in terrestrial vegetation after increased human activity in the catchment area (i.e. cropping, deforestation, and fires).

Facies V (Grey laminated tephra). This facies corresponds to bands of grey to light-brown tephras 1 to 10 cm thick. These materials correspond to eruptions that emitted lapilli material.
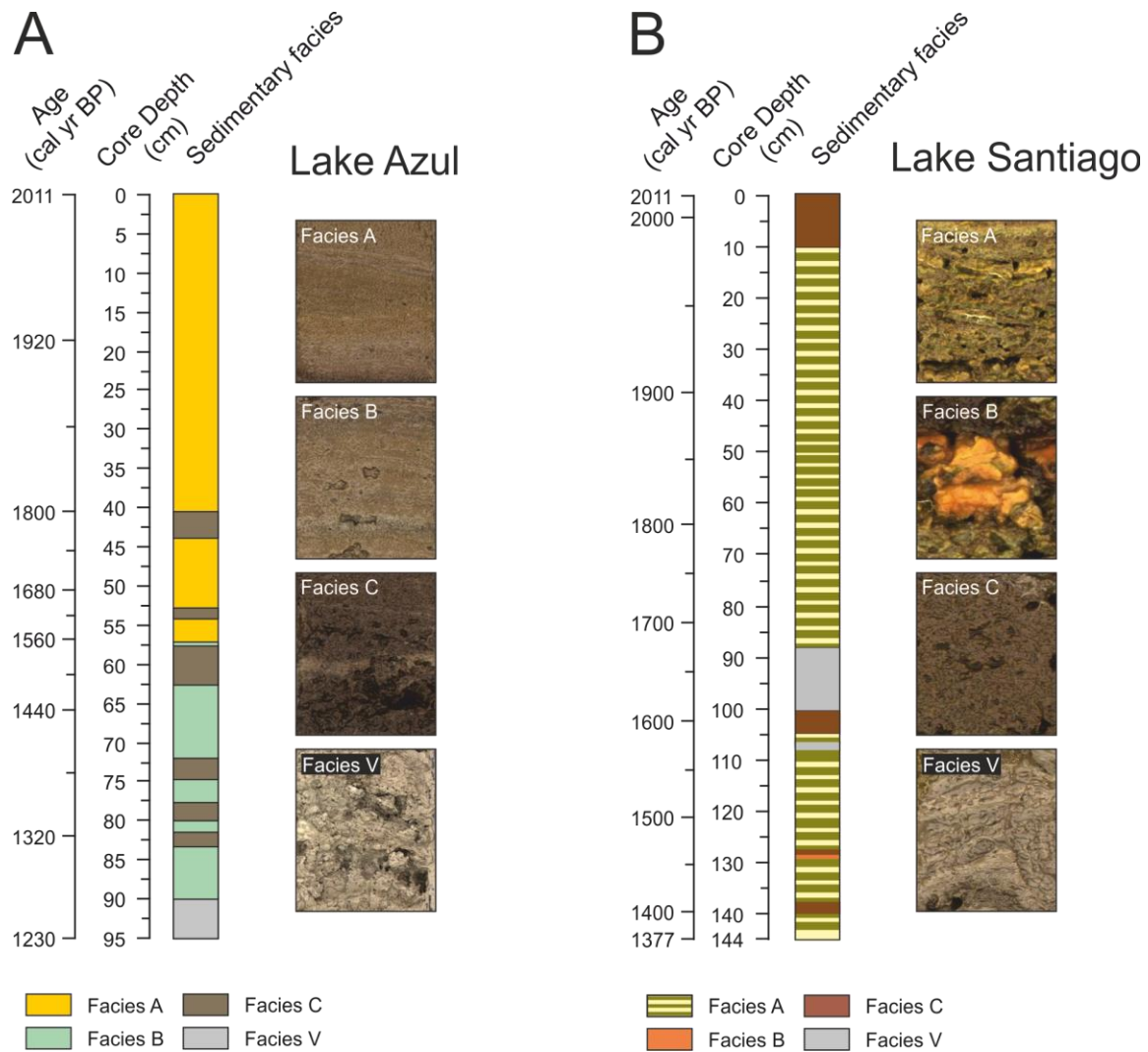
Figure 3: Sedimentary facies making up the lithological units of A) core AZ11-02 and B) core SA11-02

5.2 Chronological framework. Sedimentation rates

The age-depth models show that the studied sedimentary records of lakes Azul and Santiago spanned the last 780 and 638 yr, respectively (Table 1).

