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Paleolimnological studies of Laguna Chica of San Pedro (VIII Region): Diatoms, hydrocarbons and fatty acid records

Estudio Paleolimnológico de Laguna Chica de San Pedro (VIII Región): Diatomeas, hidrocarburos y ácidos grasos

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ABSTRACT

Diatom, hydrocarbons and fatty acid sedimentary records were used for reconstructing the recent (last 150 years) palaeolimnological history of Laguna Chica of San Pedro (Concepción, VIII Región, Chile). Cluster analyses (Constrained Incremental Sum of Squares) on the diatom data revealed three distinct periods. The first period (1883-1940's) showed a pronounced increase in sedimentation rate and a slight increase in organic matter accumulation. In this period, eutrophic species (*Aulacoseira granulata* and *Staurosira construens*) became increasingly dominant. From the 1940s until the 1970s the diatom signal is more equivocal: after the initial decrease in the relative abundance of *A. granulata* and *S. construens* their numbers fluctuate without a clear pattern. Sedimentation rates strongly fluctuate in this period. From 1978 onwards eutrophic species are in decline while indicators of oligotrophic conditions, such as *Cyclotella stelligera* and *Aulacoseira distans*, become more abundant. This shift in the lake trophic status could not be attributed to a reduction in the nutrient load from the catchment and we hypothesize that the invasion of the lake by the submersed macrophyte *Egeria densa* has altered nutrient availability to the plankton communities. This is in agreement with the hydrocarbons and fatty acid analyses which demonstrate a shift in carbon number distributions from short chain alkanes and alkanoic acids (typical for microalgae) to long chain molecules (characteristic for higher plants) in the upper layers of the lake sediment.

Key words: diatoms, hydrocarbons, fatty acids, paleolimnology, land use.

RESUMEN

Se realizó la reconstrucción histórica de los últimos 150 años de Laguna Chica de San Pedro (Concepción, VIII Región, Chile), a través de la utilización de los restos de diatomeas, hidrocarburos y ácidos grasos contenidos en la columna de sedimento. El análisis estratigráfico de las diatomeas reveló la presencia de tres períodos diferentes. El primer período (1883-1940's), mostró un marcado aumento de las tasas de sedimentación y un leve aumento en la acumulación de materia orgánica; en este período se registra un incremento de las especies eutróficas (*Aulacoseira granulata* y *Staurosira construens*). Desde los años cuarenta hasta la década del setenta el cambio en la comunidad de diatomeas fue más evidente y las tasas de sedimentación variaron fuertemente. A partir de 1978 disminuyen las especies eutróficas y aumentan las indicadoras de condiciones oligotróficas (*Cyclotella stelligera* y *Aulacoseira distans*). El cambio en el estado trófico del lago, no se atribuye a una reducción de los aportes de nutrientes desde la cuenca, sino que se hipotetiza que la invasión de la macrófita *Egeria densa*, alteró la disponibilidad de nutrientes en las comunidades planctónicas. Esto concuerda con el análisis de hidrocarburos y ácidos grasos, registrándose una mayor concentración de compuestos de cadena larga (característicos de plantas superiores) en los estratos superficiales, mientras que en los estratos más profundos se detectó una mayor concentración de hidrocarburos y ácidos grasos de cadena corta (característicos de microalgas).

Palabras clave: diatomeas, hidrocarburos, ácidos grasos, paleolimnología, uso del suelo.

INTRODUCTION

The San Pedro lacustrine system (composed of the lakes "Laguna Grande" and "Laguna Chica") has undergone four different periods of land use during the last 500 years (Cisternas et al. 1999). The first period, dominated by occasional vegetation burning and agriculture activities, began ca. 1570, after the foundation of Concepcion city (1550) and the construction of the San Pedro fort (1603), initiating large scale "fires" of the original native forest (Oliver & Zapata 1950, Morales 1989). The second period, started in the early nineteenth century, and was characterized by intensive agricultural activity which reached a maximum in 1848, as a consequence of the extensive harvesting of cereals by the so-called "golden fever" in North America (Campos-Harriet 1982). The majority of the coastal dry lands were used for intensive wheat production, through tillage by ancestral techniques inherited from the spanish conquerors. As a consequence of this, early in the twentieth century, the coastal mountain lands became degraded and eroded, being only appropriate for reforestation.

Towards the end of the nineteenth century the third period began, characterized by use of the land through forestation and the introduction of the first plantations of exotic tree species (pines and eucalyptus) by the Lota Coal Mining Company, in order to satisfy its requirements of wood and to control erosion (Astorquiza 1929, Contesse 1987). This replacement process of the native forest with commercial plantations intensified in the mid twentieth century, reaching its maximum expression nowadays. Finally, from 1968, began the fourth period, characterized by human settlement in the watersheds of the lacustrine system.

Although the human impact on the San Pedro lacustrine system has occurred since the arrival of the Spanish conquerors in Chile, the most important land use alterations of the lacustrine system catchment were produced in the last sixty years. Several researchers (Cisternas et al. 1999) have reported that in 1943 the native forest occupied ca. 70% of the total catchment surface and that in 1994 only covered ca. 13% of the total surface, as a result of a systematic replacement with exotic species.

On the contrary, tree plantations occupying less than 5% of the catchment surface in 1943, occupied ca. 46% of the surface in 1994. Accordingly, the residential use of the lacustrine system, which was not present during the 1940's, reached its maximum development of ca. 6% cover in the mid 1990's.

Cisternas et al. (1999) carried out a comparative study of pollen grains and diatom records of the sediments of both lakes (Laguna Grande and Laguna Chica). The results revealed that the catchment of the San Pedro lacustrine system has undergone drastic environmental changes from the pre-hispanic times until today. However, that study did not establish the timing and periodicity in which the identified changes occurred. Accordingly, the objective of this study is to identify through biological and chemical records of the sediments, the trends and rhythm to which the Laguna Chica of San Pedro lacustrine system has evolved during the last 150 years.

MATERIALS AND METHODS

Study area

Laguna Chica of San Pedro (36°51"S, 73°05"W) is a small lake located in the coastal mountain range of Nahuelbuta in Central Chile at approximately 3.5 km from the Pacific Ocean (Fig. 1). Mountains of metamorphic basement surround the eastern side while the western side consists of fluvial basaltic sediments (Acencio 1994). The lake has a simple bathymetry, with a single basin, that reaches its maximal depth (18 m) in the center. A complete limnological and morphological description will be discussed in future work (Urrutia et al.. in press).

Sampling

A short core was collected with a Kayak corer from the deepest part of the Laguna Chica of San Pedro. The sealed core was transported to the laboratory in an ice cooler and was sectioned into 1 cm intervals. Fifteen samples were weighed and dried at 60 °C for 48 hours. X-ray analysis was used to check possible physical or biological disturbances in the cores. The core was vertically extruded, sliced into 1-cm slices (subsamples), which were carefully sealed to avoid contamination. For each subsample, routine measurements of dry density (drying at 105°C), ^{210}Pb and Organic Matter were performed.

Geochronology, sedimentation rates and land use

Radiometric analyses were performed for ^{210}Pb (halflife = 22.3 yr) using alpha spectrometry (Häsanen 1977). The supported ^{210}Pb (the amount in equilibrium with radium in the sediment matrix) was estimated from the constant values of the three deepest subsamples (Cisternas 1999). Age and sedimentation rates of the core were determined using the Constant Rate of Supply (CRS) model (Goldberg 1963; Appleby & Oldfield

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[1] DEBELS P, M CISTERNAS, R URRUTIA, A ARANEDA & R SANHUEZA (1999) Cambios en el uso del suelo y tasas de sedimentación en ecosistemas lacustres, un caso de esudio: Laguna Chica de San Pedro, VIII Región, Chile. Resúmenes VI Conferencia Latinoamericana de usuarios de ARC/INFO y ERDAS.

1978). The historical land use patterns were obtained from Cisternas et al. 1999 and Debels et al. (1999[1]).

Diatom analysis

Approximately 0.1 g of dry sediment from each core segment was processed for diatom analyses using sulfuric acid, potassium permanganate and oxalic acid (Hasle & Fryxell 1970). Processed material was dried onto coverslips which were then mounted in Hyrax (Ir = 1.7) mounting medium. Diatoms were identified and enumerated (relative abundance) with a Carl Zeiss Axioplan microscope at a magnification of 1000x with an oil immersion objective. A minimum of 500 frustules were counted in random transects. Diatoms were identified using Rivera (1970), Rivera et al. (1973), Rivera (1974), Rivera et al. (1982) and Krammer & Lange-Bertalot (1986-1991); nomenclature follows the most recent changes in the literature (i. e. since Round et al. 1990). Autecological characteristics of the most important species with respect to total phosphorus (TP) and/or trophic state were mainly obtained from Cumming et al. (1995).

Hydrocarbons and fatty acids

The fatty acid and hydrocarbon compounds were extracted from the sediment core in a Soxhlet system with n-hexane for 8 hours. The extracts were concentrated in a rotary evaporator under reduced pressure using n-hexane as eluent until final volume of 0.5 ml. The determination of the compound was performed using a Shimadzu model 9A Gas Chromatograph equipped with a FID detector and a HP-5MS capillary column (30 m x 0.25 mm). Determinations were carried out under the following conditions: injector temperature, 250°C; detector temperature 300°C; column temperature program, 100°C for 2 min, increase from 100°C to 260°C at 10°/min, hold for 15 min. The identification and quantification of the compounds were made using the internal and external standard methodology (Bourdonniere & Meyers 1996). The Carbon Preference Index (CPI) was determined and results were normalized in relation with the organic matter content.

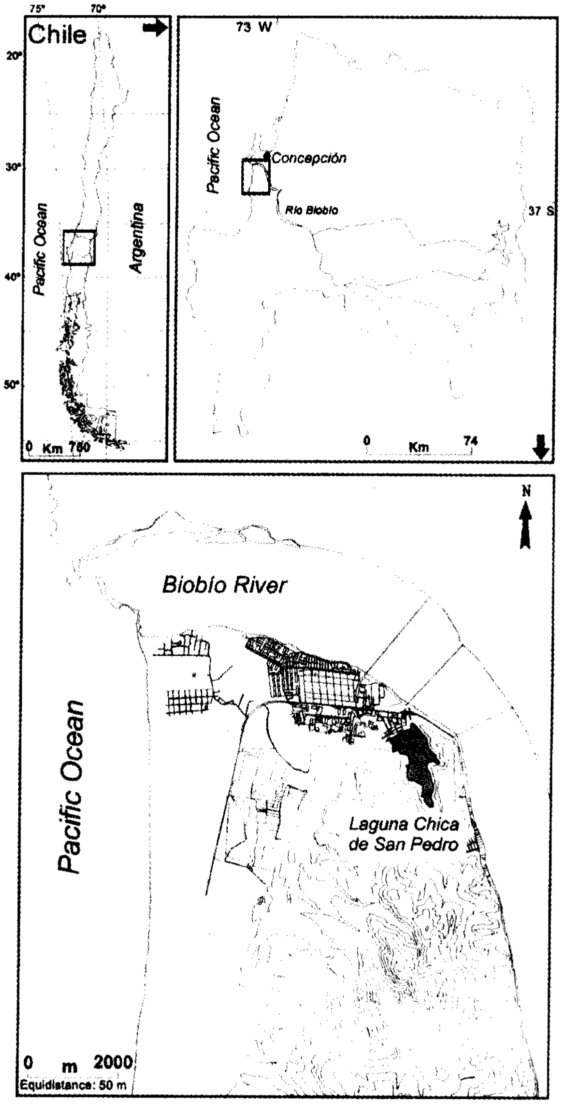

Fig. 1. Location of Laguna Chica of San Pedro.
Ubicación de Laguna Chica de San Pedro.

The relative contributions of the suite of different n-alkanes included in the total extractable hydrocarbon fractions provide information about the sources of these compounds. The presence of C_{27}, C_{29} and C_{31} n-alkanes in the sediment extracts shows that land-plant waxes have been important sources of hydrocarbons to the sediments (Cranwell 1973, Rieley et al. 1991). Microalgal contributions are indicated by the presence of n-C_{17} (Giger et al. 1980, Cranwell et al. 1987). The higher values of the ratios of terrigenous to aquatic n-alkanes ($TAR_{HC} = C_{27} + C_{29} + C_{31} / C_{15} + C_{17} + C_{19}$) indicate increased watershed sources of lipid matter relative to aquatic sources. Long chain n-alkanoic acids, such as C_{24}, C_{26} and C_{28}, are major components to the waxy coatings on terrestrial plant leaves, flowers and pollen (Rieley et al. 1991). Shorter chain C_{12}, C_{14} and C_{16} n-acids are produced by all plants but are dominant lipid components of microalgae (Cranwell et al. 1987). The higher values of the ratios of terrigenous to aquatic n-alkanoic acids ($TAR_{FA} = C_{24} + C_{26} + C_{28}$

/ $C_{12} + C_{14} + C_{16}$), may indicate increased watershed sources of lipid matter relative to aquatic sources, but they may also indicate preferential degradation of aquatic fatty acids relative to land-derived components.

Data analysis

Zonation of the diatom stratigraphy was done applying stratigraphically constrained cluster analysis using the Tilia program version 1.12 (Grimm 1991). Diagrams were plotted with Tiliagraph program. Only species that reached a relative abundance of 2 % in at least one core sample were selected.

RESULTS

Geochronology, sedimentation rates and organic matter content

X-ray radiograph of the sediment core showed a clear sedimentary stratigraphy in the form of easily distinguishable layers without indications of physical or biological disturbances. The ^{210}Pb activity in a core declines smoothly with depth from a maximum at the top to a constant value - the supported ^{210}Pb activity- in equilibrium with ^{226}Ra in the sediments. Under these conditions, the downward decrease in unsupported ^{210}Pb activity is controlled solely by the age of the deposit (Cisternas 1999).

In the core, unsupported 2^{10}Pb activity shows an overall decrease downward (Fig. 2 A). Interpreted with the CRS model, in which ^{210}Pb fallout does not change with time , this trend implies that the top 15 cm of the core spans a little more than a century (Figs 2 B y 2 C). The earliest date inferred from this model, for deposits 15 cm below the surface, is 1883. For the top of the core, we fit the model to a date of 1996 and computed intermediate dates at 1 cm intervals.

During the past 120 years, sedimentation rates in Laguna Chica de San Pedro have fluctuated considerably, ranging between 5.2 mg cm^{-2} y^{-1} at the end of 1890´s and 60.0 mg cm^{-2} y^{-1} in the 1990´s, with an average of 35.39 mg cm^{-2} y^{-1} (Fig. 2 C). Three periods of high sedimentation rates can roughly be distinguished, viz. 1883-1948, 1951-1968, 1972-1994. They are separated by short periods with lower values.

Fluctuations in organic matter content throughout the core were relatively small, ranging between 13.1 and 15.8 % (Fig. 2 D). After an initial increase in organic matter content (1883-1942), a decrease can be observed, reaching a minimum in 1968. A second period of increasing values ends in 1978, after which values slowly

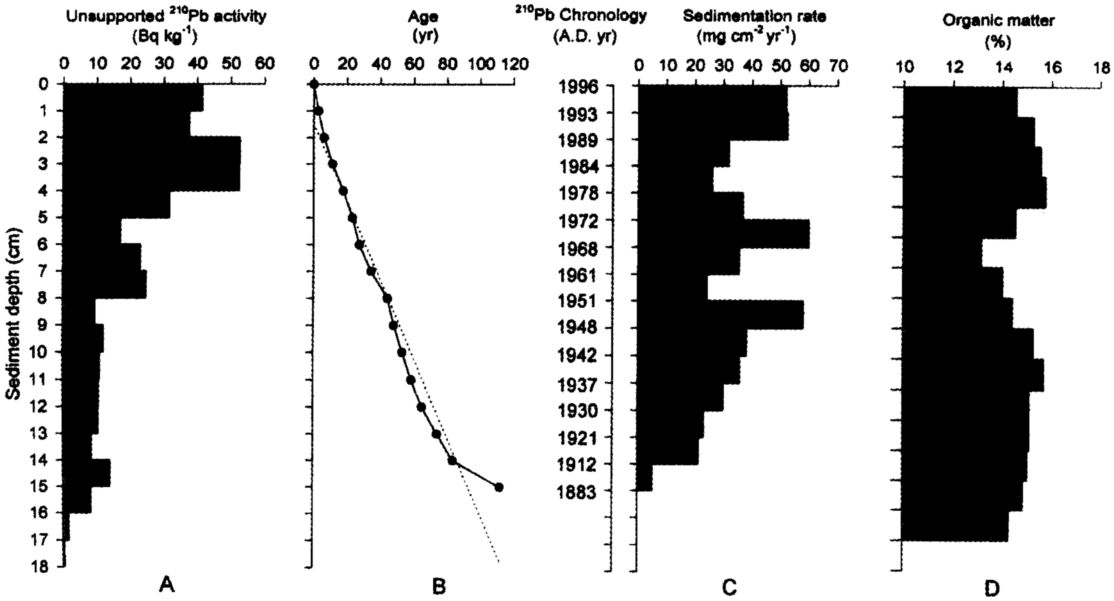

Fig. 2. A) Unsupported ^{210}Pb activity ; B) Age vs depth profile ; C) Sedimentation rate and geochronology ; D) % Organic matter.

A) Actividad 2^{10}Pb en exceso ; B) Perfil edad vs profundidad ; C) Tasas de sedimentación y geocronología ; D) % Materia Orgánica.

decrease until the present. The observed pattern was confirmed by observations made on a core taken in January 1999 (not shown) which revealed a similar pattern, with one peak in the 1930's – 1940's and a second one at the end of the 1970's.

Diatom stratigraphy

X-ray radiographs of the sediment cores showed a clear sedimentary stratigraphy in the form of easily distinguishable layers without physical or biological disturbances. A total of 97 diatom taxa were identified in Laguna Chica of San Pedro core (Table 1), only 14 of these reached a relative abundance of 2 % in at least one layer. Most taxa are benthic (87 %); only 13 % are planktonic. The most abundant taxa are *Staurosirella pinnata* (23-44%), *Staurosira construens* (4.1-35%), *Aulacoseira granulata* (3.3-20%), and *Cyclotella stelligera (2.6-23.3%)*, *Diploneis* cf. *subovalis* (0-14 %) and *Surirella guatimalensis* (1-6 %).

Stratigraphically constrained cluster analysis revealed three distinct zones (Fig. 3). The first period (1883-1942) is characterized by dominance of *Staurosirella pinnata*, *S. construens*, *Aulacoseira granulata* and, to a lesser degree, *Planothidium ellipticum*. *A. granulata* and *S. construens* gradually increase in relative abundance throughout this period, while there is a steady decrease in the abundance of the other two species. All four species have relatively high optima for total phosphorus (TP) (14.2 – 29 µg/L, Cumming et al. 1995) and can therefore be considered as indicative of meso- to eutrophic conditions. The fact that the relative abundance of *A. granulata* (TP 23.3-29 µg/l) increases towards the end of this period indicates that total phosphorus levels in the lake must have been rising.

The second period stretches from the end of the 1940's until the beginning of the 1970's; the lower boundary of this zone is typified by distinct shifts in the above-mentioned trends of the first period: the relative abundances of *Aulacoseira granulata* and *Staurosira construens* are abruptly halved while *Staurosirella pinnata* reaches peak abundance at this time. At the same time, small peaks of *Staurosira construens* fo. *subsalina* and var. *venter*, both absent from the lower zone, appear. The latter species has a TP optimum of 8-11.9 µg/l (Cumming et al. 1995). After 1948, most taxa maintain a more or less constant relative abundance throughout the rest of this zone, except for *Staurosira construens* whose relative abundance is restored to former levels.

Finally, the last period (from 1978 onwards) is characterized by some pronounced shifts in species abundance: the contribution of *Aulacoseira granulata*, *Planothidium ellipticum* and especially *Staurosira construens* further decrease, while *Cyclotella stelligera* and *Diploneis* cf. *subovalis* strongly increase in relative abundance. *Aulacoseira distans* first appears in the core in 1989. *C. stelligera* (TP optimum 7-9.7 µg/l) and *A. distans* (7.7-8 µg/l) are both oligotrophic species (e. g. Denys 1991, Wunsam et al. 1995). *Staurosirella pinnata* remains the most important

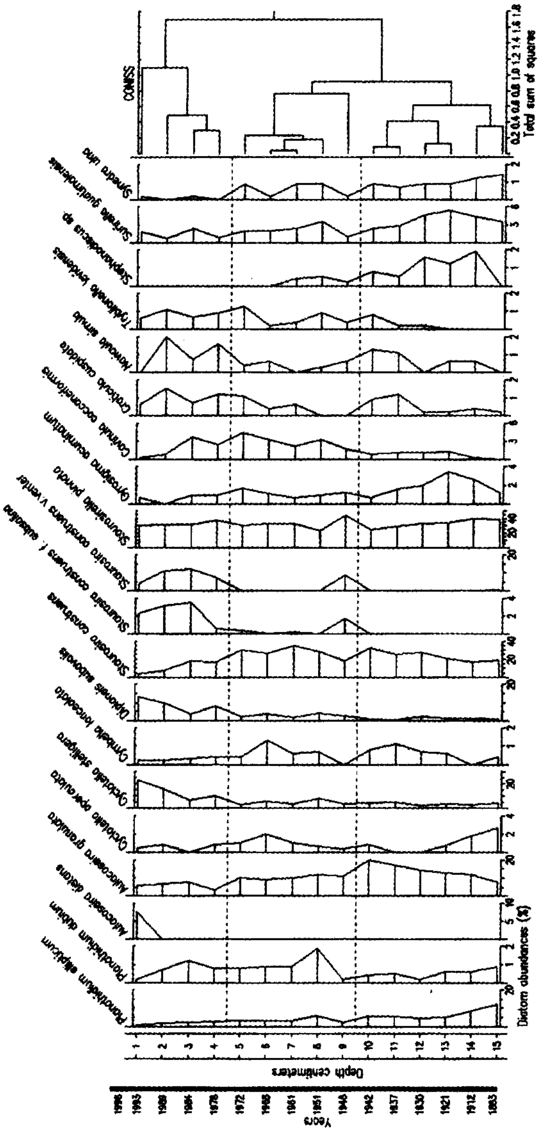

Fig. 3. Relative frequency diatom biostratigraphy for sediment core from Laguna Chica of San Pedro.

Perfil estrafigráfico de diatomeas en la columna de sedimento de Laguna Chica de San Pedro.

TABLE I

Diatom taxa identified in core from Laguna Chica of San Pedro

Taxa identificados en la columna de sedimento de Laguna Chica de San Pedro

- *Achnanthes* Bory
  - *pinnata* Hustedt
- *Achnanthidium* Kützing
  - *affine* (Grunow) Czarnecki
  - *exiguum* (Grunow) Czarnecki
  - *pinnata* Hustedt
- *Amphora* Ehrenberg
  - *veneta* Kützing
- *Asterionella* Hassall
  - *formosa* Hassall
- *Aulacoseira* Agardh
  - *distans* (Ehrenberg) Simonsen
  - *granulata* (Ehrenberg) Simonsen
- *Caloneis* Cleve
  - sp.
- *Cavinula* Mann
  - *cocconeiformis* (Gregory) Mann & Stickle
- *Cocconeis* Ehrenberg
  - *placentula* var. *euglypta* (Ehrenberg) Grunow
- *Craticula* Grunow
  - *cuspidata* (Kützing) Mann
- *Cyclotella* (Kützing) Brébisson
  - *meneghiniana* Kützing
  - *operculata* (Agardh) Kützing
  - *stelligera* (Cleve & Grunow) Van Heurck
- *Cymbella* Agardh
  - *affinis* Kützing
  - *lanceolata* (Agardh) Agardh
- *Diatoma* Bory
  - *tenue* Agardh
  - *vulgare* Bory
- *Diadesmis* Kützing
  - *contenta* (Grunow in Van Heurck) Mann
- *Diploneis* Ehrenberg
  - *ovalis* (Hilse) Cleve
  - cf. *Subovalis* Cleve
- *Encyonema* Kützing
  - *gracile* Rabenhorst
  - *minutum* (Hilse ex Ralfs) Mann
- *Epithemia* Brébisson
  - *adnata* (Kützing) Brébisson
  - *sorex* Kützing
  - sp.
- *Eunotia* Ehrenberg
  - *fallax* A. Cleve
  - *flexuosa* Brébisson ex Kützing
  - *flexuosa* var. *Linearis* (Brébisson) Okumo
  - *sudetica* O. Müller
- *Fragilaria* Lyngbye
  - *capucina* var. *lanceolata* Grunow
  - *construens* var. *javanica* Hustedt
  - *vaucheriae* (Kützing) Petersen
- *Frustulia* Rabenhorst
  - *amphipleuroides* (Grunow in Cleve et Grunow) A. Cleve-Euler
- *Gomphonema* Agardh
  - *acuminatum* Ehrenberg
  - *angustatum* (Kützing) Rabenhorst
  - *gracile* Ehrenberg
  - *gracile* var. *Dichotomum* (W. Smith) Van Heurck
  - *parvulum* (Kützing) Kützing
  - *truncatum* var. *capitatum* (Ehrenberg) Patrick
- *Geissleria* Lange-Bertalot & Metzeltin
  - *decussis* (Østrup) Lange-Bertalot & Metzeltin
- *Gyrosigma* Hassall
  - *acuminatum* (Kützing) Rabenhorst
- *Hantzschia* Grunow
  - *amphioxys* (Ehrenberg) Grunow
- *Hippodonta*
  - *hungarica* (Grunow) Lange-Bertalot, Metzeltin & Witkowski
- *Luticola* Mann
  - *cohnii* (Hilse) Mann
  - *mutica* (Kützing) Mann
- *Navicula* Bory
  - *anglica* var. *subsalsa* (Grunow) Cleve
  - *bryophila* Petersen
  - *cluthensis* Gregory
  - *lapidosa* Krasske
  - *lateropunctata* Wallace
  - *radiosa* Kützing
  - *rhynchocephala* Kützing
  - *simula* Patrick
  - *trivialis* Lange-Bertalot
  - *viridula* (Kützing) Ehrenberg
  - *viridula* var. *rostellata* (Kützing) Cleve
- *Neidium* Pfitzer
  - *iridis* (Ehrenberg) Cleve
- *Nitzschia* Hassall
  - *amphibia* Grunow
  - *amphibia* var. *umbrosa* Cleve-Euler
  - *invisitata* Hustedt
  - *kuetzingiana* Hilse
  - *linearis* (Agardh) W. Smith
  - *philippinarum* Hustedt
- *Pinnularia* Ehrenberg
  - *acuminata* W. Smith
  - *brevicostata* Cleve var. *intermedia* Manguin
  - *dactylus* Ehrenberg
  - *divergens* W. Smith
  - *gibba* Ehrenberg
  - *gibba* var. *Sancta* (Grunow) Meister
  - *lata* (Brébisson) W. Smith
  - *latevittata* Cleve
  - *latevittata* var. *Domingensis* Cleve
  - *major* (Kützing) Rabenhorst
  - *major* var. *Transversa* (Schmidt) Cleve
  - *substomatophora* Hustedt
- *Planothidium* Round & Bukthiyarova
  - *dubium* (Brébisson) Round & Bukthiyarova
  - *ellipticum* (Cleve) Round & Bukthiyarova
  - *hauckianum* (Grunow) Round & Bukthiyarova
- *Reimeria* Kociolek & Stoermer
  - *sinuata* (Gregory) Kociolek & Stoermer
- *Rhopalodia* O. Müller
  - *gibba* (Ehrenberg) O. Müller
- *Sellaphora* Mereschkowsky
  - *pupula* (Kützing) Mereschkowsky
  - *rectangularis* (Gregory) Lange-Bertalot & Metzeltin
- *Stauroneis* Ehrenberg
  - *phoenicenteron* (Nitzsch) Ehrenberg
- *Staurosira* Ehrenberg
  - *construens* Ehrenberg
  - *construens* f. *Subsalina* (Hustedt) Bukhtiyarova
  - *construens* var.*venter* (Ehrenberg) Hamilton
- *Staurosirella* Williams & Round
  - *pinnata* (Ehrenberg) Williams & Round
- *Stenopterobia* Brébisson
  - *sigmatella* (Gregory) Ross
- *Stephanodiscus* Ehrenberg
  - sp.
- *Surirella* Turpin
  - *biseriata* Brébisson
  - *brebissonii* Krammer & Lange-Bertalot
  - *guatimalensis* Ehrenberg
  - *nervosa* (Schmidt) Meyer
  - *tenera* Gregory
  - *Synedra* Ehrenberg
  - *ulna* (Nitzsch) Ehrenberg
- *Tryblionella* W. Smith
  - *levidensis* W. Smith

species, maintaining constantly high relative abundances (> 30 %). Although *Staurosirella pinnata* also has a relatively high TP optimum (14-15 µg/l) it appears to have a high amplitude with regard to lake trophic status (cf. Hofmann 1993, Krammer & Lange-Bertalot 1991). Interestingly, *S. construens* var. *subsalina* and var. *venter* again appear in this period with peak values (up to 14 % for the latter) around 1984.

Hydrocarbons

Concentration of long-chain hydrocarbons was higher in the superficial sediments than in the deeper samples, where the short-chain hydrocarbons were more prevalent. The concentration of hydrocarbons showed variation from a minimum of 0.32 mg/g at centimeter 16, to a maximum of 6.68 mg/g at centimeter 5, indicating a clear tendency to increasing concentration towards the surface layers (Fig. 4). The hydrocarbon concentrations were twice to three times higher in the superficial sediments than in the deeper layers.

On the other hand, the ratio TAR$_{HC}$ (Terrestrial/Aquatic hydrocarbons) indicates that the deepest sediments have the lowest values for this relationship. The TAR$_{HC}$ is generally greater than 1, with a maximum value of 5.4, and quite variable in all the core for sediments deposited since ~1920, but it is smaller than 1 and less variable in the older sedimentary record from Laguna Chica of San Pedro, distinguishing two periods of increased TAR values. One period starts around 1920 and goes on until 1968, the other period goes from 1972 until 1996 (Fig. 4)

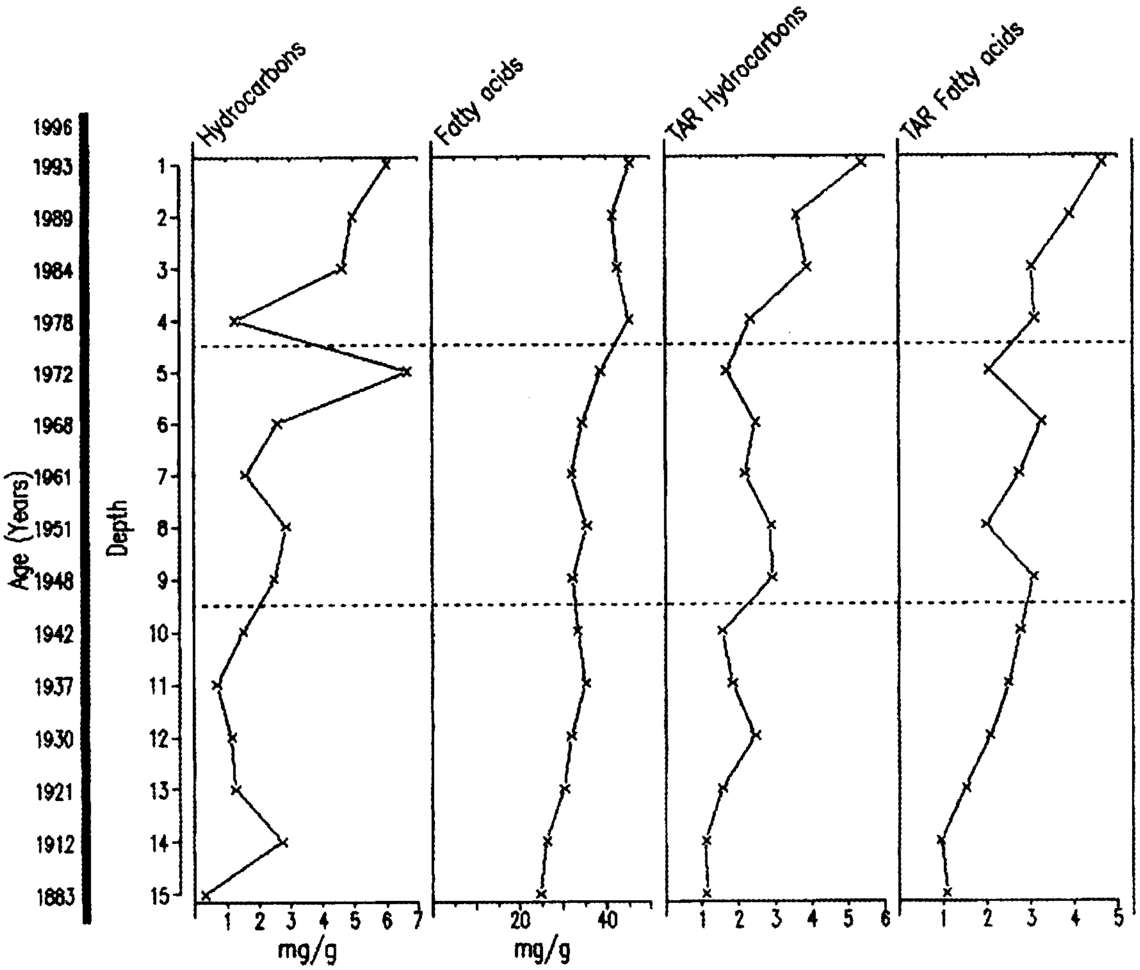

Fig. 4. Depth profiles of hydrocarbons, fatty acids, TAR$_{HC}$, and TAR$_{FA}$ in sediment core of Laguna Chica of San Pedro.

Perfil estratigráfico de hidrocarburos, ácidos grasos, TARH$_C$ y TAR$_{FA}$ en la columna de sedimento de Laguna Chica de San Pedro.

Fatty acids

Fatty acid concentration was five times greater than the hydrocarbon concentration. As described for the hydrocarbons, the concentration of long-chain fatty acids was higher in the upper part of the core, and the older sediments showed higher concentration of short-chain fatty acids. The values varied between 24.8 mg/g at centimeter 16 and 45.4 mg/g at surface layer (Fig. 4).

The TAR_{FA} (Terrestrial/Aquatic Fatty Acids) profile showed an increase toward the top of the core, with values 4-5 times higher than the deeper sediments. Like the TAR_{HC} profiles, with the TAR_{FA} patterns it was possible to distinguish two periods of increase, one between 1972 and 1996 and another between 1920 and 1968 (Fig. 4).

DISCUSSION

A total of 97 diatom taxa were identified in Laguna Chica of San Pedro short core. The most abundant taxa are *Staurosirella pinnata*, *S. construens*, *Aulacoseira granulata*, *Cyclotella stelligera*, *Diploneis* cf. *subovalis* and *Surirella guatimalensis*. Of the total diatom taxa (97), 19 were reported by Rivera (1970), which means that 78 diatom taxa are reported for the first time in Laguna Chica of San Pedro. Previous studies on the diatom flora of this lake were restricted to the phytoplankton component, collected with plankton nets with mesh sizes > 30 µm (Rivera 1970); the total number of species reported in these studies is therefore much lower (29), the most abundant species reported being *Surirella guatimalensis, Aulacoseira granulata ("Melosira granulata"), A. italica ("Melosira italica"), Synedra ulna, Synedra rumpens* var. *familiaris* and *Ceratoneis arcus*. Most other species were only represented by one or two frustules (Rivera 1970). This can largely be attributed to the large number of benthic taxa in the core. However, if we consider that the total number of species present in each stratum ranged between 24-37, the difference in the number of taxa is not so pronounced.

The diatom stratigraphy documents the existence of three distinct periods in the limnological history of this lake. While changes in diatom species composition are rather gradual during the first two periods, there are marked and rapid shifts in community structure in the last period. From 1883 to 1942, eutrophic species (such as *Aulacoseira granulata*, *Staurosira construens* and *Gyrosigma acuminata*) were dominant; there is even a gradual but distinct increase in the relative abundance of the first two species during this period. It thus appears that the lake was becoming increasingly eutrophic, something which could be related to the logging of native forest in the catchment area. Logging must have been quite gradual at the beginning of the century (by 1943 native forest still occupie 70 % of the catchment area). However, by 1955 another 17 % of forest appears to have been logged, which could explain the sedimentation rate peak in stratum 9 (1948), at the beginning of the second period. It is well-known that logging of indigeneous forests can significantly increase sedimentation rates in catchment lakes (cf. Page & Trustrum 1997), usually accompanied by a concomitant runoff of organic material (and inorganic nutrients) from catchment soils (Hornung & Reynolds 1995). Indeed, organic matter concentrations in the lake sediments increase slightly until the beginning of the 1940's. The ratio between the longer and shorter chainlength hydrocarbons and fatty acids also increases, which is indicative of the increased importance of higher plant materials in the bulk of fatty acids. As no extensive submerged water plant cover was present in Laguna Chica of San Pedro at that time, this material must have come from terrestrial sources in the catchment.

During the second period (1948-1972) there is a second maximum in sedimentation rates (1968), but this is not accompanied by an increase in organic matter content of the sediment. On the contrary, organic matter content is lowest when the peak in sedimentation rate occurs. This decline in organic matter content could be due to the fact that after 1961 the total surface area of native forest remained more or less intact (at around 34 %) until the late 1970's. The sedimentation peak in 1968 must then have mainly been caused by shifts in land uses (forestry, pasture, clear cut areas and mixed scrub vegetation) within the remainder of the catchment area. These shifts would not have caused an additional supply of organic material to the lake as logging of the native forest in this area, earlier on in the century, would have largely depleted the organic matter of the top soil. Note however that the ratio of longer to shorter chainlength fatty acids does show a maximum value at stratum 6 so although the total concentrations of fatty acids in this period do not peak, the contribution of terrestrial macrophyte material is higher than in the two previous strata.

The diatom data are in accordance with this observation: the eutrophication trend of the first period culminates with the appearance of *Staurosira construens* var. *venter* and fo. *subsalina* in 1948, when sedimentation rates and organic matter content reached a first maximum. These two taxa have often been associated with rapid changes in water chemistry, and especially trophic status, e. g., in lakes following deglaciation (leaching of the bed material) (cf. Denys 1990). During the second sedimentation peak in 1968, both taxa were absent.

In the third period, which was characterized by increased sedimentation rates and levels of organic matter, *Staurosira construens* var. *venter* and fo. *subsalina* re-appear. Strikingly, they reach their highest abundances when the turnover in diatom species composition is most pronounced, from a community characterized by meso- and eutrophic (e.g., *Staurosira construens*) to an assemblage with a considerable proportion (about 30 %) of oligotrophic species (mainly *Aulacoseira distans* and *Cyclotella stelligera*). A similar phenomenon can be seen in diatom stratigraphies shown in Brenner et al. (1999) where *S. construens* var. *venter* peaks when the dominant taxon abruptly decreases.

As already mentioned, the third zone is characterized by a marked increase of indicators for oligotrophic conditions. This is in accordance with present values for nutrients which show that Laguna Chica of San Pedro should be classified as a dys- to oligotrophic lake (Lampert & Sommer 1997). This may appear paradoxical for a number of reasons. First, sedimentation rates reach a new maximum from the 1980's onwards. This rise in sediment input into the lake coincides with a strong decline in the remaining surface area of native forest in the catchment basin (from 34 % in 1978 to 13 % in the 1990's). One would therefore expect, as with the first sedimentation rate maximum at the end of the 1940's, that relatively undegraded forest top soils, rich in organic matter and nutrients, would have been exposed to erosion. Second, the introduction of new forestry management methods has led to an increasing use of fertilizer in the plantations (which occupy about 50 % of the total catchment surface by 1994) during the last decade. Even if this does not lead to increasing nutrient concentrations in the lake, one would certainly not expect a decrease.

We therefore postulate that the introduction of the submersed macrophyte *Egeria densa* in the mid-eighties is responsible for the apparent oligotrophication of the lake. It is now well-established that dense beds of submersed macrophytes can have a significant impact on the nutritional economy of lakes. During the growing season, they take up and store nutrients, which are then not available for the phytoplankton. Their structured environment also influences biogeochemical processes such as denitrification and phosphorus availability, which can affect nutrient conditions in the pelagic (Søndergaard & Moss 1998). Although the latter processes are complex and submersed macrophytes can, under certain conditions (which also depend on macrophyte type and density), actually increase the potential for e. g., phosphorus release from the sediment, the overall effect of extensive macrophyte growth is one of reducing nutrient availability to the phytoplankton. The presence of macrophytes can not only affect phytoplankton biomass, but also species composition. Beklioglu and Moss (1996) observed a significant decline in *Aulacoseira granulata* in the presence of macrophytes in mesocosm experiments.

In the study of a short core (spanning the last 150 years) from Orange Lake (Florida, USA), Brenner et al. (1999) noted a shift in diatom species composition when submersed macrophytes were introduced in the 1930's. In addition, this shift mainly concerned a transition from a planktonic community dominated by the eutrophic plankton species *Aulacoseira ambigua* to a community which largely consisted of periphytic taxa, which is mainly due to the fact that Orange Lake is very shallow ($Z_{mean} < 2$ m). However, diatom-based limnetic total P inferences still indicated that total P concentrations had significantly decreased over the last 60 years. Interestingly, this occurred despite strong indications that the actual nutrient loading in the lake had increased during the last decades due to human disturbances.

Furthermore, an additional limitation exists to interpret changes registered in the diatom associations of Laguna Chica, which is the lack of information regarding the autoecology of the species present in the continental waters of Chile. A good evaluation of the past environmental conditions, depends on the actual ecological knowledge of the species (Anderson & Ripey 1994). Therefore, previous use of any biological indicator, in the interpretation of the past environmental conditions, the optimum ecology and tolerance ranges of the species should be quantified and evaluated (Smol & Glew 1992). Recently, most of this information was obtained directly from literature, that is, it was only possible to recognize qualitative changes in the taxonomic composition of the diatoms deposited in the sediments (e.g., "the presence of these taxa suggests that the lake was oligotrophic").

The three periods identified by the stratigraphic analysis of diatom associations, agree with the three sedimentologic events established through the sedimentation rates. Sedimentation rates, which are the base to evaluate the erosion rates, are influenced by a many factors, such as size proportion of the basin with respect to the lake, pedologic and geological characteristics and especially human activities, i.e., the use of soil developed over the basin. According to Cisternas (1999), the basin of Laguna Chica has been impacted in the last fifty years (1943-1994), by land use change and the increase of the erosion rates. This means that only 9% of the total basin surface remained without intervention.

A trend toward increasing proportions of hydrocarbons at the beginning of 1940 in the core may record progressively greater delivery of hydrocarbons from watershed sources. The TAR_{HC} is generally greater than 1 and quite variable in all the core for sediments deposited since ~1920, but it is lesser than 1 and less variable in the older sedimentary record from Laguna Chica of San Pedro. Typically, contribution of land-derived organic matter contains higher proportions of n-alkanes than those from aquatic algae; therefore parameters like TAR_{HC} may overrepresent the absolute amounts from terrigeous sources (Goossens et al. 1989, Meyers & Ishiwatari 1993). Nevertheless, this ratio is valuable for determining changes in relative contributions of organic matter from land and lake flora. The contrast between the low TAR_{HC} values in older sediments and the higher and more variable values since the ~1920 reflects a change in the geolipids delivery to the lake. This pattern reflects the increasingly deforestation of the watershed, which has accelerated the erosion and land runoff from the catchment.

Concentrations of total extractable fatty acids are six times greater than the total hydrocarbons and they decrease with sediment depth in the core. As noted for the contributions of total hydrocarbons to the lake sediments, fatty acids can originate from both lake and land sources. Similarities between fatty acid patterns for the core and hydrocarbon patterns suggest that source change rather than degradation, have been the major factors controlling fatty acids concentration in the sediments. Fatty acids as a group are ten times more susceptible to degradation than hydrocarbons (Haddad et al. 1992, Meyers and Eadie 1993).

As described for the hydrocarbon compositions of the sediment core, we used a ratio of biomarker n-alkanoic acid source indicators to determine possible changes in the terrigenous-aquatic mixture of fatty acids. Like the TAR_{HC} profiles, the TAR_{FA} patterns are dominated by land-derived material, particularly in sediments deposited between 1972 and 1996. An increase in the TAR_{FA} values starting ~1920.

In both profiles, it is possible to distinguish two periods of increased TAR values. One period starts around 1920 and goes on until 1968, the other period goes from 1972 until 1996. It is thought that the elevated TAR values of the first period reflect the effects of the gradual deforestation of the watershed, which has accelerated the erosion and runoff from the catchment. The even higher values measured for the second period are probably result of the invasion of the lake by the exotic submersed macrophyte *Egeria densa,* which causes an increase in the input of long-chained hydrocarbons and fatty acids. Unfortunately, the hydrocarbon and fatty acid compositions of the aquatic plant *Egeria densa* and land plants are very similar, so it is not possible to distinguish between both sources when interpreting the TAR values.

It is important to keep in mind that although the trophic state of the lake, as inferred from the diatom stratigraphy, appears to have improved considerably during the last 15 years; there are no indications to believe that the actual nutrient input in the lake has decreased during this period. On the contrary, recreation, urbanization and intensive exotic forestry (with increasing use of fertilizer) have all increased in the watershed of Laguna Chica of San Pedro during this period. In the above-mentioned study on Orange Lake (Brenner et al. 1999), there are strong indications that despite a decrease in inferred total P concentrations during the last sixty years, the actual nutrient loading in the lake had increased due to human disturbances. This is mainly due to the buffering effect of macrophyte stands on increasing nutrient input (Balls et al. 1989). Temporary macrophyte control measures in Orange Lake during the 80's immediately caused a brief increase in inferred limnetic total P (Brenner et al. 1999). It is therefore not unlikely that the present trophic state of Laguna Chica of San Pedro could change abruptly if the buffering effect of the macrophyte were to disappear.

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