Geochemical evidence (C, N and Pb isotopes) of recent anthropogenic impact in South-Central Chile from two environmentally distinct lake sediment records

Nathalie Fagel¹, Sébastien Bertrand², Nadine Mattielli³, Delphine Gilson³, Luis Chirinos⁴, Gilles Lepoint⁵, and Roberto Urrutia⁶

(1) AGEs, Clays, sedimentary and environmental Geochemistry, Geology Department, University of Liège, Allée du 6 Août B18, B-4000 Liège, Belgium. (Tel: +32.4.3662209; Fax: +32.4.3662029; nathalie.fagel@ulg.ac.be);
(2) Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, MA02543, Woods Hole, USA (sbertrand@whoi.edu);
(3) DSTE, Université Libre de Bruxelles, Belgium;
(4) Departamento de Ingeniería, Universidad Católica del Perú, Peru;
(5) Marine Research Centre (MARE), Laboratoire d’Océanologie, Université de Liège, Belgium;
(6) Centro de Ciencias Ambientales EULA-Chile, Universidad de Concepción, Concepción, Chile.
Abstract

In this paper, we compare the elemental and isotopic (C, N, Pb) geochemistry of lake sediments from two contrasted environments in South-Central Chile. The first lake, Laguna Chica de San Pedro (LCSP), is situated in the urbanized area of the Biobío Region (36°S). The second lake, Lago Puyehue (40°S), is located 400 km to the southeast of LCSP and belongs to an Andean national park. Our aim is to identify environmental impacts associated with increasing industrial activities and land-degradation during the last 150 years. In LCSP, shifts in C/N atomic ratios, $\delta^{13}$C and $\delta^{15}$N from 1915–1937 to the late 80’s are attributed to successive land-degradation episodes in the lake watershed. Based on a Pb isotopic mixing model, we estimate that up to 20% of lead in LCSP sediments is supplied from urban atmospheric pollution. By contrast, human impact in the watershed of Lago Puyehue is very limited. We observe no change in organic geochemistry during the last 150 years and lead contamination remains lower than 5%, even during the last decades. Although contamination levels are much higher in LCSP than in Lago Puyehue, a peak in anthropogenic Pb is recorded during the same period (1974–1976) at both sites. This maximum contamination level is consistent with increased industrial activity in the vicinity of Concepción.

Supporting information may be found in the online version of this article.

Keywords: anthropogenic activity, geochemistry, lead isotopes, lake sediment, Chile
1. Introduction

Lake sediments constitute sensitive archives of environmental changes affecting the lakes and their catchments (e.g., Smol, 2008). Since geochemistry of lake sediments is largely controlled by the nature and the processes occurring in the lake catchment (Mackereth, 1966; Engstrom and Wright, 1984), sedimentary geochemistry is one of the best methods to reconstruct paleoenvironmental changes that occurred in lake watersheds. Moreover, recent improvements in dating techniques (e.g., $^{210}$Pb, $^{14}$C) of recent sediments allow sediment cores to be used as faithful recorders of recent human impacts (Smol, 2008). For instance, variations in sedimentation rates have been used to study historical changes in erosion processes and assess land-use changes during historical times (Debels et al., 1999; Luque and Julia, 2002). Paleolimnological approaches have also been used to support studies of identification of metal pollution in aquatic environments (Smol, 2008). Among metals, lead is a good pollution indicator that is immobile in natural environment archives such as lake sediments (Bränvall et al., 2001). Recently, stable Pb isotopic signatures of lake sediments have been used to trace the source of anthropogenic contaminations associated with Pb (e.g., Gallon et al., 2005, Hou et al., 2006, Couillard et al., 2008).

Carbon to nitrogen elemental ratios, as well as stable carbon ($\delta^{13}$C) or nitrogen ($\delta^{15}$N) isotope ratios of sedimentary organic matter is frequently used to reconstruct sources of sedimentary organic matter and past lake productivity (e.g., Schelske and Hodell, 1991; Brenner et al., 1999; Meyers, 2003; Perdue and Koprivnjak, 2007; Das et al., 2008). Organic geochemistry reflects the autochthonous or allochtonous origin of the organic matter, i.e., aquatic-derived organic matter vs. terrestrial vegetation. Since terrestrial plants are characterized by C-rich and protein-poor structural material, their C/N atomic ratios is generally well above 20 (Meyers and Terranes, 2001). On the contrary, the C/N ratio of lake plankton averages 8 to 10, which makes the C/N ratio of lake sedimentary organic matter a useful tool to reconstruct organic matter origin, and environmental changes that occurred in lakes and their watersheds. Similarly, the carbon isotopic composition of organic matter in lake sediments is influenced by both organic matter sources and paleoproduction rates (Meyers and Terranes, 2001). Therefore combining organic geochemical composition and stable carbon or nitrogen isotopic signature of lake sedimentary organic matter generally reveals important clues about past lake productivity and changes in terrestrial supplies.
Lead isotopes analysis has been applied to diverse materials in order to assess spatial and temporal changes of recent pollution from industries and from leaded gasoline (e.g., Shirahata et al., 1980; Rosman et al., 1993; Véron and Church, 1997). The sources of lead preserved in sedimentary archives are diverse and can be traced using their isotopic signature (Renberg et al., 2002), which depends on the geological origin and age of the original lead-bearing rocks and sediments (Faure, 1986). Naturally, lead is transported to sedimentary environments through weathering of soils and bedrock or more directly within mineral matter eroded from the catchment. The anthropogenic source of lead is associated with airborne particles from leaded gasoline and industries. Alkyl-lead, a common man-made organic form of lead, has been used as a fuel additive to reduce "knock" in combustion engines since the 1920s (Bollhöfer and Rosman, 2000). Other major sources of atmospheric Pb are mining, smelting, refining of non-ferrous metal, waste incineration and coal burning (Nriagu and Pacyna, 1988, Bollhöfer and Rosman, 2000). Lead is also associated with the emission of other pollutants and it has been used to study long range transport and atmospheric mixing processes responsible for the pollution of remote environments (e.g., Duce et al., 1983).

Prior to the advent of lead pollution, atmospheric deposition contributed an insignificant fraction of lead accumulated in lake sediments relative to the supply from the catchment (Bindler et al., 2001). However, since ancient times, lead derived from a variety of human activities has been transported atmospherically and deposited on lakes and their catchments (Renberg et al., 2002). In modern times, anthropogenic lead accounts for approximately 95% of the global lead cycle (Settle and Patterson, 1980). On a global scale, ~85% of industrial Pb emissions are introduced in the atmosphere in the Northern Hemisphere (Schaule and Patterson, 1981). Taking into account the residence time of Pb-rich aerosols in the atmosphere (~10 days — Settle and Patterson, 1991), those Northern Hemisphere emissions have a negligible impact on the Southern Hemisphere (Bollhöfer and Rosman, 2000).

Early studies of atmospheric contamination of lake sediments focused on long-established industrialized regions of Europe and North America (Boyle, 2001). More recently, work has been undertaken in the newly industrialized countries and in areas less directly influenced by industrial activities. However, the Southern Hemisphere remains relatively understudied. Here, we use stable lead isotopes (new data) and organic geochemistry (new data and data from Bertrand et al., 2005) to identify the environmental impacts associated with increasing industrial activities and land-
degradation during the last 150 years in South-Central Chile. We compare sedimentary geochemical records from two contrasting lake settings, i.e., Laguna Chica de San Pedro, which is located in an urbanized area and thus immediately affected by pollution, and Lago Puyehue, which is located in an Andean national park with very limited human activities. Our aim is to investigate the local and global impacts of anthropogenic activities in Chile, i.e., one of the most industrialized countries in South America, with over 90% of its population living in urban areas.

2. Material and study area

2.1. Location

Laguna Chica de San Pedro (LCSP; 36°51´S, 73°05´W) is a mesotrophic coastal lake located in the vicinity of Concepción, at approximately 3.5 km from the Pacific Ocean (Fig. 1). It is situated in an industrial and highly populated region (population density is 32 x the Chilean average), at an altitude of 5 m.a.s.l. The bathymetry of the lake is rather simple, with a single basin that reaches a maximum depth of 18 m in its center (Urrutia et al., 2000a). LCSP presents a surface area of 0.82 km² and a small drainage basin of 4.5 km² (Urrutia et al., 2000a, Parra et al., 2003), which belongs to the metamorphic mountain range of Nahuelbuta. LCSP is surrounded by mountains of Precambrian metamorphic rocks (shale, phyllite) on its eastern side and by Late Pleistocene and Holocene fluvial sandy sediments on its western side (Acencio, 1994; Chirinos, 2005). The watershed of LCSP is a narrow basin, elongated in a North-South direction with steep western and eastern flanks (Debels et al., 1999). It is covered by alfisols (soils developed under temperate forests), which are characterized by a clayey matrix with some quartz grains (Cisternas, 2000). Only one small river drains the watershed of LCSP, and flows into the lake in its southern part. Since the late 19th century, human activities have affected the lake and its watershed through clear-cutting of the native forest, wheat growing, introduction of exotic trees, and urbanization (Cisternas et al., 1999). The native forest occupied 70% of the lake watershed in 1943, and decreased to 13% in 1994. The introduction of the macrophyte Egeria densa in the mid 1980’s has created apparent oligotrophic conditions (Urrutia et al., 2000b).

Lago Puyehue (40°40´S, 72°20´W) is an oligotrophic, moraine-dammed lake located at the foothill of the Cordillera de Los Andes, at approximately 50 km from the city of Osorno (Fig. 1). The lake lies at an elevation of 185 m.a.s.l. and has a complex bathymetry, with several sub-basins separated by a continuous bathymetric ridge and
with a series of small bedrock islands in its centre (Charlet et al., 2008). The lake has a surface area of 164 km² and a maximum depth of 123 m, and is located in a Tertiary valley over-deepened by Quaternary glacial advances (Campos et al., 1989). The watershed of the lake covers 1267 km² and is composed of Quaternary volcanic rocks that are generally buried under several meters of post-glacial andosols (i.e., Trumaos) (Laugenie, 1982; Bertrand and Fagel, 2008). Several active volcanoes surround the lake: the Antillanca and Puyehue-Cordón de Caulle volcanic complexes eastward, and the Osorno volcano to the South (Fig. 1). The eastern part of the lake watershed belongs to a natural park (the Parque Nacional Puyehue) that is virtually free of anthropogenic influence. The population is concentrated in small lowly-populated villages along the southern shore of the lake. The whole region is dominated by westerly winds and the lake is fed by Rio Golgol to the East and by several smaller rivers (Fig. 1). Its outlet, i.e., Rio Pilmaiquen, merges with Rio Bueno and flows into the Pacific westward. Since 1944, Rio Pilmaiquen has been dammed by a hydro-electric station 6 km downstream of Lago Puyehue (Laugenie, 1982). The lake is monomictic, with stratification in summer and mixing during the winter months (Campos et al., 1989).

2.2. Coring and core processing

In May 2003 duplicate sediment cores were taken in the central part of LCSP, at a depth of 17 m (Chirinos et al., 2005b). The sampling site was selected with the aid of a Lowrance X-16 sonar and sediment cores were obtained by divers using 1 m long Plexiglass tubes with an inner diameter of 5.8 cm. The sediment cores were then capped, sealed and stored at 4 ºC until analysis. For this work, one of the cores has been sampled in 1 cm thick slices. The core is 60 cm long and is composed of dark silty mud containing less than 5% of sand particles (Chirinos et al., 2005b). The sediment is dominated by detrital minerals (clays, plagioclase and quartz) with only a few diatoms (biogenic silica ~3–4%). Microscopically, the sediment is homogeneous without any laminations.

In Lago Puyehue, the selection of the coring site is based on high-resolution seismic profiles obtained in February 2002 (Charlet et al., 2008). Site PU-II is located on a sub-aquatic moraine ridge at 48.4 m depth in the southern part of the lake (Fig. 1). The site is under the influence of interflows from the Golgol river. At PU-II site, five short cores were taken using a Uwitec short gravity coring device. For this paper, core PU-II-P4 has been opened described and sampled every 1 cm. Organic geochemistry was
measured on parallel core PU-II-P5. Macroscopically, sediment core PU-II-P4 is composed of homogeneous to finely laminated silty sediments, and contains a few tephra layers. The core contains two fine green layers representing the in-situ alteration of pumices at 4.0–4.5 cm and at 8.5–9.0 cm, and two sandy tephra layers at 12.0–12.5 cm and 42.0–42.2 cm (Bertrand et al., 2005, 2008). Microscopic observations reveal the occurrence of annually laminated sediments composed of an alternation of terrigenous clays and diatomaceous clays, except for a massive layer between 3.5 and 6 cm (Boës and Fagel, 2008).

In addition to the sediment cores, soil and river sediment samples were collected in the watersheds of both lakes. In the watershed of LCSP, we sampled two soil profiles, as well as the sediment of the only river flowing into the lake (Fig. 1). In the watershed of Lago Puyehue, we collected 21 river sediment samples and 12 soil sediment samples from two distinct profiles. The results obtained on these samples are detailed in Bertrand et al. (in press). In both cases, the samples have been sieved at 105 μm and the fine fraction of the sediment has been analyzed for bulk organic geochemistry according to the methods described hereafter. Some of these samples have also been analyzed for lead isotopes (see Tables 3a and 3b, online supporting information).

2.3 Chronology

The age-depth model of LCSP sediment core (Fig. 2) is based on $^{210}$Pb concentrations (Chirinos et al., 2005a). Ages have been estimated using the constant rate of supply model (CRS) and are listed in Table 2a (online supporting information). The oldest available $^{210}$Pb date corresponds to AD 1880 ± 26 years, at a depth of 18 cm. Here, we focus on the upper 20 cm of the sediment core, which represents the last ~150 years. Low sedimentation rates have been calculated between 14 and 18 cm (as low as 0.04 mm/yr), and the highest sedimentation rates occur at 9–10 cm (1.5 mm/yr, AD 1976–1977).

For the sediments of PU-II coring site, the age-depth model (Fig. 2) is based on varve-counting results obtained on parallel core PU-II-P5 (Boës and Fagel, 2008). They are in agreement with radionuclide profiles ($^{210}$Pb and $^{137}$Cs; Arnaud et al., 2006) and with the recognition of historically-documented event deposits (Boës and Fagel, 2008, Bertrand et al., 2008). In particular, the massive layer microscopically described at 3.5–6 cm has been attributed to the 1960 Valdivia earthquake and used as a time-marker (Boës and Fagel, 2008). In this paper, we focus on the upper 22 cm of PU-II-P4.
sediment core, which covers the last ∼150 years (1833–1842 AD at 21.5 cm). Sedimentation rates vary from 0.7 to 1.7 mm/year (Table 2b, online supporting information).

3. Methods

3.1 Bulk organic geochemistry

Stable isotope ratios of carbon and nitrogen were measured by continuous flow isotope ratio mass spectrometry after sample combustion to CO₂ and N₂ at 1000°C in an on-line elemental analyzer. For PU-II-P5 sediments, approx 25 mg of sediment was oven-dried, ground and homogenized in an agate mortar, and analyzed on a Fisons NA 1500 NC elemental analyser in line with an Optima mass spectrometer (GV Instrument, Lab. Océanologie, ULg, Belgium). The other samples (LCSP, river and soils samples) were freeze-dried, ground and homogenized in an agate mortar, decarbonated using 1N sulphurous acid and analyzed at the UC Davis Stable Isotope Facility, USA, on an Europa Hydra 20/20 mass spectrometer in line with an ANCA-GSL elemental analyzer. Before introduction to the IRMS the gases were separated on a Carbosieve G column. Isotopic measurements are presented as δ values (‰) expressed relative to VPDB (δ¹³C) or AIR (δ¹⁵N) standards. The precision is calculated by replicate analysis of internal standards, i.e., sucrose (ULg, δ¹³C = -10.3 ± 0.2 ‰) or a mixture of ammonium sulfate and sucrose (UC Davis, δ¹³C = -23.83 ‰, δ¹⁵N = 1.33 ‰). For δ¹³C, the precision is 0.04 ‰ (UC Davis) or 0.20 ‰ (ULg), and the precision for δ¹⁵N is 0.18 ‰ (UC Davis).

3.2 Inorganic geochemistry and Pb isotopes

Total Pb and Ti concentrations of LCSP sediments were determined by ICP-OES with an accuracy of 16% for Pb and 1.5% for Ti (2 RSD, Chirinos et al., 2005b). For sediment core PU-II-P4, total Ti concentrations were determined by XRF on fused glass beads, with an accuracy of 3% (Bertrand et al., 2005) and total Pb was estimated by MC-ICP-MS (accuracy: 10%). For Pb isotopes, ∼500 mg of sediment was heated at 550°C overnight to volatilize organic matter. The weight loss-on-ignition at 550°C ranges between 13 to 16% for LCSP sediments (Chirinos, 2005) and vary between 1.5 and 11% for PU-II-P4 sediments (Bertrand et al., 2005). The samples (∼50 mg for LCSP and 100 mg for PU-
II-P4) were subsequently dissolved in closed Teflon beakers in an HF-HNO₃ mixture, and placed on a hot plate (110°C) for 3 days. The solution was then evaporated to dryness, re-dissolved in HCl, re-evaporated and finally dissolved in 0.8N HBr. Lead (Pb) was chemically extracted using an AG1-X8 anionic resin loaded in a 2 ml column in an HBr environment (Manhès et al., 1978). Pb isotopes were measured using a Nu-Plasma Multi Collector-Inductively Coupled Plasma-Mass Spectrometer (MC-ICP-MS) at the 'Département des Sciences de la Terre et de l'Environnement' (DSTE - Université Libre de Bruxelles). As an internal isotopic standard, a thallium solution was added to each sample and standard to monitor and correct for mass dependent isotopic fractionation. Whilst the samples were characterized by a large variability in Pb concentrations, the sample solutions were prepared to obtain a beam intensity in the Axial collector (²⁰⁴Pb) of minimum 100 mV, and a Tl/Pb ratio of ~ 0.2, matching the Pb and Tl concentrations of the NBS981 standard (200 ppb in Pb, added with 50 ppb in Tl). Tl/Pb ratio was relatively stable from one day of analysis to another. For PU-II-P4 sediments, Tl/Pb ranges between 0.14 and 0.23. For LCSP, this ratio is usually less than 0.5, except for one sample (0.58). In the course of the study, measurements of NBS981 yielded weighted average values of 36.7158 ± 0.027 (2SD) for ²⁰⁸Pb/²⁰⁴Pb, 15.4969 ± 0.011 for ²⁰⁷Pb/²⁰⁴Pb, 16.9399 ± 0.0011 for ²⁰⁶Pb/²⁰⁴Pb, 0.9148 ± 0.0001 for ²⁰⁷Pb/²⁰⁶Pb, and 2.1674 ± 0.0007 for ²⁰⁸Pb/²⁰⁶Pb, which are in good agreement with long term laboratory values (n = 1000, ²⁰⁸Pb/²⁰⁴Pb = 36.7130 ± 0.012 (2SD), ²⁰⁷Pb/²⁰⁴Pb = 15.4950 ± 0.004 (2SD), ²⁰⁶Pb/²⁰⁴Pb = 16.9393 ± 0.0044 (2SD)), with the TIMS values published by Galer and Abouchami (1998), and with the MC-ICP-MS values of Weis et al. (2006). These values are also in agreement with TIMS triple-spike values previously published by Galer and Abouchami (1998). Although the NBS981 standard results were within error of the triple-spike values after online correction for instrumental mass bias by Tl addition, the results were further corrected by the sample-standard bracketing method (as described by White et al. (2000) and Weis et al. (2006)) to circumvent any instrumental drift during the analytical session. Duplicates of the entire analytical procedure (n = 7) are reported in Table 3 (online supporting information), and all fall within error bars.

4. Results

4.1. Laguna Chica de San Pedro
The TOC and TON profiles of LCSP are roughly parallel, with the TOC and TON values ranging from 3.1 to 5.0 % and 0.3 to 0.5 %, respectively (Fig. 3a). The C/N atomic ratio varies from 11.2 to 15.2. The carbon and nitrogen isotopic values range from -22.8 to -27.6 ‰ and 2.7 to 4.6 ‰, respectively. Two significant changes are observed in all the variables at around 5 cm and 14 cm depth (Fig. 3a). The samples collected in the lake watershed show values typical for terrestrial organic matter (C/N: 16.5 ± 1.0; δ¹³C: -25.8 ± 0.9; δ¹⁵N: 7.6 ± 2.5), with no significant difference between the river sediment sample and the soil samples (Table 1a, online supporting information).

Lead concentration and isotopic composition has been determined in thirteen samples from LCSP sediment core and on a few samples from the catchment (soil profiles and river sediments, see location on Figure 1) (Figs. 4-6; Tables 2a and 3a, online supporting information). The Pb composition of LCSP sediments remains relatively stable in the lower core section, i.e., in the interval between 11 and 20 cm corresponding to sediments older than 1972 A.D (Fig. 5). For instance the mean Pb/²⁰⁴Pb ranges around 18.533 ± 0.022 (2 SD). Then a shift to lower Pb/²⁰⁴Pb, Pb/²⁰⁷Pb and Pb/²⁰⁸Pb ratios is observed in the upper 10 cm (Figs. 5 and 6). It is especially pronounced in the last 3 cm, i.e., in sediments younger than 1992 (Fig. 5). The Pb/²⁰⁴Pb ratio decreases down to 18.257 ± 0.022 in the upper 0–1 cm sample. The range of variation in Pb/²⁰⁴Pb ratio (standard deviation = 0.079) reached in the upper section is 4-fold higher than in the lower section. Note that the general trend in the Pb isotopic profile, in particular the uppermost sharp shift, is confirmed by the three duplicate analyses reported on Fig. 5. The signature of the soil and river samples is more scattered, with Pb/²⁰⁴Pb ranging between 18.481 and 18.768 (mean = 18.628; standard deviation = 0.11, online supporting information table 3a). The river sediments and the lower soil sample of site 2 display the highest isotopic ratios. The lowest isotopic ratios (e.g., Pb/²⁰⁴Pb = 18.4807 ± 0.0010) are recorded in the upper soil sample at site 2 (see Fig. 1 for location). At site 1 the two soil samples collected from the upper brown to black and lower red to brown horizons give similar Pb composition (e.g., 18.5847 ± 0.0009 < Pb/²⁰⁴Pb < 18.5869 ± 0.0009, online supporting information table 3a). Those Pb ratios are more radiogenic than the lacustrine sediments values. For instance, all the Pb/²⁰⁴Pb values for LCSP are lower than 18.5644 ± 0.0018. The mean soil signature displays slightly more radiogenic Pb/²⁰⁴Pb ratios (18.593) than the lower core section (Fig. 5).
4.2 Lago Puyehue

The TOC and TON profiles of the upper 22 cm of PU-II-P5 sediment core are roughly parallel (Fig. 3b), with particularly low values at 13.5 cm, which are due to the occurrence of a tephra layer (Bertrand et al., 2005). The lake sediments (excluding the tephra layer) are characterized by TOC and TON values ranging from 1.9 to 3.6 %, and 0.3 to 0.2 %, respectively, and slightly decreasing towards the bottom of the core. The C/N ratio and the $\delta^{13}$C values do not show any particular trend, and the values range between 12.8 and 14.7 for C/N and -27.8 to -28.8 ‰ for $\delta^{13}$C. The river sediment samples are characterized by more terrestrial values that do not vary significantly between the different rivers (C/N: 13.1 ± 1.0 and $\delta^{13}$C: -27.2 ± 0.5). Details regarding each particular river are given in Bertrand et al (in press).

The Pb elemental and isotopic composition of 10 bulk sediment samples from sediment core PU-II-P4 are reported in figures 4, 5 and 6, and the data are presented in tables 2b and 3b (online supporting information). The Pb isotopic ratios vary within a narrow range in most of the studied core section. For instance, the $^{206}$Pb/$^{204}$Pb values are comprised between 18.5069 ± 0.0007 and 18.6097 ± 0.0008 (Fig. 5). Similarly to the LCSP record, a slight excursion to lower $^{206}$Pb/$^{204}$Pb, $^{207}$Pb/$^{204}$Pb and $^{208}$Pb/$^{204}$Pb ratios occur in the upper sediment section. The change is gradual. It appears within the upper 3 cm, i.e., since at least 1976 AD (Fig. 5). Again, duplicates (n=5, online supporting information table 3a) confirmed the observed isotopic trend.

5. Discussion

5.1 Sources of organic matter and land-use changes over the last 150 years

Here, we use the bulk organic geochemical data obtained on the sedimentary organic matter of LCSP and PU-II-P5 to reconstruct the variations in the main sources of organic carbon during the last 150 years. In lake systems, terrestrial plants and lake plankton generally have very similar $\delta^{13}$C values (-25 to -30 ‰ for lake plankton, -22 to -30 ‰ for C3 terrestrial plants) but significantly distinct C/N atomic ratios (Meyers and Teranes, 2001). Therefore, our interpretation in terms of sources of sedimentary organic matter is primary based on the carbon to nitrogen ratio data.

5.1.1 Laguna Chica de San Pedro
In LCSP, the lake sedimentary organic matter represents a mixture of terrestrial organic matter (C/N: 16.5 ± 1.0) and lake plankton (C/N generally between 6 and 10, Meyers and Terranes, 2001). Shifts towards higher C/N ratios are interpreted as a higher supply of terrestrial organic matter and/or lower lake productivity and vice versa. At LCSP, the measured C/N atomic ratios and isotopic values display significant and concomitant shifts, evidencing a variable contribution of lake versus terrestrial organic matter during the last ~150 years. In the deepest part of the core (20–14 cm, i.e., 1880–1953 AD) the C/N ratios are relatively low (~12), evidencing a high contribution of lake plankton compared to the supply of terrestrial organic matter. Then, around 1950–1955, the C/N ratios and the TOC sharply increase, which probably represents a higher supply of terrestrial organic matter, with approx. ~80% of the organic matter originating from the lake watershed. The C/N values remain high until around 1986, where they gradually decrease towards the present-day conditions, reflecting a decrease in the terrestrial supply of sedimentary organic matter and/or higher lake productivity during the last 2 decades. During the last 17 years, the TOC values are generally low, evidencing that the shift in the C/N atomic ratio at around 5 cm is most likely due to a decrease in the supply of terrestrial organic matter. A shift towards less negative $\delta^{13}$C and a concomitant decrease of the $\delta^{15}$N values (Fig. 3) between in ~1953 AD are in agreement with an increased supply of terrestrially-derived organic carbon during the 1953–1986 AD period.

The significant increase in the supply of terrestrial organic matter to LCSP at around 1953 is strikingly consistent with a rapid increase in the total mass accumulation rate of sediment in the same core (Chirinos et al., 2005a) and in another core from the same lake (Cisternas and Araneda, 2001; Cisternas et al., 2001). In addition, Urrutia et al. (2000b) observed a significant increase in terrestrial hydrocarbons and fatty acids in ~1945 in agreement with our interpretation.

The observed changes in the supply of terrestrial organic carbon are most likely linked to anthropogenic activities in the watershed of LCSP, mostly related to deforestation. Although the replacement of the native forest by commercial plantation in the watershed of LCSP began at the end of the 19th century, it only became intensive in the mid 20th century (Debels et al., 1999; Urrutia et al., 2000b, Cisternas et al., 2001). In 1943, the native forest still occupied 70% of the watershed area and no area had been left deforested (Cisternas et al., 2001). Between 1943 and 1955, 17% of the forest had been logged and replaced by exotic species. Most of the
Deforestation and denudation of the soil cover generally result in increased soil erosion and runoff of soil particles (including organic matter), which in turn triggers higher sedimentation rates in lake sediments (e.g., Page and Trustrum, 1997). The increased supply of terrestrial organic matter in the sediments of LCSP between 1953 and 1986 is in good agreement with the peak of anthropogenic activities in the lake watershed, especially deforestation, clear-cutting of indigenous species and human settlement. After 1986, our results show a decrease in TOC and C/N, which reflects a decrease in the supply of terrestrial organic matter into the lake. This change is very likely related to the stabilization of the soils in the lake watershed in response to reforestation after 1981. It is noteworthy that the anthropogenic introduction of the macrophyte *Egeria densa* in LCSP in the mid-eighties (Urrutia *et al.*, 2000b) is not directly recorded in the lake sediments (i.e., no increase in C/N), although it acted as a sink for nutrients, resulting in the actual apparent oligotrophication of the lake.

5.1.2 Lago Puyehue

The sedimentary organic matter of core PU-II-P4 is composed of a mixture of terrestrial and aquatic end-members that are characterized by average C/N atomic ratios of 13.7 (river sediment), 14.6 (soils and paleosoils), and 8.5 (lake plankton), respectively (Bertrand *et al.*, in press). By contrast with the sediments of LCSP, the sediments of Lago Puyehue show rather stable C/N and δ¹³C values during the last 150 years (Fig. 3), ranging around 13.4 and 28.4 ‰, respectively. No significant trend is observed and the only excursions of the C/N ratio occur at 8–9 and 13–14 cm, in relation with a clay layer (weathered pumices) and a sandy tephra layer, respectively. Because of the remote location of Lago Puyehue and its situation within a national park, anthropogenic impacts in the lake watershed are very minor, and do not affect the soil erosion and the terrestrial runoff. Neither can they modify the lake trophic conditions. Therefore, the composition of the bulk sedimentary organic matter in Lago Puyehue reflects the natural supply and export production of...
terrestrial and aquatic organic matter. Changes in its composition over longer time-
scales are driven by natural variations in lake productivity, resulting from natural
changes in the supply of nutrients to the lake (Bertrand et al., 2005). The sediments
of Lago Puyehue are therefore a good archive of paleoclimate changes over the last
millennia (Bertrand et al., 2005) and even since the Last Glacial Maximum (Bertrand
et al., in press), but do no contain any evidence of anthropogenic impact.

5.2. Sedimentary Pb isotopes: a record of human activities over the last 150 years

Stable Pb isotopes in lake sediments are widely used in environmental studies as
tracers of historical pollution (e.g., Bränvall et al., 1997; Arnaud et al., 2004; Vermillon
et al., 2005; Couillard et al., 2008). Lead pollution in lake sediments can be traced using
two distinct methods. The first one, generally less accurate than the second, uses lead
concentrations. The second method, using lead stable isotopes, is much more precise,
and generally allows to trace the sources of lead. Here, we compare estimates calculated
by both methods.

5.2.1 Estimation of anthropogenic lead using Pb concentrations

Lead concentrations in sediments (Pbsample) integrate both the natural Pb
associated with the sediment matrix, and the Pb supplied from atmospheric pollution.
Therefore, the easiest method to estimate the anthropogenic fraction of Pb
(Pbanthropogenic) in lake sediments is by subtracting the natural Pb concentration from
the sample concentration (Fig. 4). To take into account the variations of Pb
concentration related to change in sediment composition (i.e., dilution effect), the
natural Pb fraction is estimated for each sample by using the sample concentration of
a naturally-derived conservative element (Arnaud et al., 2004). Assuming that the
natural Pb/Ti ratio is constant in the whole core, the anthropogenic Pb concentration
is calculated following equation (1):

Pbanthropogenic = Pbsample - [(Ti sample * Pb/Tinatural)]

where Pb/Tinatural is the Pb/Ti ratio measured in pre-anthropogenic sediments.

The assumption that the Pb/Tinatural ratio of pre-anthropogenic sediments is
constant in the whole core is usually valid for lakes with catchments characterized by
a relatively small size (like for LCSP) and/or by a simple and homogeneous geology
(like for both lakes: metamorphic rocks in LCSP, dominant volcanic andesitic or
basaltic rocks in Puyehue).
In order to compare distant records, anthropogenic Pb fluxes are generally more appropriate than concentrations (Arnaud et al., 2004). Therefore, we calculated the flux of bulk \( F_{\text{bulk}} \) and anthropogenic \( F_{\text{anthropogenic}} \) lead using the concentration data, the dry density \( D \) (g/cm\(^3\)) and the sediment accumulation rate SAR (cm/yr) estimated from the respective age models:

\[
F_{\text{bulk}} = D \times \text{SAR} \times \text{Pb}_{\text{sample}} \quad (2)
\]

\[
F_{\text{anthropogenic}} = F_{\text{bulk}} \times \%\text{Pb}_{\text{anthropogenic}} \quad (3)
\]

For PU-II-P4 sediment samples, the total Pb concentrations are low and vary around 8 ppm (standard deviation: 2 ppm), with slightly higher values after 1962 (Fig. 4). This value is close to the natural background Pb concentrations (7 ppm) in the regional andosols (Deraymaeker, 2003). The calculated Pb\(_{\text{anthropogenic}} \) reaches its maximum (5 ppm) in the sample corresponding to year 1976, where it represents more than 40% of the total Pb (Fig. 4). It corresponds to the highest anthropogenic flux (1.0 mg/m\(^2\)/yr).

In LCSP sediments, the total lead concentration increases from 40 ppm in the pre-industrial samples (before 1965) up to a maximum of 58 ppm in the sample corresponding to year 1974 (Fig. 4). It corresponds to 18 ppm of Pb\(_{\text{anthropogenic}} \) and an anthropogenic flux of 10 mg/m\(^2\)/yr. The flux of Pb\(_{\text{anthropogenic}} \) is the highest in 1985 (16.1 mg/m\(^2\)/yr) but is generally well above 10 mg/m\(^2\)/yr between 1974 and 1991, where it represents up to 30% of the total Pb.

In both lakes, we evidence a peak in Pb concentration in 1974–1976 (Fig. 4). Taking into account the error in age model and the sampling resolution, it corresponds to a synchronous change despite the contrasted environments of the two lake settings. Such change underlines the global character of the Pb contamination in Chile. The contamination by industrial airborne particles is approximately 10 times greater in LCSP than in Lago Puyehue, reflecting the natural setting characterizing the region of Puyehue. Interestingly, the inception of airborne pollution in LCSP is consistent with the detection of spheroidal carbonaceous particles, i.e., residue of fossil fuel combustion, in LCSP sediments. Indeed, using the same sediment core, Chirinos et al. (2005a) have detected the occurrence of SCP only in sediments younger than 1976 (first 11 cm of the sediment core). Detection of contamination in newly industrialized countries and in areas remote from industry can be difficult and it is important to pay attention to estimation of the natural concentrations, especially in region where atmospheric contamination is minor (Boyle, 2001), as it is the case
in Chile. Even if Concepción is one of the most industrialized cities in Chile, the flux of anthropogenic Pb recorded in the sediments of LCSP (10–15 mg/m²/yr) is still 2–3 times lower than in the French Alps and in Canada (30 mg/m²/yr, Arnaud et al., 2004; Ndzangou et al., 2005).

5.2.2 Estimation of anthropogenic lead using Pb stable isotopes

The anthropogenic lead content can similarly be calculated using lead stable isotopes, with the main advantage that we can now discuss the possible sources of anthropogenic lead. The downcore records of the $^{206}$Pb/$^{204}$Pb ratio are illustrated in Fig. 5. They show that the Pb isotopic composition of the two sedimentary environments depicts a similar trend through the last ~150 years, with less radiogenic values in the most recent sediments. The isotopic sedimentary Pb signatures are relatively constant in older sediments (Fig. 5). The $^{206}$Pb/$^{207}$Pb and $^{208}$Pb/$^{206}$Pb results are illustrated in Fig. 6. At both sites, we note a decrease of the $^{206}$Pb/$^{207}$Pb and an increase of $^{208}$Pb/$^{206}$Pb ratios towards the surface (Fig. 6b). The shift seems to start earlier in the sediments of LCSP than in those of Lago Puyehue, (i.e., between 1969 and 1976 and between 1976 and 1990, respectively), although this might be affected by the relatively low sampling resolution. These trends evidence a supply of anthropogenic Pb than can be estimated using Pb isotopes after identification of the isotopic signatures of the natural and anthropogenic sources. In both lakes, the lead isotopic compositions ($^{206}$Pb/$^{207}$Pb – $^{208}$Pb/$^{206}$Pb) are distributed along two different trends (Fig. 6), which can be interpreted as mixing lines between two end-members. One end-member represents the regional natural background sedimentation. The other end-member, characterized by lower $^{206}$Pb/$^{207}$Pb and higher $^{208}$Pb/$^{206}$Pb ratios, coincides with the anthropogenic source.

a. Identification of the natural sources of lead

In lake sediments the “old” or pre-industrial samples are usually used as representative of the isotopic composition of the sediment matrix (e.g., Arnaud et al., 2004). In Lago Puyehue, a long record of the sedimentary Pb composition is available (Deraymaeker, 2003). The range of variation of Pb ratios measured on an 11 m-long core (PU-II) is narrow. The Holocene and deglacial sediments are characterized by stable Pb isotopic signatures. Their averaged signature ratios ($^{206}$Pb/$^{207}$Pb ~1.191; $^{208}$Pb/$^{206}$Pb ~2.071) are therefore used to characterize the natural end-member. The definition of this natural end-member is consistent with regional
soil and volcanic rock data (Fig. 6). The Puyehue catchment is covered by volcanic-derived soils (“Trumaos”, Bertrand and Fagel, 2008), characterized by $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios of 1.192 and 2.070, respectively. The Trumaos signature is therefore in good agreement with the sedimentary pre-anthropogenic Pb isotopic composition (Deraymaeker, 2003; Fig. 6). The average Pb isotopic composition of the volcanic rocks from the surrounding area also perfectly agrees with the composition of the pre-industrial sediments. For instance the mean $^{206}\text{Pb}/^{204}\text{Pb}$ value calculated for the Southern Volcanic Zone (SVZ) between 36 and 41°S (18.5984 ± 0.0619, online supporting information table 3b) perfectly agrees with the sedimentary $^{206}\text{Pb}/^{204}\text{Pb}$ values of PU-II-P4 below 3 cm (Fig. 5). In the $^{208}\text{Pb}/^{206}\text{Pb}$ - $^{206}\text{Pb}/^{207}\text{Pb}$ biplot (Fig. 6), the mean SVZ signature ($^{206}\text{Pb}/^{207}\text{Pb}$: 1.192, $^{208}\text{Pb}/^{206}\text{Pb}$: 2.068–2.070) is adjacent to the Trumaos-representative signature.

According to the $^{210}\text{Pb}$ age model, the sediment core from LCSP can be divided into a pre-industrial period before 1915 (below 16 cm) and an industrial period after 1915 (Chirinos et al., 2005b). We can therefore estimate the natural Pb isotopic signature by averaging the results of the 3 lowest samples, resulting in $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios of 1.186 and 2.084, respectively (online supporting information table 3a). Unfortunately, there is a lack of data regarding the Pb isotopic composition of rocks in the region of Concepción. However, in January 2007 we collected and analyzed several sediment samples from soils outcropping around the lake and from the only river flowing into LCSP. Although we are aware this sampling is not exhaustive, it gives an estimate of the scattering of the natural Pb isotopic composition of the LCSP watershed. The mean watershed signature ($^{206}\text{Pb}/^{207}\text{Pb}$: 1.192, $^{208}\text{Pb}/^{206}\text{Pb}$: 2.079) and the mean soil signature ($^{206}\text{Pb}/^{207}\text{Pb}$: 1.190, $^{208}\text{Pb}/^{206}\text{Pb}$: 2.080) are comparable to the Pb isotopic composition of the pre-industrial LCSP sediment samples (Fig. 6). The only outlier is soil 2A, which has been collected in the upper part of an outcrop in the southern part of the lake watershed, and may therefore contain industrial lead.

**b. Identification of the anthropogenic sources of lead**

The composition of the anthropogenic end-member is influenced by Pb atmospheric emissions related to alkyl-lead and industrial activities. Bollhöfer and Rosman (2000) have analyzed aerosols collected between 1994 and 1999 at >70 sites widespread in Southern Hemisphere in order to define the modern isotopic signature.
for atmospheric lead. The isotopic composition in Chile is characterized by low 206Pb/207Pb ratios (down to 1.06 at the Southern tip of Chile), probably reflecting the supply of alkyl-lead from the UK producer Associated Octel, i.e., the world’s primary alkyl-lead producer. Associated Octel has used Pb from different ores (e.g., Broken Hill in Australia) in variable proportions with time and location (Véron et al., 1999). In Chilean airborne samples, the 206Pb/207Pb ratio, for instance, increases northward, from Punta Arenas (1.063) via Villarica (1.069) and Concepción (1.103) up to a maximum ratio of 1.150–1.182 in Santiago (see online supporting information table 3). This shift can be explained either by different market shares in petrol (different alkyl-lead mixings provided to different cities) or by a change in relative contribution of industrial Pb and leaded petrol. Industrial activities may be a more important source of atmospheric Pb in Santiago than at the Southern tip of the country. Keeping in mind this spatial variability, we selected the lead isotopic signature of airborne particles from the closest city of each lake (Concepción for LCSP, Villarica for Puyehue) to characterize the anthropogenic end-member of each location.

c. Estimation of natural vs. anthropogenic lead contribution using Pb isotopes

Assuming that the lead isotopic composition of each sample is a mixture of only two sources, i.e., natural lead derived from soil and rocks from the catchment (ISnatural) and anthropogenic lead (ISanthropogenic), we can estimate the relative contribution of natural and anthropogenic lead using a simple binary mixing model (equation 4 — e.g., Renberg et al., 2002):

\[
\text{IS}_{\text{sample}} = \alpha \ast \text{IS}_{\text{anthropogenic}} + \beta \ast \text{IS}_{\text{natural}}, \text{with } \alpha + \beta = 1
\]  

The end-members used in our calculation and the calculated mixing-lines are reported on figure 6b. In the region of Puyehue the contribution of anthropogenic Pb always remains lower than 5% during the last 150 years (Fig. 6). This low environmental contamination level persists during the late decade. At LCSP, the fraction of anthropogenic Pb significantly increases during the recent years (Fig. 6), from less than 5% between 1945 and 1994, to 10% in 1998 and even 20% in 2002 (Fig. 6b).

5.2.3 Anthropogenic lead: general interpretation and comparison of the two estimates
Although several studies suggest that the main process of anthropogenic lead incorporation into lake systems is direct atmospheric deposition (Dillon and Evans, 1982; Blais and Kalff, 1993), others show that pollutants previously deposited in lake catchments also contribute significantly to the global supply of Pb to lake sediments (Miller and Friedland, 1994). These studies however show that the anthropogenic lead, mainly deposited in lake catchments after 1960, will not be released to upland streams before the middle of the next century (Miller and Friedland, 1994), and has therefore no influence on the lake sedimentary records of Pb pollution. In addition, the recent increase in anthropogenic lead at LCSP can only represent a direct atmospheric supply since the reforestation of the LCSP watershed has stabilized soils and reduced the sediment supply to the lake. Keeping in mind that small variations in concentration may be difficult to interpret (Bränvall et al., 2001), we consider that the anthropogenic estimates using Pb concentrations fit noticeably well with our Pb isotopic approach. Although the estimates using Pb concentrations are constantly higher than the estimates using Pb isotopes, both methods show an increased anthropogenic lead supply for the last 30 years, which is much more distinct in the region of Concepción than around Puyehue.

6. Summary and conclusion

We used a geochemical approach combining elemental and isotopic carbon, nitrogen and lead, to compare the anthropogenic impact in South-Central Chile, as recorded in two contrasted lake settings, i.e., LCSP located near the city of Concepción (36°S) and Lago Puyehue, situated in a National Park at the foothills of the Chilean Andes (40°S).

For the region of Puyehue both methods underline the minimal impact of anthropogenic activities on the natural sedimentation processes. Although the lake receives a small amount of anthropogenic lead from atmospheric deposition, its relative contribution is always lower than 5%. Since no industrial activity takes place in the watershed of the lake, the anthropogenic lead deposited in Lago Puyehue probably originates from relatively long-distance atmospheric transport. A fraction of the Puyehue anthropogenic lead may also originate from road transport to Argentina, as one of the main routes to cross the Andes runs along the southern shore of the lake.
Recent sedimentation in LCSP reflects variable human activities in the region of Concepción during the 20th century. The bulk organic geochemical data provide clear evidence for deforestation episodes in the lake watershed from 1915–1937 to the late 80’s, with an accentuation between 1943 and 1987, when most of the native forest has been logged and replaced by exotic species. Using two different approaches, we demonstrate that airborne pollution in the region of Concepción started to become significant sometime between 1974 and 1982. We estimate that anthropogenic lead constitutes up to 10 to 20% of total Pb supplies during the last decade. This interpretation is consistent with the detection of spheroidal carbonaceous particles, i.e., residue of fossil fuel combustion, in lake sediments deposited after 1976.

Although the contamination levels are much higher around Concepción than in the region of Puyehue (the Pb anthropogenic flux is 10 times lower at Puyehue than at LCSP), the maximum Pb contamination is observed in the mid-seventies (1974–1976) at both sites, suggesting a large-scale Pb pollution.

7. Acknowledgements

This research was partly supported by the Belgian OSTC project EV/12/10B "A continuous Holocene record of ENSO variability in southern Chile", by the Scientific Co-operation Exchange Program between University of Concepción (Chile) and University of Liège (Belgium) funded by the Belgian CGRI (Commissariat Général aux relations internationales de la Communauté Française de Belgique), and by Fondecyt project N° 1070508. We acknowledge Alberto Araneda for the collection of sediment core LCSP, and Virginie Renson for her help with sample preparation. S.B. is supported by a BAEG fellowship (Belgian American Educational Foundation), and by an EU Marie Curie Outgoing Fellowship under the FP6 programme. The authors acknowledge Dr Ana Moreno for her constructive comments and suggestions.

8. References


Bertrand S, Castiaux J, Juvigné E. 2008. Tephrostratigraphy of the Late Glacial and Holocene sediments of Puyehue Lake (Southern Volcanic Zone, Chile, 40\(^\circ\)S). *Quaternary Research* 70 (3): 343–357. DOI: 10.1016/j.yqres.2008.06.001


Chirinos L. 2005. Registros sedimentarios lacustres de contaminacion atmosferica derivada de los procesos de combustion en la provincia de Concepción – Chile en los


Luque JA, Julia R. 2002. Lake sediment response to land-use and climate change during the last 1000 years in the oligotrophic Lake Sanabria (northwest of Iberian Peninsula). *Sedimentary Geology* **148**: 343–355


835 **Figure captions**

836 Figure 1 – Location of Laguna Chica de San Pedro (LCSP) and Lago Puyehue in
837 South-Central Chile. Bathymetric maps are from Campos et al., 1989 (Puyehue) and
838 Urrutia et al., 2000a (LCSP). LCSP1 and 2 indicate the location of the soil samples
839 collected in the watershed of LCSP.

840 Figure 2 – Age–depth models of cores LCSP and PU-II-P4, based on $^{210}\text{Pb}$
841 analysis (LCSP, data from Chirinos et al., 2005a) and varve-counting (PU-II-P4, data
842 from Boës and Fagel, 2008). For Puyehue, the open squares represent the average
843 age of the 1-cm thick sediment samples used in this study and the error bars are
844 calculated as the cumulated varve-number difference between three independent
845 counts.

846 Figure 3 – Bulk organic geochemistry of cores LCSP (a) and PU-II-P4 (b).
847 Total Organic Carbon (TOC) and Total Organic Nitrogen (TON) are in weight
848 %, and $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ are in ‰ relative to VPDB and AIR, respectively. Zones 1, 2
849 and 3 (LCSP) indicate changes in bulk organic geochemistry, resulting from
850 anthropogenic activities in the lake watershed (see text). Data are presented in tables
851 1a and 1b (online supporting information).

852 Figure 4 – Total, natural and anthropogenic lead concentrations (a), and flux of
853 anthropogenic Pb (b) in sediment cores LCSP and PU-II-P4.
854 In (a), the error bars cumulate errors associated with the geochemical analysis of Pb
855 ($\pm 10\%$ for PU-II-P4, $\pm 16\%$ for LCSP) and Ti ($3\%$ for PU-II-P4 and $1.5\%$ for LCSP).
856 In (b), the error bars cumulate the errors on anthropogenic lead concentrations, sediment
857 accumulation rates and density. See online supporting information for data.

858 Figure 5 – Temporal evolution of $^{206}\text{Pb}/^{204}\text{Pb}$ ratios measured on bulk lake
859 sediments from LCSP and Lago Puyehue. The grey symbols correspond to duplicate
860 analyses. “SVZ” (upper dashed arrow and dark grey area) refers to the isotopic
861 composition of rocks from the Southern Volcanic Zone of Chile. “Trumaos” (vertical
862 dashed arrow) refers to the isotopic composition of soils in the vicinity of Puyehue.
863 “LCSP soils” (lower dashed arrow and light grey area) refers to the mean isotopic
composition of soils in the watershed of Laguna Chica de San Pedro. Data are presented in tables 3a and 3b (online supporting information).

Figure 6 – $^{206}\text{Pb}/^{207}\text{Pb}$ vs. $^{208}\text{Pb}/^{206}\text{Pb}$ isotopic biplots.

(a) Close up on the data obtained on the lake sediment samples. Open symbols represent duplicate analyses. The values calculated for the natural end-members are also indicated. SVZ: Southern Volcanic Zone.

(b) Extended biplot showing the data obtained on the lake sediment samples, the selected end-members, and the mixing-lines (with 10% increments).

For data and/or references see tables 3a and 3b (online supporting information).
A. Laguna Chica de San Pedro

B. Lago Puyehue

Fagel et al – Figure 3
Fagel et al – Figure 5
Fagel et al – Figure 6