Plotting ages derived from the chronological models versus core depths gives different estimates of sedimentation rates (Fig. 4). According to its age model, sedimentation rates in Lake Azul range from 0.51 mm yr^{-1} between c. 1475 and c. 1770 cal yr AD and 2.75 mm yr^{-1} between 1989 and 2011 cal yr AD (Fig. 5). By contrast, Lake Santiago shows sedimentation rate values ranging from 1.84 mm yr^{-1} between 1377 and 1593 cal yr AD and 3.96 mm yr^{-1} between 1955 and 2011 cal yr AD (Fig. 6). Both lakes show a sharp increase in sedimentation rates in recent times.
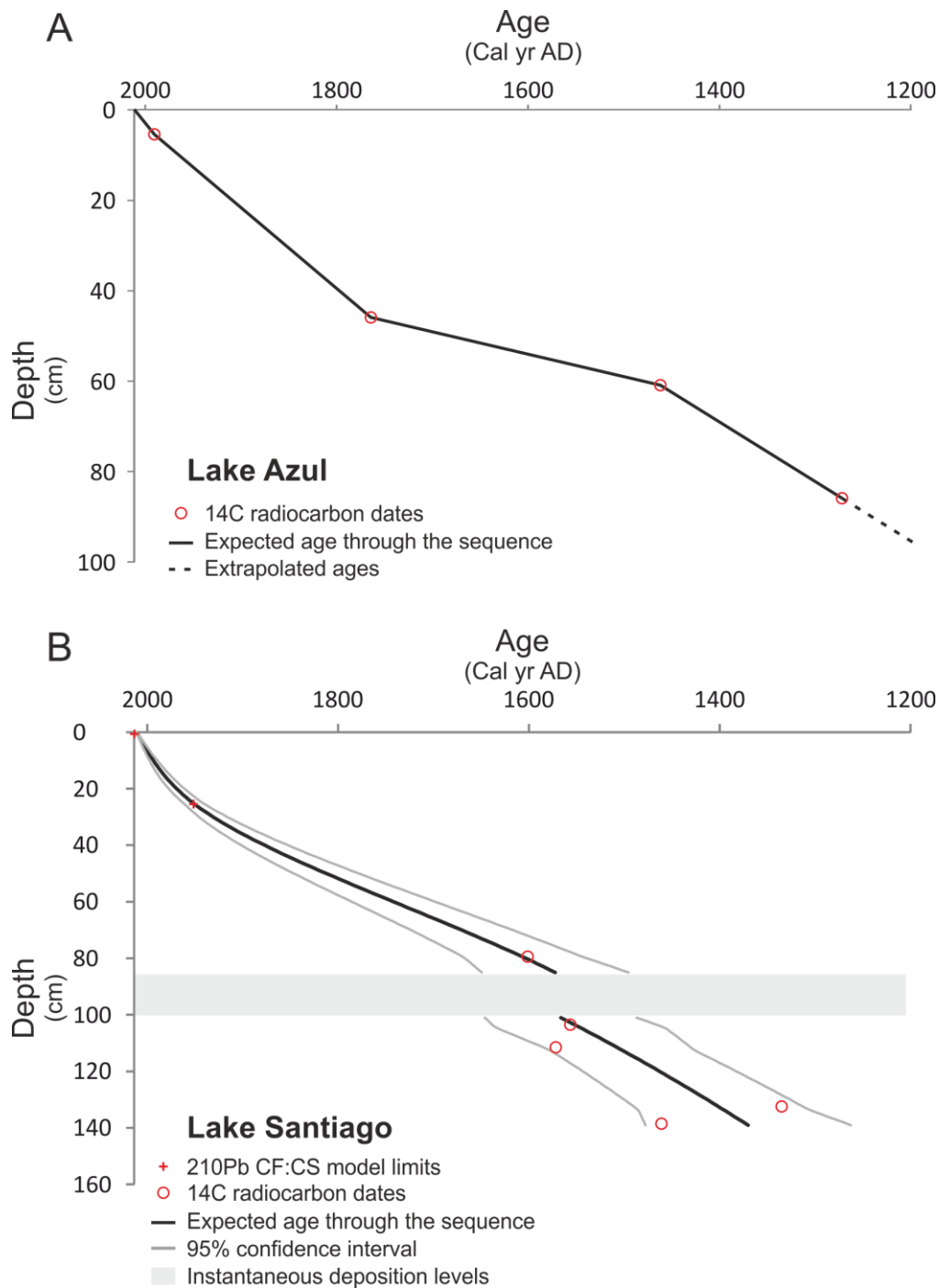
Figure 4: Sedimentation rate curves for A) core AZ11-02, and B) core SA11-02

5.3 Diatom accumulation rates, TOC, and TOC/TN signature

Results on DARs, TOC and values of the TOC/TN ratio are presented according to the previously defined Diatom Assemblage Zones (DAZs) (Figs. 5 and 6) based on the main taxa constituting the diatom record of Lakes Azul and Santiago (Vázquez-Loureiro *et al.*, in prep.)

5.3.1 Lake Azul

DAZ-1 (94 cm – 36 cm; 1231 - 1824 cal yr AD). This zone shows low values for DARs, which however show a peak at 66 cm (2.50 x 10^8 valves cm^{-2} yr^{-1}) and a secondary peak at 32 cm (2.22 x 10^8 valves cm^{-2} yr^{-1}). Most of this zone shows TOC values around 0.5%, with two peaks at 50 cm

and 45 cm, both yielding values of ~3.5%. TOC/TN, shows, in general, quite constant values of ~10, but with a steady rise that is magnified by sharp increases at 76-77 cm, reaching values ~14, and at 50-45 cm, where the values reach ~20 and ~22, respectively.

DAZ-2 (36 cm – 11 cm; 1824- 1961 cal yr AD). After an initial decrease, DARs experience an increase in this zone, reaching the maximum value for the whole record at 12 cm (3.36 x 10^8 valves cm^{-2} yr^{-1}) and a secondary peak at 21 cm (2.34 x 10^8 valves cm^{-2} yr^{-1}). TOC is characterized in this zone by an increasing trend up to a peak value of, ~3% at 15cm. The TOC/TN ratio, however, shows fairly constant values of ~10.

DAZ-3 (10 cm – 0 cm; 1961- 2011 cal yr AD). This zone shows a large variability in DARs, ranging from 0.37 x 10^8 at 10 cm to 3.96 x 10^8 at 5 cm. TOC shows a sharp net decline up to a minimal value of ~1% at 3 cm. The TOC/TN ratio shows a very slight uprising trend.

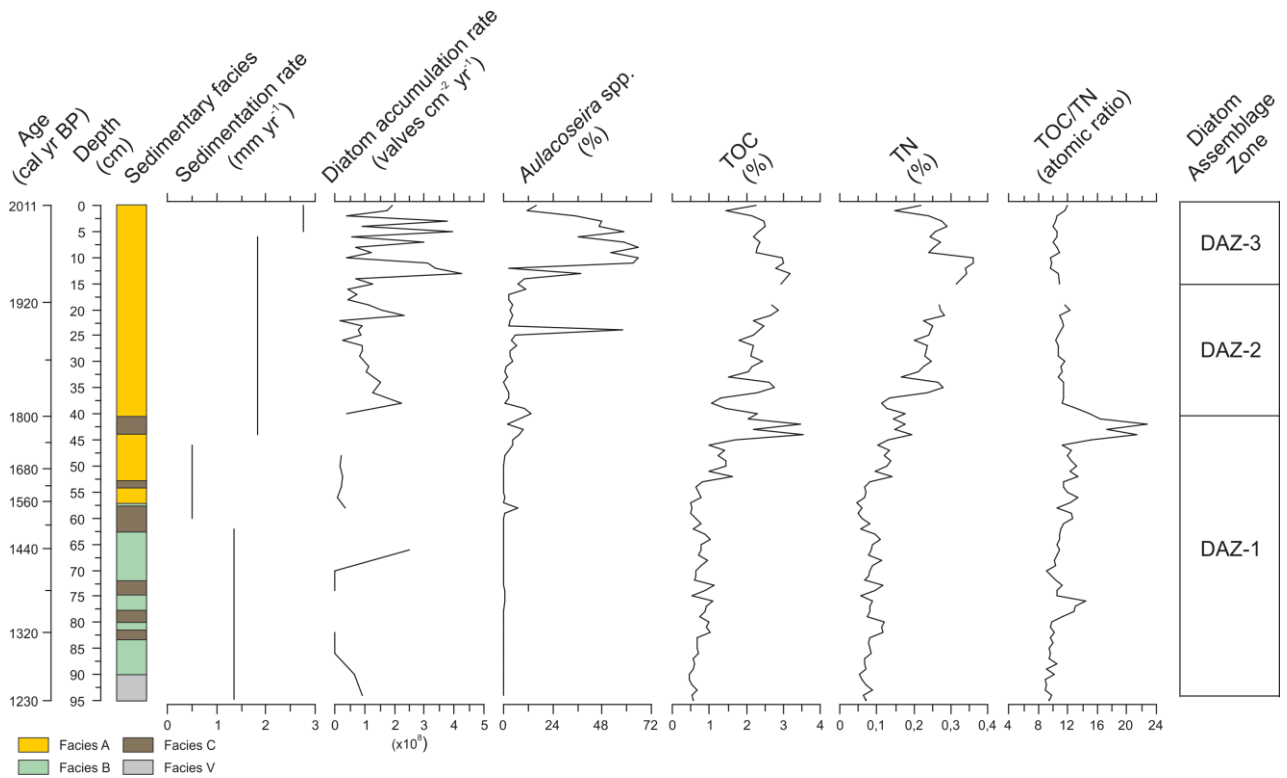*Figure 5: Sedimentological, geochemical and diatom data from core AZ11-02 plotted against depth and age (cal yr AD). Percent values of Aulacoseira spp. according to Vázquez-Loureiro et al. (in prep.)*

5.3.2 Lake Santiago

DAZ-1 (144 cm – 86 cm; 1377 – 1686 cal yr AD). The main feature of this zone is the presence of a tephra at its top, between 102-86 cm. Below this tephra, DARs values are low. Fluxes up to 16.86 x 10^8 valves cm^{-2} yr^{-1} at 130 cm are followed by a steady decrease up to values close to 0 just below the tephra. TOC and the TOC/TN ratio show very similar curves, with an increasing trend from the bottom to approximately 110 cm (values of 4.9% and 11.02, respectively), when a decline starts until the deposition of the tephra.

DAZ-2 (86 cm – 10 cm; 1686 – 1986 cal yr AD). DARs show a continuous net increase up to 75.21 x 10^8 valves cm^{-2} yr^{-1} at 10 cm, the maximum for the entire record. Secondary peaks are found at 31 cm (42.01 x 10^8 valves cm^{-2} yr^{-1}) and at 18 cm (62.79 x 10^8 valves cm^{-2} yr^{-1}). TOC values show a net increasing trend up to 10.5 % at 54 cm, declining thereafter. The TOC/TN ratio also starts with a rise from the bottom to 72 cm when it reaches a value of 12.7. After a decrease afterwards, it maintains in quite constant values (12.4 to 9.9) until the top of this zone.

DAZ-3 (10 cm – 0 cm; 1986 – 2011 cal yr AD). This zone starts with a sharp decrease in DARs (up to 8.4 x 10^8 valves cm^{-2} yr^{-1}), partially recovering in the topmost part (25.53 x 10^8 valves cm^{-2} yr^{-1}). Quite similar rends can be seen in the TOC curve, ranging from ~5 to ~7. Almost no variation is found in the TOC/TN ratio that maintains in approximately 10.5 values.
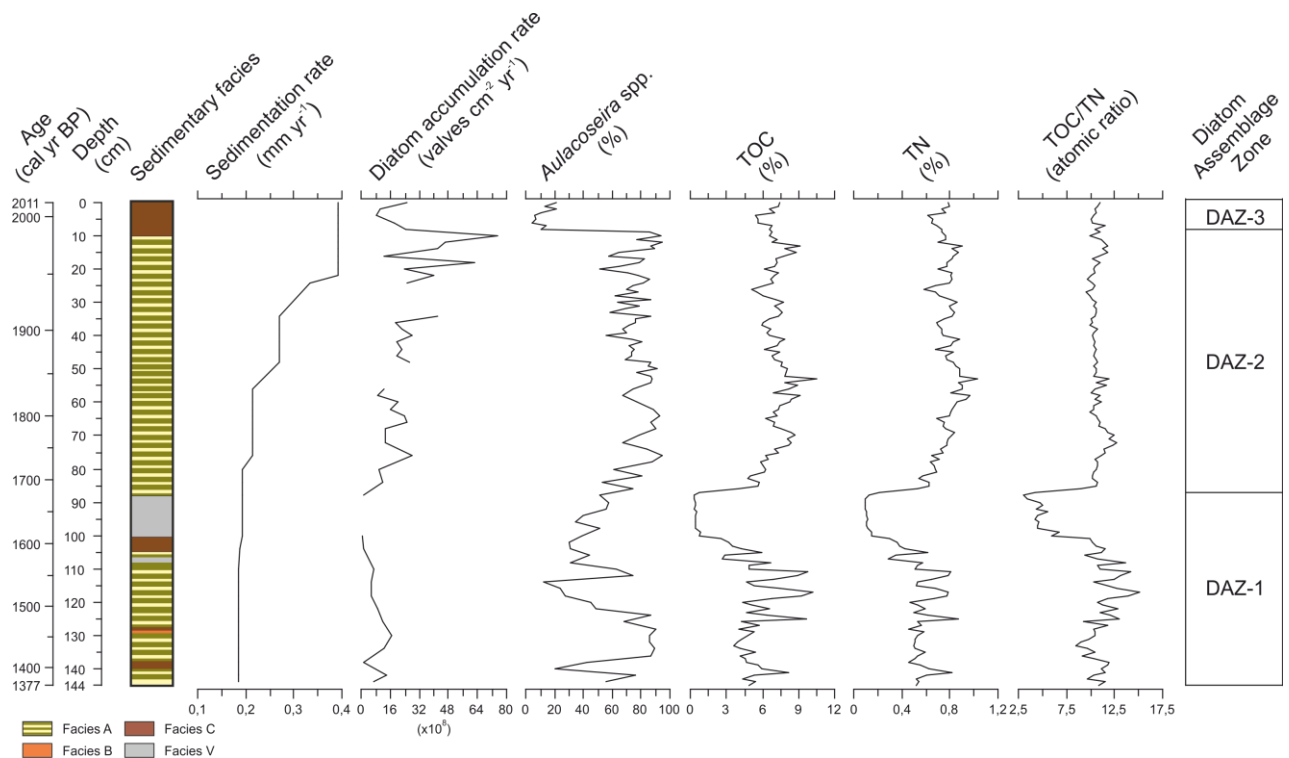
Figure 6: Sedimentological, geochemical and diatom data from core SA11-02 plotted against depth and age (cal yr AD). Percent values of Aulacoseira spp. *according to Vázquez-Loureiro et al. (in prep.)*

6. Discussion

Changes in DARs, TOC and in the TOC/TN ratio over time allowed to reconstruct the main trajectories in paleoproductivity in Lake Azul and Lake Santiago and the likely causes behind the main detected changes.

6.1 Paleoproductivity changes in Lake Azul

Three distinct productivity-related stages in the paleoenvironmental evolution of the lake were identified. These stages also roughly correspond to the preliminar DAZs defined for core AZ11-02 (Vázquez-Loureiro *et al.*, in prep.)

Stage 1 (c. 1230 to 1810 cal yr AD)

The recent history of Lake Azul began after the last volcanic intracaldera eruption, as recorded by the basal tephra layer (Facies V). In spite of the gradual increase in TOC throughout this section (Fig. 5), and its maximum peak recorded in c. 1780 cal yr AD that corresponds to a flood event, TOC content shows low values indicative of reduced productivity conditions during the entire stage. DARs also show a reduced flux of diatoms to the bottom of the lake, in spite of a peak of 2.50×10^8 valves cm^{-2} yr^{-1} dated at c. 1440 cal yr AD. This inferred productivity is compatible with the oligotrophic conditions of a shallow lake still in the initial phases of its ontogeny (Margalef, 1983). Interestingly, however, the DAR peak at c. 1440 cal yr AD coincides with the start of a net increase in the planktonic/periphytic diatom ratio, an indicator of water level fluctuations (Wolin & Stone, 2010), and therefore of a water-level rise trend (Vázquez Loureiro *et al.*, 2015). These punctual moderate diatom productivity conditions did not however persist for the rest of this stage. Both the lithofacies (Facies C, Fig. 3) and peaks in the TOC/TN ratio show that several flood events took place throughout all this stage (Fig. 5), probably associated with an intensified or more regular precipitation regime. With the possible exception of the before mentioned DAR peak, the probable increased input of nutrients associated to these flood events seem to have had no major influence

16

on diatom productivity.

Stage 2 (c. 1810 to 1960 cal yr AD)

The record of this stage is characterized by higher values of both DARs and TOC content compared to the previous stage (Fig. 5), indicating enhanced productivity conditions. However, whereas TOC shows a continuous gradual increase throughout this stage, DARs experience a net decline only interrupted by a peak at c. 1910 cal yr AD. This lack of correspondence between the trends of the two proxies is probably indicating that other primary producers rather than diatoms are contributing to total primary productivity. It is not likely that macrophytes significantly contributed to the increase in productivity, because the lake level rise initiated during Stage 1, that still persists during this stage, would have reduced the total area of littoral habitats necessary for macrophytic growth. On the other hand, the TOC/TN ratio during this stage shows minor variations (Fig. 5) and it keeps in the values characteristic of a dominant planktonic origin of organic matter. Preliminary data on algal pigment analysis shows that green algae significantly increased throughout this stage (Buchaca, pers. comm.), therefore becoming a very likely candidate as a major primary producer instead of diatoms. The prevalence of green algae over diatoms can also be interpreted as an indicator of a predominant stratified water column (Margalef, 1983).

The causes behind the productivity increase from Stage 1 to Stage 2 are not clear but, besides the natural increased nutrient availability of lakes over time (Margalef, 1983), it can be hypothesized that an ecological change of state (Brönmark & Hansson, 2005) might have occurred. According to historical sources, artificial fish species introduction in previously Azorean fishless lakes (Vicente, 1956; Flor de Lima, 1993) could be one of the main environmental impacts in the archipelago. It is known that cyprinids were first introduced in 1792 cal yr AD (Valois & Silva, 1886), approximately at the same time when Stage 2 starts. Fish introductions can contribute to major changes in aquatic communities and eutrophication, prompting cascading effects on the trophic chain (Brönmark & Hansson, 2005). The Alternative Stable State Theory of Shallow Lakes (Scheffer *et al.*, 1993; Scheffer & Van Nes, 2007) suggests that introduction of planktivorous fishes reduces zooplankton biomass, which promotes phytoplankton growth. As a consequence, a change of state towards a phytoplankton-dominated state occurs. Because phytoplankton growth prompts an increase in turbidity that causes a shade that inhibits macrophyte development, this state is called the turbid state. Conversely, the clear state, associated to reduced nutrient loads, would be characterized by clear water, large zooplankton and low phytoplankton biomass, extensive beds of submerged macrophytes, and a balanced fish community with a high proportion of piscivores. The quasi-synchronous introduction of the planktivorous cyprinids in Lake Azul and increase in productivity is compatible with this scenario. Moreover, the TOC increase is paralleled by a decline in pollen percentages of the macrophyte *Myriophyllum* sp. (Rull, pers. comm.) and of epiphytic diatoms likely attached to this and other available aquatic plants (Vázquez-Loureiro *et al.*, 2015). All these data support the hypothesis of an ecological change of state from a clear to a turbid state prompted by the introduction of non-native planktivorous fishes in the lake.

Stage 3 (c. 1960 to 2011 cal yr AD)

This stage is characterized by a decrease in TOC whereas DARs, although very shifting, show some of the highest values for the entire record (Fig. 5). Diatom assemblages also show maximum values of the euplanktonic and eutrophic of *Aulacoseira* spp. which however decrease towards the top of this stage (Vázquez-Loureiro *et al.*, 2015). Pigment data also indicate a significant decrease in green algae (Buchaca, pers. comm.).

The sharp increase in DARs and *Aulacoseira* spp. is very probably a consequence of enhanced nutrient loads associated to the extensive use of fertilizers since c. 1960 cal yr AD (Gonçalves, 1997). In spite of increased diatom productivity, TOC values show a negative trend towards the top of this stage, suggesting that total primary productivity diminished. Interestingly, the change from Stage 2 to Stage 3 is coincident with a significant negative excursion in $\delta^{13}C_{org}$ values (Vázquez-Loureiro *et al.*, 2015). The main reason for this change might be different fractionation of organic carbon produced by periphytic vs. planktonic algae (Vázquez-Loureiro *et al.*, in prep.). Periphyton is usually enriched in ^{13}C when compared to phytoplankton due to a higher CO_2 limitation of primary

producers in the littoral zone (France 1995). According to this interpretation, the use of fertilizers would have prompted planktonic productivity to the detriment of benthic productivity during Stage 3, probably as a consequence of shading (Brönmark & Hansson, 2005). This would be the reason behind the total primary productivity decrease indicated by the declining TOC values. Besides this, the change from a phytoplankton community dominated by green algae towards another dominated by *Aulacoseira* spp. would be indicative of a shift to a more turbulent water column regime, since heavy silicified diatoms such as *Aulacoseira* require well mixed waters to avoid sinking from the euphotic zone (Margalef, 1983).

6.2 Paleoproductivity changes in Lake Santiago

Data on DARs, TOC and the TOC/TN ratio reveal for this lake a higher trophic status for this lake compared to Lake Azul (with DARs ranging from 0.44×10^8 to 75.21×10^8 valves cm^{-2} yr^{-1}). Three productivity-related stages, also roughly related to the preliminar DAZs defined for core SA11-02 (Vázquez-Loureiro *et al*., in prep.), have been established:

Stage 1 (c. 1380 to 1680 cal yr AD)

This stage shows a correspondence between the net increasing trend in DARs and TOC content at its early history, but a quite opposite trend from 1470 cal yr until the deposition of tephras dated in c. 1680 cal yr AD (Fig. 6). DARs however show similar trends than percent abundances of *Aulacoseira* spp. (Vázquez-Loureiro *et al*., in prep.). This correspondence suggests that DARs are predominantly indicating phytoplanktonic rather than benthic productivity. Moreover, the time interval from c. 1470 to 1680 cal yr AD, when TOC and DARs follow distinct patterns, is coincident with an increase in benthic diatoms (Vázquez-Loureiro *et al*, in prep.) and in the TOC/TN ratio (reaching values up to 11, Fig. 6). The latter suggest a mixed origin of the organic matter, with incorporation of vascular plant materials (Meyers & Teranes, 2001). It seems however unlikely that the very steep shores of this lake could have maintained significant periphytic and/or macrophytic communities, so the allochthonous provenance of this organic matter cannot be disregarded.

Stage 2 (c. 1680 to 1985 cal yr AD)

Although the DAR record shows interruptions due to the lack of samples from some intervals, there is a consistent pattern among TOC content, DARs, and the percent abundance of *Aulacoseira* spp. of steady increase until c. 1860 cal yr AD, decline thereafter until c. 1960 cal yr AD, and peak values for the whole record at the top of this stage dated in c. 1965 to 1985 cal yr AD (Fig. 6). The TOC/TN ratio shows very minor variations, maintaining in values characteristic of organic matter of planktonic origin (Meyers & Teranes, 2001).

The correspondence among the three curves suggests that most primary productivity is due to planktonic diatoms. This is also corroborated by the examination of sediment smear slides, made up almost exclusively by planktonic diatoms (Sáez, pers. comm.), and by pigment data, which also show the dominance of diatoms throughout the whole sequence (Buchaca, pers. comm.). The TOC content, DARs, and *Aulacoseira* spp. data also suggest that after tephra deposition a progressive eutrophication took place until c. 1860 cal yr AD. This eutrophication process could be related to the extractive phase in which forests were felled by the Portuguese colonizers for construction, ship-building and charcoal production (Dias, 1996 in Connor *et al*., 2012). This stage started in Sâo Miguel in c. 1509 AD, so forest clearance could have facilitated the delivery of nutrients from the basin into the lake and, thus, the increase in primary productivity that is already recorded since the previous stage. Conversely, the decline in all the studied productivity proxies from c. 1860 to c. 1960 cal yr AD could be roughly related to the massive afforestation with the conifer *Cryptomeria japponica* D. Don that started c. 1845 (Dias, 1996 in Connor *et al*., 2012) that would hinder the input of nutrients from the basin. According to some peak values of DARs (up to 75.21×10^8 valves cm^{-2} yr^{-1}) and the maximum percent abundance of *Aulacoseira* spp. (94%) of the entire record, maximum diatom productivity and eutrophic conditions could have been reached in the interval c. 1965 to 1985 cal yr AD. Although the start of this interval coincides approximately with the time of the first extensive use of fertilizers in c. 1960 cal yr AD (Gonçalves, 1997), it is not likely that cultural eutrophication could have affected this lake, since no agricultural activities have been recorded in

the basin were lake Santiago is located. There is not a clear explanation for the increase in productivity for this interval.

Stage 3 (c. 1985 to 2011 cal yr AD)

This stage is characterized by a sharp decrease in DARs, as well as in the percent abundance of *Aulacoseira* spp. which during this interval are partially replaced by the also euplanktonic *Asterionella formosa* Hassal and *Fragilaria crotonensis* Kitton (Fig. 6). TOC content also show a parallel decrease, but still maintaining moderate values.

Recent increases of long pennate planktonic diatoms such as *A. formosa* and *F. crotonensis* at the expense of heavily silicified *Aulacoseira* taxa are quite common elsewhere, including other lakes of the Azorean archipelago (Gonçalves, 2008). These changes have been explained by both the addition of nutrients, as well by warming-related changes to lake properties (Rühland *et al.*, 2015). Because the increase may be a response to a combination of stressors, it is difficult to explain the observed decrease in DARs and TOC in relation to the sharp shift in the composition of the diatom assemblages.

7. Conclusions/ Conclusiones/ Conclusións

Conclusions

1. TOC, TN and DARs data allowed to distinguish three major stages in paleoproductivity conditions in Lake Azul in the approximately last 800 yr. During Stage 1 (c. 1230-1810 cal yr AD), low productivity conditions were recorded, probably because the lake was still in the early times of its ontogeny after the last volcanic explosive eruption took place. In spite of the recurrence of flood events associated to intense precipitations, these seldom produced significant changes in productivity levels. During Stage 2 (c. 1810-1960 cal yr AD) the lake showed an increase in productivity associated to the rise in green algae and decline of diatoms that suggest the prevalence of stratified water column conditions. The coincidence of the uprising trend in productivity with the artificial introduction of non-native planktivorous fishes in the lake suggest, according to the Alternative Stable State Theory of Shallow Lakes, that a change from a clear to a turbid state could have taken place. The most recent history of the lake, recorded by Phase 3 (c. 1960-2011 cal yr AD), shows an increase in planktonic productivity coincident with the start of the use of fertilizers and a shift to a more turbulent water column regime

2. Three productivity-related stages in the approximately last 640 yr could also be distinguished in Lake Santiago from TOC, TN and DARs data. Stage 1 (c. 1380-1680 cal yr AD) was characterized by a first period, up to c. 1470 cal yr AD, of dominant productivity of planktonic origin, followed by a period of net increase in productivity associated to more terrestrial sources of organic matter whose allochthonous origin cannot be disregarded. During Stage 2 (c. 1680-1985 cal yr AD) most productivity was related to diatoms, showing a first net increase up to c. 1860 cal yr AD, and a decline thereafter. Changes in the delivery of allochthonous nutrients from the basin seem the most likely driver of productivity variations, since the observed rise and decline in productivity are coincident with, on the one hand, the deforestation associated to the Portuguese colonizers and, on the other, to the massive afforestation with *Cryptomeria japponica* that began around 1860 AD, respectively. The last decades (Stage 3, c. 1985-2011 cal yr AD) are characterized by a reduction in diatom productivity, which is parallel to a significant shift from the dominance of centric to pennate planktonic diatoms, attributed elsewhere to the addition of nutrients, and/or global warming.

3. The comparison of the trajectories exhibited by productivity in the two lakes shows that the more oligotrophic conditions recorded in Lake Azul, compared to Lake Santiago, are a consequence of its younger age. The sedimentary record of both lakes also shows that they have been largely affected by anthropogenic stressors. Because of this, they are not good candidates to test whether increased primary productivity is the result of natural lake development over time.

Conclusiones

1. Los datos obtenidos a partir del estudio del TOC, TN y DARs, permitieron diferenciar en el Lago Azul tres estadios principales en las condiciones de paleoproductividad de, aproximadamente, los últimos 800 años. Durante el Estadio 1 (c. 1230-1810 cal AD), se registraron valores bajos de productividad, probablemente porque el lago se encontraba aún en un momento temprano en su ontogenia después de que la última erupción explosiva tuviera lugar. A pesar de la asiduidad con la que las inundaciones asociadas a precipitaciones intensas se produjeron, éstas raramente provocaron cambios significativos en los niveles de productividad. Durante el Estadio 2 (c. 1810-1960 cal AD) el lago mostró un aumento de la productividad asociada al incremento de algas verdes y el declive de las diatomeas, lo que apunta a la existencia de condiciones donde prevalece la estratificación de la columna de agua. El que la tendencia ascendente de la productividad y la introducción artificial de peces planctívoros foráneos en el lago coincidan sugiere, de acuerdo con la teoría de Estados Estables Alternativos en Lagos Someros que un cambio de un estado claro a uno turbio pudo haber tenido lugar. La historia reciente del lago, registrada en el Estadio 3 (c. 1960-2011 cal AD), muestra un incremento de la productividad achacable a organismos planctónicos, que coincide con el comienzo del uso de los fertilizantes y un cambio hacia un régimen de la columna de agua más turbulento.

2. En el Lago de Santiago se pueden diferenciar también tres estadios relacionados con la productividad a partir de los datos obtenidos del estudio del TOC, TN y DARs para los últimos 640 años. El Estadio 1 (c. 1380-1680 AD cal) se caracteriza por un primer período, hasta c. 1470 cal AD, de dominancia de la productividad achacable a organismos planctónicos, seguida de un periodo de incremento neto de la productividad asociada a fuentes de materia orgánica terrestre, cuyo origen alóctono no puede descartarse. Durante el Estadio 2 (c. 1680-1985 AD cal), la mayor parte de la productividad se debe a las diatomeas mostrando, primero, un incremento neto hasta c. 1860 cal AD, seguido de un declive a partir de este momento. Los cambios en la incorporación de nutrientes desde la cuenca parecen ser el motor de la variación en la productividad, ya que la subida y el descenso observados en sus niveles coinciden, por un lado, con la deforestación asociada a la colonización portuguesa y, por otra, con la repoblación intensiva con *Cryptomeria japponica* que comenzó alrededor de c. 1860 AD cal. Las últimas décadas (Estadio 3, c. 1985-2011 cal AD) se caracterizan por la reducción de la productividad achacable a las diatomeas, que es paralela a un cambio significativo de la dominancia de diatomeas plactónicas céntricas a pennales, atribuible a la adición de nutrientes y/o al calentamiento global.

3. La comparación de las trayectorias de la productividad de ambos lagos muestra que las condiciones más oligotróficas registradas en Lago Azul son una consecuencia de su corta edad. El registro sedimentario de ambos lagos permite apreciar que ambos han estado ampliamente afectados por impactos antropogénicos.. Debido a esto, no podemos considerar a ninguno como un buen candidato para comprobar si el incremento de la producción primaria es el resultado del desarrollo natural del lago a través del tiempo.

Conclusións

1. Os datos obtidos a partir do estudo do TOC, TN e DARs, permitiron diferenciar no Lago Azul tres estadios principais nas condicións de paleoprodutividade de, aproximadamente, os últimos 800 anos. Durante o Estadio 1 (c. 1230-1810 cal AD), rexistraron valores baixos de produtividade, probablemente porque o lago se encontraba aínda nun momento temprano na súa ontoxenia despois da última erupción explosiva tivera lugar. A pesar da asiduidade ca que as inundacións asociadas ás precipitacións

intensas se produciron, éstas raramente provocaron cambios significativos nos niveis de produtividade. Durante o Estadio 2 (c. 1810-1960 cal AD) o lago mostrou un aumento da produtividade asociada ó incremento de algas verdes e ó declive das diatomeas, o que apunta á existencia de condicións onde prevalece a estratificación da columna de auga. Que a tendencia ascendente da produtividade e a introducción artificial de peixes planctívoros foráneos no lago coincidan suxire, de acordo ca teoría de Estados Estables Alternativos en Lagos Someros que un cambio dun estado claro a un turbio puido ter lugar. A historia recente do lago, rexistrada no Estadio 3 (c. 1960-2011 cal AD), mostra un incremento da produtividade achacable a organismos planctónicos, que coincide co comezo do uso dos fertilizantes e un cambio hacia un réxime da columna de auga máis turbulento.

2. No Lago de Santiago pódense diferenciar tamén tres estadios relacionados ca produtividade a partir dos datos obtidos do estudo do TOC, TN e DARs para os últimos 640 anos. O Estadio 1 (c. 1380-1680 AD cal) caracterízase por un primeiro período, até c. 1470 cal AD, de dominancia da produtividade achacable a organismos planctónicos, seguida dun periodo de incremento neto da produtividade asociada a fontes de materia orgánica terrestre, cuxa orixe alóctona non pode descartarse. Durante o Estadio 2 (c. 1680-1985 AD cal), a meirande parte da produtividade se debe ás diatomeas mostrando, primeiro, un incremento neto até c. 1860 cal AD, seguido dun declive a partir deste momento. Os cambios na incorporación de nutrientes dende a cunca parecen ser o motor da variación na produtividade, xa que a subida e o descenso observados nos niveis coinciden, por un lado, ca deforestación asociada á colonización portuguesa e, por outra, ca repoboación intensiva con *Cryptomeria japponica* que comenzou arredor de c. 1860 AD cal. As últimas décadas (Estadio 3, c. 1985-2011 cal AD) caracterízanse pola redución da produtividade achacable ás diatomeas, que é paralela a un cambio significativo da dominancia de diatomeas plactónicas céntricas a pennales, atribuible á adición de nutrientes e/ou ó quencemento global.

3. A comparación das traxectorias da produtividade de ámbo-los dous lagos mostra que as condicións máis oligotróficas rexistradas en Lago Azul son unha consecuencia da súa curta idade. O rexistro sedimentario de ámbo-los dous lagos permite apreciar que estiveron ampliamente afectados por impactos antropoxénicos. Debido a isto, non podemos considerar ningún como un bo candidato para comprobar se o incremento da producción primaria é o resultado do desenvolvemento natural do lago a través do tempo.

8. Acknowledgments

The author of this dissertation participated in the micropaleontological analyses, calculation of the diatom accumulation rates, and construction of the age models. She also

integrated all the available sedimentological, geochemical, micropaleontological, and geochronological data to perform the interpretations.

9. References

Agostinho, J. 1948. Clima dos Açores. Contribuição para o estudo da sua variação secular. Açoreana 4, 263–66

Anderson, N.J., 1990. Inferring diatom paleoproduction and lake trophic status from fossil diatom assemblages, In: Kociolek, J.P. (Ed.), Proceedings of the 11th International Diatom Symposium, San Francisco, California. California Academy of Sciences Mem. 17, San Francisco, pp. 539-547.

Appleby, P.G., 2001. Chronostratigraphic techniques in recent sediments, In: Last, W.M., Smol, J.P. (Eds.), Tracking Environmental Change Using Lake Sediments. Volume 1: Basin Analysis, Coring, and Chronological Techniques. Kluwer Academic Publishers, Dordrecht, pp. 171-203.

Azevedo, A.2006: O anticiclone dos Açores. João Azevedo Editor, Ponta Delgada, 73 pp.

Battarbee, R.W., Jones, V.J., Flower, R.J., Cameron, N.G., Bennion, H., Carvalho, L., Juggins, S., 2001. Diatoms, En: Smol, J.P., Birks, H.J.B., Last, W.M. (Eds.), Tracking Environmental Change Using Lake Sediments. Volume 3: Terrestrial, Algal, and Siliceous Indicators. Kluwer Academic Publishers, Dordrecht, pp. 155-202.

Battarbee, R.W., Kneen, M.J., 1982. The use of electronically counted microspheres in absolute diatom analysis. Limnology and Oceanography 27, 184-188.

Birks, H.J.B., Juggins, S., Lotter, A.F., Smol, J.P., 2012. Tracking Environmental Change Using Lake Sediments. Volume 5: Data Handling and Numerical Techniques. Kluwer Academic Publishers, Dordrecht, p. 745.

Connor, S.E., van Leeuwen, J.F.N., Rittenour, T.M., van der Knaap, W.O., Ammann, B., Björck, S., 2012. The ecological impact of oceanic island colonization – a palaeoecological perspective from the Azores. Journal of Biogeography 39, 1007-1023.

Constância, J.P., Braga, T.J., Nunes, J.C., Machado, E., Silva, L., 2001. Lagoas e Lagoeiros da Ilha de Sâo Miguel. Amigos dos Açores - Associaçao Ecológica.

Björck, S., Wohlfarth, B., 2001. 14C chronostratigraphic techniques in paleolimnology, In: Last, W.M., Smol, J.P. (Eds.), Tracking Environmental Change Using Lake Sediments. Volume 1: Basin Analysis, Coring, and Chronological Techniques. Kluwer Academic Publishers, Dordrecht, pp. 205-245.

Brönmark, C., Hansson, L.A., 2005. The Biology of Lakes and Ponds. Oxford University Press, Oxford.

Deevey, E.S., 1955. The obliteration of the hypolimnion. Memorie dell'Istituto Italiano di Idrobiologia, Suppl 8, 9-38.

Digerfeldt, G., Håkansson, H., 1993. The Holocene paleolimnology of Lake Sämbosjön, southwestern Sweden. Journal of Paleolimnology 8, 189-210.

Dokulil, M.T., Kaiblinger, C., 2009. Phytoplankton productivity, In: Likens, G.E. (Ed.), Encyclopedia of Inland Waters. Academic Press, pp. 210-218.

Engstrom, D.R., Fritz, S.C., Almendinger, J.E., Juggins, S., 2000. Chemical and biological trends during lake evolution in recently deglaciated terrain. Nature 408, 161-166.

Gonçalves, V., 2008. Contribuçao para o estudo da qualidade ecológica das lagoas dos Açores. Fitoplâncton e diatomáceas bentónicas. PhD. Dissertation, Universidade dos Açores, Ponta Delgada, p. 343.

Hall, R.I., Smol, J.P., 2010. Diatoms as indicators of lake eutrophication, In: Smol, J.P., Stoermer, E.F. (Eds.), The Diatoms: Applications for the Environmental and Earth Sciences. Cambridge University Press, Cambridge, pp. 122-151.

Heegaard, E., Birks, H.J.B., Telford, R.J., 2005. Relationships between calibrated ages and depth in stratigraphical sequences: an estimation procedure by mixed-effect regression. The Holocene 15, 612-618.

Ishiwatari, R., Negishi, K., Yoshikawa, H., Yamamoto, S., 2009. Glacial–interglacial productivity and environmental changes in Lake Biwa, Japan: A sediment core study of organic carbon, chlorins and biomarkers. Organic Geochemistry 40, 520-530.

Kaland, P.E., Stabell, B., 1981. Methods for absolute diatom frequency analysis and combined diatom and pollen analysis in sediments. Nordic Journal of Botany 1, 697-700.

Margalef, R., 1983. Limnología. Ediciones Omega, Barcelona.

Meyers, P.A., 2003. Applications of organic geochemistry to paleolimnological reconstructions: a summary of examples from the Laurentian Great Lakes. Organic Geochemistry 34, 261-289.

Meyers, P.A., Lallier-Vergés, E., 1999. Lacustrine Sedimentary Organic Matter Records of Late Quaternary Paleoclimates. Journal of Paleolimnology 21, 345-372.

Meyers, P.A., Teranes, J.L., 2001. Sediment organic matter, In: Smol, J.P., Birks, H.J.B., Last, W.M. (Eds.), Tracking Environmental Change Using Lake Sediments. Volume 2: Physical and Geochemical Methods. Kluwer Academic Publishers, Dordrecht, pp. 239-269.

O'Sullivan, P.E., Reynolds, C.S., 2004. The Lakes Handbook. Volume 1. Blackwell Publishing, Malden, MA, p. 699.

Reimer, P. J., Baillie, M. G. L., Bard, E., Bayliss, A., Beck, J. W., Blackwell, P. G., Bronk Ramsey, C., Buck, C. E., Burr, G. S., Edwards, R. L., Friedrich, M., Grootes, P. M., Guilderson, T. P., Hajdas, I., Heaton, T. J., Hogg, A. G., Hughen, K. A., Kaiser, K. F., Kromer, B., McCormac, F. G., Manning, S. W., Reimer, R. W., Richards, D. A., Southon, J. R., Talamo, S., Turney, C. S. M., van der Plicht, J., & Weyhenmeyer, C. E. (2009). IntCal09 and Marine09 radiocarbon age calibration curves, 0-50,000 years cal BP. Radiocarbon, 51(4), 1111-1150Renberg, I., 1990. A procedure for preparing large sets of diatom slides from sediment cores. Journal of Paleolimnology 4, 87-90.

Rühland, K., Paterson, A., Smol, J., 2015. Lake diatom responses to warming: reviewing the evidence. Journal of Paleolimnology, 1-35.

Santos FD, Valente MA, Miranda PMA, Aguiar A, Azevedo EB, Tome AR, Coelho F. 2004. Climate Change Scenarios in the Azores and Madeira Islands. World Resource Review 16: 473–491Scheffer, M., Hosper, S.H., Meijer, M.L., Moss, B., Jeppesen, E., 1993. Alternative equilibria in shallow lakes. Trends in Ecology and Evolution 8, 275-279.

Scheffer, M., van Nes, E., 2007. Shallow lakes theory revisited: various alternative regimes driven by climate, nutrients, depth and lake size. Hydrobiologia 584, 455-466.

Smol, J.P., 2008. Pollution of Lakes and Rivers. A Palaeoenvironmental Perspective. Blackwell Publishing, Malden.

Theriot, E., 2001. Diatoms, Encyclopedia of Life Sciences. John Wiey and Sons, Chichester.

Vázquez-Loureiro, D., Bao, R., Gonçalves, V., Rubio-Inglés, M.J., Sáez, A., Hernández, A., Raposeiro, P.M., Pueyo, J.J., Masqué, P., Trigo, R.M., Giralt, S., 2015. Diatom responses to precipitation and anthropogenic disturbances in an Azorean lake during the last seven centuries. Geophysical Research Abstracts 17, EGU2015-11990.

Wetzel, R.G., 2001. Limnology. Academic Press, San Diego.

Wolin, J.A., Stone, J.R., 2010. Diatoms as indicators of water-level change in freshwater lakes, In: Smol, J.P., Stoermer, E.F. (Eds.), The Diatoms: Applications for the Environmental and Earth Sciences. Cambridge University Press, Cambridge, pp. 174-185.