

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

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18 **Abstract**

19 In this paper, we compare the elemental and isotopic (C, N, Pb) geochemistry of
20 lake sediments from two contrasted environments in South-Central Chile. The first lake,
21 Laguna Chica de San Pedro (LCSP), is situated in the urbanized area of the Biobio
22 Region (36°S). The second lake, Lago Puyehue (40°S), is located 400 km to the
23 southeast of LCSP and belongs to an Andean national park. Our aim is to identify
24 environmental impacts associated with increasing industrial activities and land-
25 degradation during the last 150 years. In LCSP, shifts in C/N atomic ratios, $\delta^{13}\text{C}$ and
26 $\delta^{15}\text{N}$ from 1915–1937 to the late 80's are attributed to successive land-degradation
27 episodes in the lake watershed. Based on a Pb isotopic mixing model, we estimate that
28 up to 20% of lead in LCSP sediments is supplied from urban atmospheric pollution. By
29 contrast, human impact in the watershed of Lago Puyehue is very limited. We observe
30 no change in organic geochemistry during the last 150 years and lead contamination
31 remains lower than 5%, even during the last decades. Although contamination levels are
32 much higher in LCSP than in Lago Puyehue, a peak in anthropogenic Pb is recorded
33 during the same period (1974–1976) at both sites. This maximum contamination level is
34 consistent with increased industrial activity in the vicinity of Concepción.

35

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

37

38 **Keywords:** anthropogenic activity, geochemistry, lead isotopes, lake sediment, Chile

39 **1. Introduction**

40 Lake sediments constitute sensitive archives of environmental changes affecting the
41 lakes and their catchments (e.g., Smol, 2008). Since geochemistry of lake sediments is
42 largely controlled by the nature and the processes occurring in the lake catchment
43 (Mackereth, 1966; Engstrom and Wright, 1984), sedimentary geochemistry is one of the
44 best methods to reconstruct paleoenvironmental changes that occurred in lake
45 watersheds. Moreover, recent improvements in dating techniques (e.g., ^{210}Pb , ^{14}C) of
46 recent sediments allow sediment cores to be used as faithful recorders of recent human
47 impacts (Smol, 2008). For instance, variations in sedimentation rates have been used to
48 study historical changes in erosion processes and assess land-use changes during
49 historical times (Debels *et al.*, 1999; Luque and Julia, 2002). Paleolimnological
50 approaches have also been used to support studies of identification of metal pollution in
51 aquatic environments (Smol, 2008). Among metals, lead is a good pollution indicator
52 that is immobile in natural environment archives such as lake sediments (Bränvall *et al.*,
53 2001). Recently, stable Pb isotopic signatures of lake sediments have been used to trace
54 the source of anthropogenic contaminations associated with Pb (e.g., Gallon *et al.*,
55 2005, Hou *et al.*, 2006, Couillard *et al.*, 2008).

56 Carbon to nitrogen elemental ratios, as well as stable carbon ($\delta^{13}\text{C}$) or nitrogen
57 ($\delta^{15}\text{N}$) isotope ratios of sedimentary organic matter is frequently used to reconstruct
58 sources of sedimentary organic matter and past lake productivity (e.g., Schelske and
59 Hodell, 1991; Brenner *et al.*, 1999; Meyers, 2003; Perdue and Koprivnjak, 2007; Das *et*
60 *al.*, 2008). Organic geochemistry reflects the autochthonous or allochthonous origin of the
61 organic matter, i.e., aquatic-derived organic matter *vs.* terrestrial vegetation. Since
62 terrestrial plants are characterized by C-rich and protein-poor structural material, their
63 C/N atomic ratios is generally well above 20 (Meyers and Terranes, 2001). On the
64 contrary, the C/N ratio of lake plankton averages 8 to 10, which makes the C/N ratio of
65 lake sedimentary organic matter a useful tool to reconstruct organic matter origin, and
66 environmental changes that occurred in lakes and their watersheds. Similarly, the
67 carbon isotopic composition of organic matter in lake sediments is influenced by both
68 organic matter sources and paleoproductivity rates (Meyers and Terranes, 2001).
69 Therefore combining organic geochemical composition and stable carbon or nitrogen
70 isotopic signature of lake sedimentary organic matter generally reveals important clues
71 about past lake productivity and changes in terrestrial supplies.

72 Lead isotopes analysis has been applied to diverse materials in order to assess
73 spatial and temporal changes of recent pollution from industries and from leaded
74 gasoline (e.g., Shirahata *et al.*, 1980; Rosman *et al.*, 1993; Véron and Church, 1997).
75 The sources of lead preserved in sedimentary archives are diverse and can be traced
76 using their isotopic signature (Renberg *et al.*, 2002), which depends on the geological
77 origin and age of the original lead-bearing rocks and sediments (Faure, 1986).
78 Naturally, lead is transported to sedimentary environments through weathering of soils
79 and bedrock or more directly within mineral matter eroded from the catchment. The
80 anthropogenic source of lead is associated with airborne particles from leaded gasoline
81 and industries. Alkyl-lead, a common man-made organic form a lead, has been used as
82 a fuel additive to reduce "knock" in combustion engines since the 1920s (Bollhöfer and
83 Rosman, 2000). Other major sources of atmospheric Pb are mining, smelting, refining
84 of non-ferrous metal, waste incineration and coal burning (Nriagu and Pacyna, 1988,
85 Bollhöfer and Rosman, 2000). Lead is also associated with the emission of other
86 pollutants and it has been used to study long range transport and atmospheric mixing
87 processes responsible for the pollution of remote environments (e.g., Duce *et al.*, 1983).

88 Prior to the advent of lead pollution, atmospheric deposition contributed an
89 insignificant fraction of lead accumulated in lake sediments relative to the supply from
90 the catchment (Bindler *et al.*, 2001). However, since ancient times, lead derived from a
91 variety of human activities has been transported atmospherically and deposited on lakes
92 and their catchments (Renberg *et al.*, 2002). In modern times, anthropogenic lead
93 accounts for approximately 95% of the global lead cycle (Settle and Patterson, 1980).
94 On a global scale, ~85% of industrial Pb emissions are introduced in the atmosphere in
95 the Northern Hemisphere (Schaule and Patterson, 1981). Taking into account the
96 residence time of Pb-rich aerosols in the atmosphere (~10 days — Settle and Patterson,
97 1991), those Northern Hemisphere emissions have a negligible impact on the Southern
98 Hemisphere (Bollhöfer and Rosman, 2000).

99 Early studies of atmospheric contamination of lake sediments focused on long-
100 established industrialized regions of Europe and North America (Boyle, 2001). More
101 recently, work has been undertaken in the newly industrialized countries and in areas
102 less directly influenced by industrial activities. However, the Southern Hemisphere
103 remains relatively understudied. Here, we use stable lead isotopes (new data) and
104 organic geochemistry (new data and data from Bertrand *et al.*, 2005) to identify the
105 environmental impacts associated with increasing industrial activities and land-

106 degradation during the last 150 years in South-Central Chile. We compare sedimentary
107 geochemical records from two contrasting lake settings, i.e., Laguna Chica de San
108 Pedro, which is located in an urbanized area and thus immediately affected by
109 pollution, and Lago Puyehue, which is located in an Andean national park with very
110 limited human activities. Our aim is to investigate the local and global impacts of
111 anthropogenic activities in Chile, i.e., one of the most industrialized countries in South
112 America, with over 90% of its population living in urban areas.

113

114 **2. Material and study area**

115 2.1. Location

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

136 Lago Puyehue (40°40'S, 72°20'W) is an oligotrophic, moraine-dammed lake located
137 at the foothill of the Cordillera de Los Andes, at approximately 50 km from the city of
138 Osorno (Fig. 1). The lake lies at an elevation of 185 m.a.s.l. and has a complex
139 bathymetry, with several sub-basins separated by a continuous bathymetric ridge and

140 with a series of small bedrock islands in its centre (Charlet *et al.*, 2008). The lake has a
141 surface area of 164 km² and a maximum depth of 123 m, and is located in a Tertiary
142 valley over-deepened by Quaternary glacial advances (Campos *et al.*, 1989). The
143 watershed of the lake covers 1267 km² and is composed of Quaternary volcanic rocks
144 that are generally buried under several meters of post-glacial andosols (i.e., *Trumaos*)
145 (Laugenie, 1982; