PCBs in a dated sediment core of a high altitude Lake in the Chilean Altiplano: The Chungara Lake

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Environmental evidence of fossil fuel pollution in Laguna Chica de San Pedro lake sediments (Central Chile)

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The lake sediment record of SCPs shows the record of fossil-fuel derived pollution in Central Chile.

Abstract

This paper describes lake sediment spheroidal carbonaceous particle (SCP) profiles from Laguna Chica San Pedro, located in the Biobío Region, Chile (36° 51′ S, 73° 05′ W). The earliest presence of SCPs was found at 16 cm depth, corresponding to the 1915–1937 period, at the very onset of industrial activities in the study area. No SCPs were found at lower depths. SCP concentrations in Laguna Chica San Pedro lake sediments were directly related to local industrial activities. Moreover, no SCPs were found in Galletué lake (38° 41′ S, 71° 17.5′ W), a pristine high mountain water body used here as a reference site, suggesting that contribution from long distance atmospheric transport could be neglected, unlike published data from remote Northern Hemisphere lakes. These results are the first SCP sediment profiles from Chile, showing a direct relationship with fossil fuel consumption in the region. Cores were dated using the ^{210}Pb technique.

Keywords: Carbonaceous particles; Atmospheric pollution; SCP; Lake sediments; Concepción-Chile

1. Introduction

Chile is one of the most industrialised countries in Latin America, with over 90% of its population living in urban areas. As the Chilean economy grows, so does the amount of airborne pollution generated by fossil-fuel combustion, affecting air quality and human health in most industrial cities (Didyk et al., 2000; Tsapakis et al., 2002). In particular, the Biobío Region, located between 36° 00′ and 38° 20′ south latitude, hosts a large concentration of process industries including cellulose plants, sawmills, fisheries, textiles, steel making, oil refineries, petrochemical plants, electricity production and, until recently, coal mining. The region has a population density of around 51.7 inhabitants km^{-2}, double the Chilean average, mostly living in small and medium sized towns. As a result of the accelerated industrialisation process during the past 50 years in the Biobío Region, signs of water and air pollution have been identified in recent years (Barra et al., 2001a; CONAMA, 1994; Mudge and Seguel, 1999). In this respect, appropriate environmental management and prevention measures need to be defined in order to prevent further damage to the environment and public health. Moreover, the source of key pollutants should be identified as a prerequisite for effective regulatory controls. Combustion processes, from both natural and human sources, are thought to account

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for most air pollution in the Biobío Region. Wood and coal burning can be traced back to the mid-19th century, whereas oil appeared during the first part of the 20th century. In recent years, natural gas has also been introduced as a domestic and industrial fuel.

In the absence of direct measurements, or monitoring, lake sediments can be used as a natural archive to determine the temporal trends of atmospherically deposited pollutants. Fly-ash particles produced from high temperature fossil-fuel combustion are dispersed by air currents, and deposited by both wet and dry means, after travelling from their sources. Spheroidal carbonaceous particles (SCPs), a component of fly-ash, are formed from the incomplete high temperature combustion of fossil fuels such as coal and oil. In lake sediments, SCPs can be used to indicate temporal (from dated sediment cores) and spatial (from surface sediments) distribution of environmental contamination derived from industrial coal and oil burning (Rose et al., 1995). Further, SCP concentration profiles have been used to date recent lake sediments and to show the evolution of industrial combustion processes within a region (Griffin and Goldberg, 1979; Renberg and Wik, 1985; Rose et al., 1995). Although a number of papers have been published on lake and marine sediments in the Biobío Region, little has been done to associate the sediment record to the environmental impacts of fossil-fuel burning.

This paper describes dated lake sediment SCP profile from Laguna Chica San Pedro (LCSP), located near Concepción, the capital town of the Biobío Region, Chile. The SCP concentration profile is compared with results obtained from Galletué lake, a relatively pristine site located in remote highlands near the Andes, and other locations. The feasibility of such methodology as a tool to identify trends in airborne pollution is assessed.

2. Materials and methods

2.1. Study area

2.1.1. Laguna Chica de San Pedro lake (LCSP)

LCSP and Galletué lake lie in the Biobío Basin, situated within the 8th and 9th Administrative Region in Central Chile (Fig. 1). The former is a coastal lake, which lies at 36° 51′ S, 73° 05′ W, on the mountain range of Nahuelbuta, near the Pacific Ocean. This lake is surrounded by mountains of metamorphic basement geology on its eastern side and by layers of fluvial balsatic sediments to the west (Acencio, 1994).

Present environmental conditions around LCSP arise as a result of increasing land-degradation processes. Land-use changes started with the arrival of Spanish colonisers, in the early 17th century. The Spanish farming model, based on intensive ungulate cattle raising and cereal crops, displaced the pre-Columbian system, which was characterised by less environmentally aggressive practices (Cisternas and Torrejón, 2002; Torrejón and Cisternas, 2002, 2003).

During the 19th century farming activities intensified, mainly due to wheat, timber, firewood, and charcoal production, with serious consequences to native

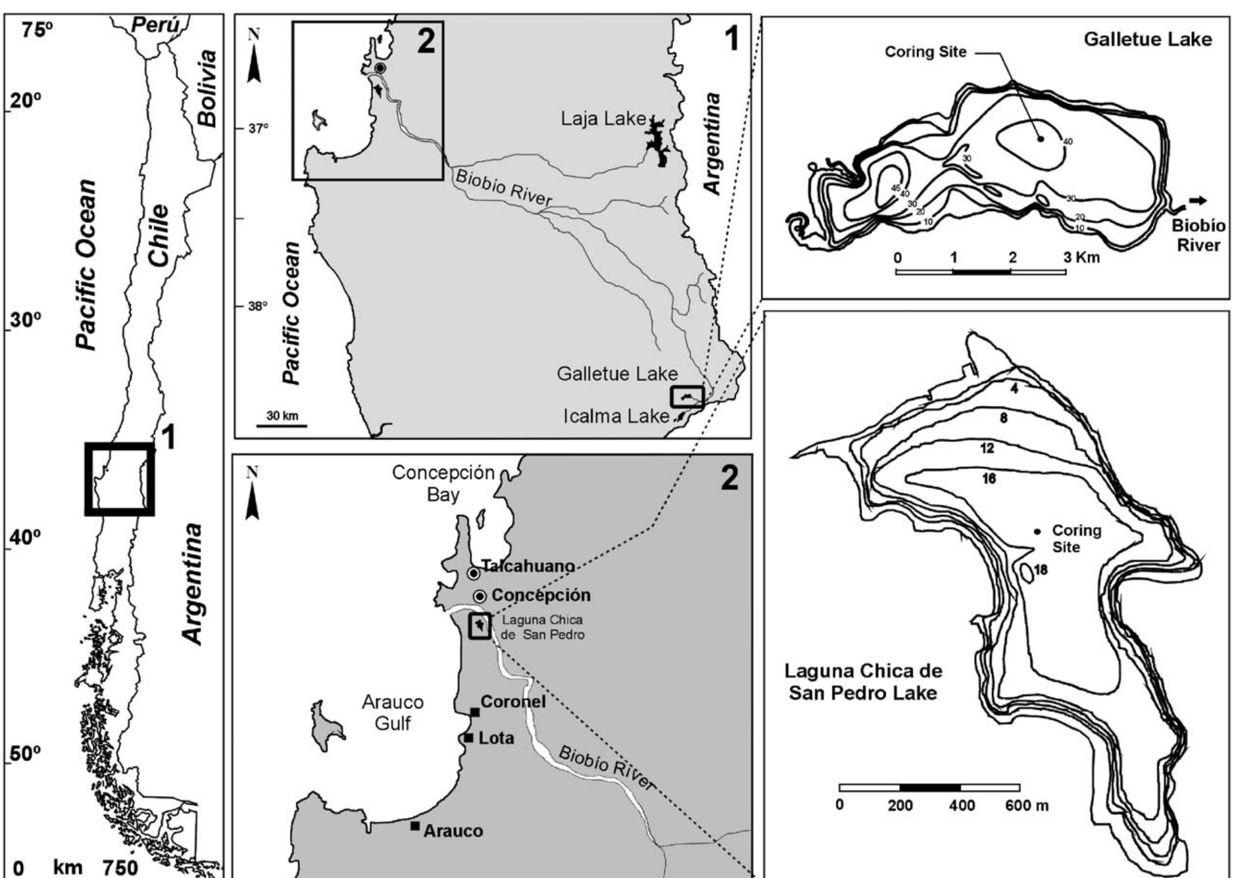

Fig. 1. Location of Laguna Chica de San Pedro and Galletué lake, bathymetric maps and coring sites.

vegetation, and land use (Azócar and Sanhueza, 1999; Sanhueza and Azócar, 2000). Furthermore, greater timber demand by coal mining boosted exotic plantations to the detriment of native forests (Astorquiza, 1929; Sanhueza and Azócar, 2000).

Throughout the 20th century, government incentives for afforestation (e.g. "Ley de Bosque" in 1931 and Decree Law "D.L. 701 de Fomento Forestal" from 1974, currently Law No. 19.561), in addition to urban development of rural zones, contributed to shape present land use structure in the study area (Azócar and Sanhueza, 1999; Cisternas, 2000). The effects of such environmental changes on water quality and lake trophic conditions (Urrutia et al., 2000a), chlorinated pesticide deposition in lake sediments (Barra et al., 2001b) and sediment yield within the basin (Cisternas et al., 2001) have all been recently studied.

The climate in the study area is Mediterranean (temperate warm), and influenced by maritime air masses, causing moderate temperatures. The mean annual temperature is 12 °C, and the difference between the hottest and coldest monthly average temperature is about 8 °C. Temperatures below 10 °C occur from June until September, while temperatures above 15 °C occur from December to February. The typical annual precipitation is around 1300 mm, occurring mainly from May to August. Southwesterly winds predominate in the area, with an annual mean within 8–11 knots and reaching a maximum of over 50 knots.

2.1.2. Galletué lake

Galletué lake is located at 38° 41′ S, 71° 17.5′ W, at 1150 m above sea level, near the Argentinean border. This high mountain lake receives drainage from Ñirreco and Miraflores pristine rivers on its western side, and discharges to the Biobío river on its opposite side (Parra et al., 1993). The area is characterised by the presence of high altitude (viz. 2000 m high) geomorphic structures to the east and volcanic cones and a granitic mountain range (peak heights >3000 m) to the west (Rondanelli, 2001). Limnological and morphological parameters corresponding to both lakes are listed in Table 1.

Changes in climatic conditions (from cold and moist to cold and dry) experienced during the last 5000 years have generated changes in vegetation around Galletué lake (Rondanelli, 1993). Currently, *Araucaria araucana*, *Nothofagus pumilio* and Gramineae species dominate local vegetation (Ugarte, 1993). The natural resilience of the environment would not have been affected by the pre-Columbian system (Torrejón, 2001). As the first settlements in the region only started at the end of 19th century, e.g. Liucura, Lonquimay (Asta-Buruaga, 1899). The present population density in rural areas is around 8.6 inhabitants km^{-2}. There is no industrial activity within 150 km of Galletué lake.

Scarce local climatic data indicates that the annual precipitation is within the range 1180–3018 mm (1990–1991), with an annual mean of around 1900 mm (Parra et al., 1993). In addition, the lowest temperature is −6 °C (wintertime) and the highest is 29 °C (summertime), and predominant wind direction is manly south west around this site.

Table 1
Morphometric parameters of Laguna Chica de San Pedro and Galletué lake

Parameters	Laguna Chica de San Pedro[a]	Galletué lake[b]
Height (m.a.s.l.)	5.0	1150.0
Maximum depth (m)	18.0	45
Mean depth (m)	10.3	27
Maximum length (km)	1.9	6.7
Maximum width (km)	0.87	3.3
Perimeter (km)	5.7	30.0
Lake area (km^2)	0.82	12.5
Catchment area (km^2)	4.5	320.0
Volume (km^3)	0.0086	0.338
Shore development	1.8	–
Mean depth/maximum depth	0.57	0.6
Catchment area/lake area	5.5	25.6
Catchment area/volume (km^{-1})	523.3	947.75

[a] Extracted from Urrutia et al. (2000b).
[b] Extracted from Parra et al. (1993).

2.2. Sediment sampling

Sediment cores were collected from the central basin of LCSP (at depth 17 m) in May 2003 and from the largest basin of Galletué lake (at 40 m depth) in February 2002. The latter was performed using a Uwitec gravity corer fitted with a 60 cm long Plexiglass tube and the former by divers operating a coring device equipped with 1 m long Plexiglass tubes with 5.8 cm internal diameter. In both cases, sampling sites were selected with the aid of a Lowerance 16 echo sounder and duplicate cores were taken 1 m apart. After recovery, cores were capped, sealed and stored at 4 °C at the Laboratories at the Environmental Science Centre until analysis.

Sediment cores were sliced in 1 cm sections, using a Plexiglass spatula and samples for mean grain size analysis were taken. LCSP sediment samples were oven dried at 60 °C until constant weight, and stored in clean plastic bags prior to dating estimations, total organic matter (TOM), inorganic carbonate ($CaCO_3$) and SCP determinations, whereas sediment samples from Galletué lake were prepared to dating analysis and SCP estimations.

2.3. Sediment analysis

LCSP sediment analyses were conducted at the Environmental Biology Laboratories of the Environmental Science Centre, Universidad de Concepción, Chile. Total organic matter (TOM) and inorganic carbonate ($CaCO_3$) content were estimated by loss-on-ignition techniques (LOI). About 1 g sample was oven dried at 105 °C for 24 h, and then heated at 550 °C for 4 h to estimate TOM. Further heating at 1000 °C for 2 h was conducted to estimate $CaCO_3$ content. Both TOM and $CaCO_3$ were determined as a percentage of dry weight (Boyle, 2001).

Wet sediment samples were segregated by ultrasound before mean grain size analysis was carried out by an Electronic Micro-particle Analyser ELZONE-282PC. The mean diameter was calculated as micrometre units.

2.4. Radiometric dating methods

2.4.1. Laguna Chica de San Pedro lake (LCSP)

^{210}Pb analysis was undertaken by alpha spectrometry of its daughter ^{210}Po according to the methodology described by Flynn (1968). ^{210}Po was autoplated onto silver disks at approximately 75 °C for 2.5 h in the presence of ascorbic acid. The activity was counted in a CAMBERRA QUAD alpha spectrometer, (model 7404) over 24–48 h, in order to achieve the desired counting statistics (1 σ error; 4–10%). Assuming that ^{210}Po activity is in equilibrium with ^{210}Pb, the former is calculated taking into account the natural radionuclide/tracer ratio, and the tracer activity at the time of plating. Further, corrections are made based on the delay between plating and counting processes, and the period elapsed between the collection date and the analysis of the samples. Spectrometer background corrections were also taken into consideration. The activities were expressed in dpm per gram based on ash weight.

^{210}Pb has been extensively used for dating recent lacustrine and marine sediments (Appleby, 2001; Appleby and Oldfield, 1978, 1983; McCaffrey and Thomson, 1980). As a result of precipitation and dry fallout, the lead isotope, ^{210}Pb, is deposited and transported to the bottom sediments where it is accumulated producing an excess over the ^{210}Pb in equilibrium with radium isotope ^{226}Ra (supported ^{210}Pb). Assuming that this excess ($^{210}Pb_{xs}$, unsupported ^{210}Pb) flux is constant (constant rate of supply model), the age of the sediment from a particular depth in the core can be estimated using the general decay equation (McCaffrey and Thomson, 1980). The $^{210}Pb_{xs}$ activity in the sediment samples was estimated from the total ^{210}Pb measured, minus the supported activity (constant values of ^{210}Pb from sections of the core in equilibrium with ^{226}Ra). The supported activity was estimated from the exponential curve of total ^{210}Pb (Appleby and Oldfield, 1978; Binford, 1990). Compaction was taken into account by using exponential bulk sediment density (Christensen, 1982). The geochronology obtained was verified with independent historical temporal tracers such as *Pinus radiata* pollen, the historical record of which is well known in Chile (Astorquiza, 1929; Contesse, 1987).

2.4.2. Galletué lake

The Galletué lake geochronology was undertaken at Sektion Analytik - Abteilung Umweltradioaktivität und -isotope UFZ zentrum, as a part of Research Project DIUC No. 230.310.0.35-1.0. Vertical distributions of total ^{210}Pb, ^{226}Ra (supported ^{210}Pb), and ^{137}Cs (temporal marker) were determined. Consideration of the unsupported ^{210}Pb profile led to the constant initial concentration (CIC) dating model being applied to estimate the dates, and verified by the ^{137}Cs activity profile. ^{210}Pb dates allowed a chronology between 2002 and 1915 to be ascribed to the 20 cm long core.

2.5. Spheroidal carbonaceous particles (SCPs) analysis

SCP analyses were carried out by chemical digestion with mineral acids according to the methodology described by Rose (1994). A known fraction (viz. 20 μl) of the remaining suspension was placed on a microscope cover slip and allowed to dry, before being fixed using "Naphrax" diatom mountant. SCP counting was carried out using a light microscope at 400–1000× magnification. Spheroidal, elliptical, and rounded fragments (>75% of the whole particle) were considered in these estimates. SCP concentration was calculated as "number of particles per gram of dry sediment" (g DM^{-1}). The detection limit was ~10 SCPs g DM^{-1}, and the finding of a single particle is enough to establish the onset of SCP presence in lake sediments.

2.6. Energy consumption by local industry

Coal and oil consumption by Chilean industry was estimated from the National Energy Council database (CNE, 2003). The consumption of these fuels in the pulp and paper, steel, petrochemical, cement and fishing industries was considered in these estimates, since these are the most important industrial activities affecting the study area.

3. Results and discussion

3.1. Sediment analysis in LCSP

3.1.1. Grain size analysis

Grain size composition shows no major changes in the upper 60 cm of the core, being dominated by fine silt mud according to the Wentworth size classification (5.1–7.5 μm) (Fig. 2). However, in the 60–65 cm section, mean grain size changes monotonically and sharply from 5.5 μm at 60 cm to 8.5 μm at 65 cm. There appears to be little change in mean grain size with depth. The majority of sorting values correspond to a 'very well sorted' classification (<0.35 ϕ), according to the definitions stated by Folk (1980). Results show that there is little variability in the core.

3.1.2. TOM and $CaCO_3$

Fig. 2 shows TOM and $CaCO_3$ content profiles. TOM content varies with depth from ~15% in the surface sediment to ~2% in the 65 cm section. Natural decomposition of organic matter could account for this. $CaCO_3$ content also decreases with depth, varying from around 6–7% for most of the core to 2% in deeper sections. The bulk density profile shows a monotonic increase with depth. However, three sections show sharp increases in bulk density (i.e. 0–6, 40–46, and 60–65 cm sections). The increase in bulk density from the 0–6 cm section could be a result of higher water content and less compaction, whereas the increase in the 60–65 cm section seems to be correlated with the changes in TOM and $CaCO_3$.

3.1.3. Lead-210 activity

Fig. 2 also shows the total ^{210}Pb profile determined from the LCSP core. The total ^{210}Pb profile declines neither monotonically with depth nor in accordance with usual radioactive decay. Some of these irregularities could result from changes in sedimentary components rather than mixing processes or benthic activity. As shown in Fig. 2, laminations observed in X-ray images show that no vertical mixing has occurred. Moreover, this variable darkening of the X-ray film at different depths would account for heterogeneities in the sediments (Axelsson, 1983). However, changes in erosion rates from the catchment could account for such irregularities in ^{210}Pb. Most of the estimated $^{210}Pb_{xs}$ is found in the uppermost 20 cm of the core. The lowest $^{210}Pb_{xs}$ occurs at 9–10 cm depth, whereas the highest $^{210}Pb_{xs}$ value occurs at 1–2 cm depth.

3.1.4. Chronology

Supported ^{210}Pb activity ($^{210}Pb_{ss}$), which is assumed to be in equilibrium in the sediment (Appleby and Oldfield, 1983; Binford and Brenner, 1986), was determined by averaging the three deepest activities until the mean plus one standard deviation was lower than the next upper activity (Binford, 1990). This value was corroborated by considering mathematical models for density and ^{210}Pb activity under sediment compaction. The corresponding model parameters are presented for comparison in Table 2.

Because of the irregular $^{210}Pb_{xs}$ activity, only the constant rate of supply (CRS) dating model was used to produce a chronology and determine sedimentation rates (Appleby and Oldfield, 1978); corresponding standard deviations were estimated by first order analysis (Binford, 1990). The $^{210}Pb_{xs}$ inventory was calculated from the equation in Turekian et al. (1980).

The $^{210}Pb_{ss}$ concentration, $^{210}Pb_{xs}$ inventory and $^{210}Pb_{xs}$ flux are shown in Table 3. These values are comparable to those obtained for Raqui and Rocuant salt marshes (Muñoz and Salamanca, 2003), Aculeo Lake in Central Chile (Jenny et al., 2002) and in Concepción Bay (Salamanca, 1993), but differ from those reported by Cisternas and Araneda (2001). Ages estimated by the CRS chronology, are shown in Table 4. The oldest available ^{210}Pb date corresponds to 1880 ± 26 at 18 cm depth. First *Pinus radiata* pollen grains appeared at 16–17 cm depth, corresponding to the 1903–1915 period, when most exotic plantations around the study area reached a state of maturity (Astorquiza, 1929). These results agree with the *Pinus radiata* pollen horizon reported by Cisternas and Araneda (2001). 1977, estimated from the CRS model to be at 10 cm depth, was adjusted to 1976 by considering the age standard deviation.

The highest and lowest sedimentation rate are observed at 10 cm section (1.48 cm yr^{-1}) and at 18 cm section (0.044 cm yr^{-1}), respectively. This would indicate that either natural or human disturbances in the drainage basin, or both, have led to an increase in sedimentation rates during the last decades (Table 4). These sedimentation rates are comparable to those reported by Cisternas and Araneda (2001). Interestingly, changes in sedimentation rate are not reflected in mean grain size, TOM, and $CaCO_3$ content due to

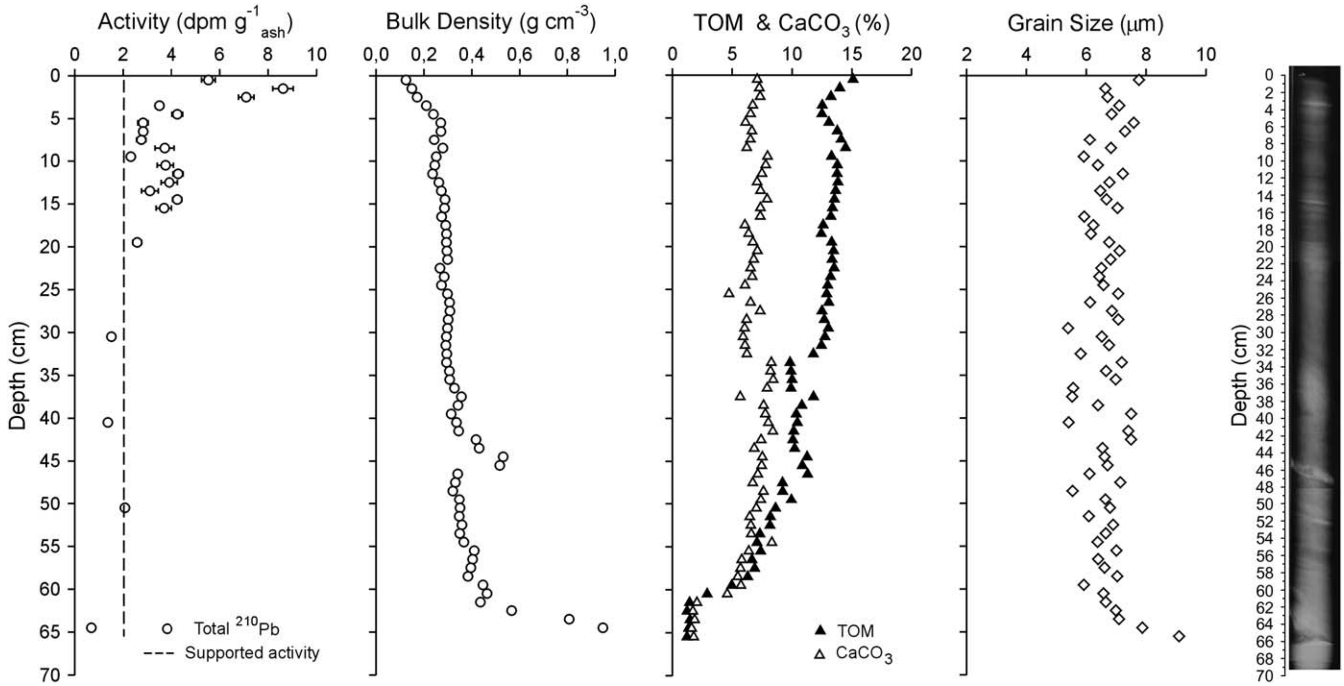

Fig. 2. ^{210}Pb total activity, bulk density; TOM and $CaCO_3$, grain size profiles and an X-ray image in lake sediments from Laguna Chica de San Pedro.

allochthonous material from the watershed is composed of clayey soils, quartz debris and terrestrial organic matter such as leaves and branches (FIA, 1990). The accuracy of the LOI method depends on both the organic matter content and the nature of the sediment. Most of the clay minerals contain structurally bound water that is released progressively on heating (Boyle, 2001); thus LOI values do not represent true organic matter content in sediments. Additionally, Urrutia et al. (2000a) demonstrated that terrestrial organic matter is greater than aquatic sources in LCSP lake sediments during high erosion periods. Moreover, the logging of indigenous forests can significantly increase sedimentation rates in the catchment area (Page and Trustrum, 1997); and also this erosion process is usually accompanied by a concomitant runoff of organic matter (and organic nutrients) from the catchment soils (Hornung and Reynolds, 1995). In this sense, it is likely that MOT, in extent $CaCO_3$, content would not reflect increments in sedimentation rates in LCSP.

3.2. SCPs in lake sediments

SEM photographs of SCP from LCSP are shown in Fig. 3, and the SCP concentration profile for LCSP is shown in Fig. 4. Triplicate measurements were taken for each core section, and up to 20 SCP were counted on each slide. Particle sizes were lower than 60 μm. SCP sizes lower than 10 μm account for about 79% of total particles, whereas about 16% and 4% are in the range 11–30 μm and 31–60 μm, respectively. No distinction is made here between SCPs from coal and oil burning processes.

The first presence of SCPs was recorded at 16 cm depth, corresponding to 1915–1937. No SCPs were found at lower depths, i.e. before the early 20th century. Historical records indicate that Lota City was a centre of active coal mining, manufacture and production from the mid-19th century (Astorquiza, 1929). However, a combination of low combustion temperatures, low emission rates, and low chimney stacks were probably responsible for fly-ash not reaching the lake catchment area at this time. This situation changed by the early 1920s, when pulverised coal started being used in high temperature industrial furnaces (above 1400 °C) associated with brick and porcelain manufacture at Lota City, and consolidation of thermoelectric generation at the end of the 1920s. As a consequence, fly-ash was emitted to the atmosphere at increasing rates and at greater heights, and therefore could travel longer distances than before, thereby reaching the lake area.

Table 2
Parameters for density and activity mathematical models under sedimentation compaction according to Christensen (1982)

Model	ρ_0	ρ_1	a	r^2 (%)	n (p)
Density	0.294 ± 0.004	0.20 ± 0.01	0.26 ± 0.04	95	21 (<0.01)
	S_0	r_1	S_1		
Activity	5.27 ± 0.84	0.023 ± 0.08	2.03 ± 0.41	76	16 (<0.01)

ρ_0, density at infinite depth (g cm^{-3}); ρ_1, difference between density at surface and depth (g cm^{-3}); a, compaction coefficient (cm^{-1}); S_0, surface activity (dpm g^{-1}); r_1, mean mass accumulation rate (cm yr^{-1}); S_1, supported activity (dpm g^{-1}).

Table 3
Comparison of relevant parameters of ^{210}Pb activity near the study area

	$^{210}Pb_{ss}$ (dpm g^{-1})	Inventory (dpm cm^{-2})	$^{210}Pb_{xs}$ flux (dpm cm^{-2} yr^{-1})
In this study	2.03 ± 0.42	7.62 ± 0.53	0.237
Muñoz and Salamanca (2003)	0.92–1.25[a]	6.8 ± 0.6–8.8 ± 1.1[a]	–
	–	7.7 ± 1.1–28.3 ± 1.9[b]	–
Salamanca (1993)	–	10.45 ± 4.1[c]	–
Jenny et al. (2002)	–	–	0.288 ± 0.03[d]
Cisternas et al. (2001)	–	4.68[e]	0.141[e]

[a] Raqui Salt Marsh. South-east Pacific coastal area (~36°S).
[b] Concepción Bay. South-east Pacific coastal area (~36°S).
[c] Concepción Bay, South pacific coastal area (~36°S).
[d] Lake Aculeo (33°50′S) Coastal Cordillera of Central Chile. Conversion from the original data: 48 ± 5 Bq m^{-2} yr^{-1}.
[e] Laguna Chica de San Pedro (36°51′S) Central Chile. Conversions from the original data: 757 Bq m^{-2}; 23.57 Bq m^{-2} yr^{-1}.

Sediment SCP concentrations steadily increased until the 1980s as a result of industrial activity and urban growth. Since the 1950s, steel-making and associated industries have operated in the Talcahuano area, located at about 15 km from LCSP. A sharp increase in SCP levels is observed between 4 and 6 cm depth, corresponding to the 1984–1990 period. This is a period characterised by a dramatic increase in both coal and fuel oil consumption, mainly by the local fishing industry (INE, 2003). Indeed, between 1984 and 1990, the local fish-meal industry increased production capacity from 100 000 tons fish flour/year to more than 800 000 tons fish flour/year, reaching a coal consumption of over 70 000 tons coal/year. Other production activities, such as pulp and paper, steel making, and the food industry also experienced significant production increases over that period. As the Chilean economy kept growing during the 1990s, so did energy consumption in both industrial and domestic activities.

Table 4
Ages estimated by CRS dating model in lake sediments from Laguna Chica de San Pedro

Depth (cm)	Total inventory[a] $^{210}Pb_{xs}$ (dpm cm^{-2})	Cumulative years	Sedimentation rate (cm yr^{-1})	Date
0–1	7.62 ± 0.53	1.90	0.52	2003–2001
1–2	7.18 ± 0.53	6.63	0.21	2001–1996
2–3	6.20 ± 0.52	11.50	0.20	1996–1992
3–4	5.33 ± 0.51	13.41	0.52	1992–1990
4–5	5.02 ± 0.50	17.01	0.27	1990–1986
5–6	4.49 ± 0.49	18.57	0.64	1986–1984
6–7	4.27 ± 0.48	20.22	0.60	1984–1983
7–8	4.06 ± 0.46	21.63	0.70	1983–1981
8–9	3.88 ± 0.45	25.77	0.24	1981–1977
9–10	3.41 ± 0.42	26.44	1.49	1977–1976[b]
10–11	3.34 ± 0.40	30.76	0.23	1976[b]–1972
11–12	2.92 ± 0.38	37.20	0.15	1972–1966
12–13	2.39 ± 0.36	44.62	0.13	1966–1958
13–14	1.90 ± 0.34	49.99	0.18	1958–1953
14–15	1.61 ± 0.30	66.26	0.06[c]	1953–1937
15–16	0.97 ± 0.27	87.76	0.04[c]	1937–1915
16–17	0.50 ± 0.23	100.48	0.07	1915–1903
17–18	0.33 ± 0.19	122.98	0.04[c]	1903–1880
18–19	0.17 ± 0.13	–	–	<1880

[a] Inventories ± 1 standard deviation.
[b] Section 9–10 is dated by CRS model as year 1977. It was adjusted to year 1976.
[c] Lowest sediment rates.

From 1994 onwards, local environmental authorities set policies to restrict atmospheric emissions (CONAMA, 1994) resulting in significant reductions particularly from industrial sources. Thus, steel, pulp and paper, and fishing industries introduced measures to reduce particulate matter emissions, favouring natural gas and increasing energy efficiency. The SCP decrease shown at 2–3 cm depth (1992–1996 period) reflects such reductions of emissions. Furthermore, between 1995 and 2002, the local fishing industry experienced a sharp reduction in fish-meal production, with a consequent decrease in fossil fuel (coal and oil) consumption (BCC, 2003) and consequently, atmospheric emissions. In the upper section (i.e. 0–2 cm depth) there is another reduction of SCP concentration and this probably reflects the effect of further emission reduction measures from the main industrial sectors. Coal and oil have been steadily replaced by natural gas as an industrial fuel in the Biobío Region, as a consequence of the commissioning of a gas pipeline from Argentina.

Interestingly, trends in SCP content and influx profiles are similar throughout the core, with the exception of 9–10 cm depth, corresponding to the period 1976–1977, when an increment in SCP influx is observed (Fig. 4).

Given this temporal agreement it is interesting to compare the SCP concentration profile in the lake with local fossil fuel industrial consumption. Fig. 5 summarises industrial coal and oil consumption in the Biobío Region after 1973, since no reliable data are available before then. As clearly seen in the figure, industrial coal consumption follows a similar pattern to that of the historical SCP concentrations and inflow in lake sediments. By contrast, a sharp decrease in industrial oil consumption is observed between 1973 and 1987, reflecting the impact of high oil prices. The increase in energy demand resulting from greater industrial activity after 1985 was met by both oil and coal supply. However, fossil fuel combustion only plays a minor role in electricity production within the study area as most electricity supply is generated by hydroelectric plants located in the Biobío river basin (CNE, 2003).

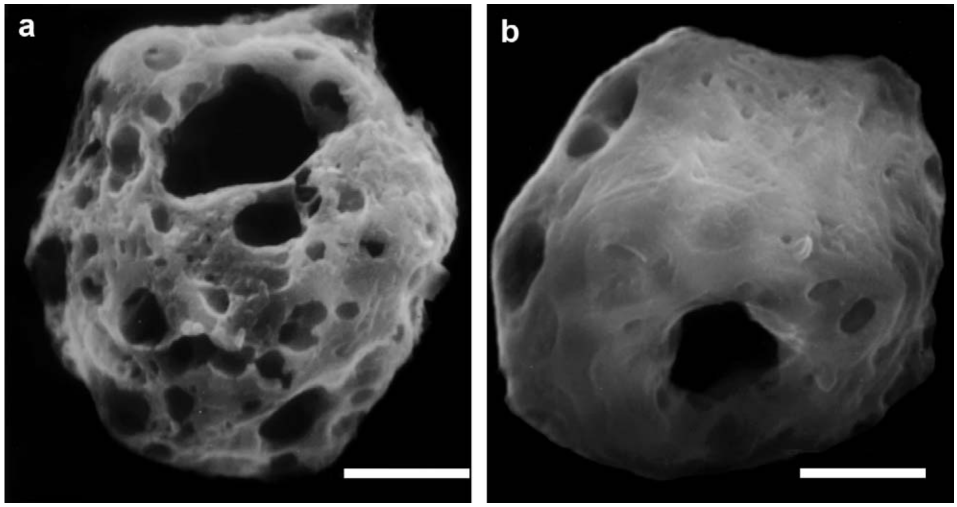

Fig. 3. SEM photographs of spheroidal carbonaceous particles in lake sediments from Laguna Chica de San Pedro. (a) bar = 2 μm (10 000×); (b) bar = 4 μm (5000×).

The SCP profile from LCSP lake shows the same sedimentary features and trends as those reported for lakes throughout Europe (Rose et al., 1995, 1999). Three distinct features are observable: (a) a steady increase in SCP concentration at start of the particle record; (b) a sharp increase in SCP concentration due to rapid industrial development; (c) an SCP subsurface maximum concentration and subsequent decrease resulting from introduced particle-arrestor technology and industrial decline. However, whilst the absolute dates for these features understandably differ between the two regions, both are seen to reliably reflect documented changes of their respective industrial developments.

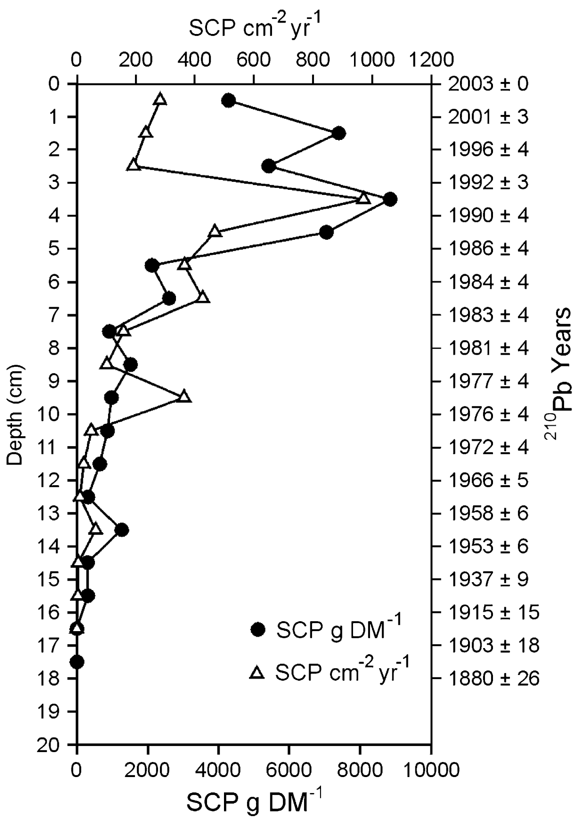

Fig. 4. Spheroidal carbonaceous particle concentration and influx profiles in lake sediments from Laguna Chica de San Pedro.

In contrast to the SCP profile from LCSP, the sediment core from Galletué lake showed no SCP presence at any depth. As mentioned above, this lake is located in a remote mountainous area at 1150 m above sea level. Anticyclonic winds from south and southwest (S-SW), between 30 and 60° S, predominate in that area during approximately 51% of the year. Moreover, north and north-west winds (N-NW), between 30 and 45° S, are present during approximately 31% of the year (Ahumada and Chuecas, 1979). Thus, the transport of atmospheric pollutants from eastern sites should be neglected. Any SCP found in Galletué lake would have been the result of long distance atmospheric transport since no local SCP sources exist. The fact that no SCP is present in the Galletué lake sediments indicates that long-range transport does not contribute significantly to SCP deposition in that area.

The SCP profile from LCSP is the first from a Chilean lake and hence, with the absence of SCPs in Galletué lake, there are no other regional data against which to compare these results. Indeed, there is a paucity of SCP data from the southern hemisphere in general. SCP profiles from two lakes in the Falkland Islands (distant about 2000 km from the study area), Adam Tarn and Lake Sulivan (Rose, unpublished data) showed quite variable profiles, although that from Adam Tarn shows some agreement with the SCP record from LCSP, as the first presence of SCPs is recorded in the 1930s and a concentration peak (~500 g DM^{-1}) was found in the 1980s. Beyond this region, Cameron et al. (1993) reported a SCP profile for a remote lake in Tasmania where peak concentrations of ~2000 g DM^{-1} were found in the surface sediments (1991).

The lack of SCPs in Galletué lake also raises questions regarding the long-range transport of SCPs in the southern

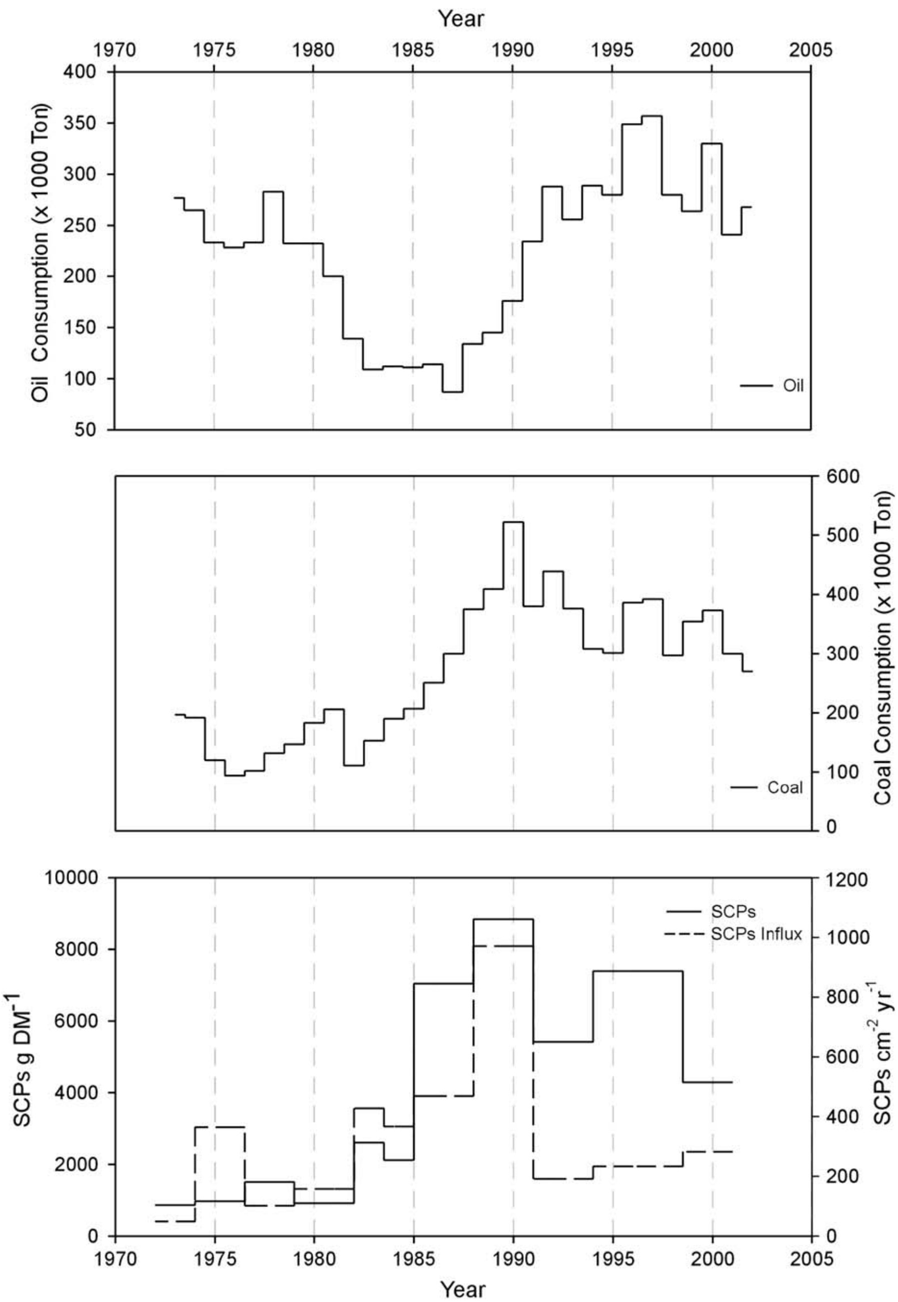

Fig. 5. Oil and coal consumption in the Biobío Region and the SCP concentration and influx profiles in lake sediments from Laguna Chica de San Pedro.

hemisphere and in particular the possibility of a 'hemispherical background' concentration similar to that postulated by Rose (1995) for the northern hemisphere, where remote lake sites showed concentrations of between 100 and 1000 g DM^{-1}. Whilst the results from Galletué lake would suggest that SCP distribution is not so ubiquitous in the southern hemisphere, presumably due to a lower level of historical industrial activity when compared with the north, Muir and Rose (2005) do report the presence of SCPs in lakes from coastal Antarctic sites and from maritime Antarctic islands (distant about 3000 km from the study area). Concentrations in these lakes are, predictably, very low at ~100 g DM^{-1} or below. These data, together with those from Galletué lake, would suggest that if a southern hemispherical background exists it is at a level considerably below that of the northern hemisphere and a SCP presence may only be detectable where analytical detection limits are exceptionally good.

4. Conclusion

The SCP profile from LCSP represents the first such data from Chile and shows that SCP concentrations can be directly related to local industrial activities, particularly steel-making, fish processing, pulp and paper production, and other local manufacturing. This suggests that SCP profiles from lake sediments could be used as temporal indicators of fossil-fuel consumption in the Biobío Region and with further data could potentially be used as an independent means of sediment dating.

However, no SCPs were found in the high mountain lake used here as a reference site, raising questions about the long distance atmospheric transport of SCPs in this region but supporting the idea that any southern hemisphere 'background' SCP concentration is considerably lower than that for comparably remote lakes in the northern hemisphere.

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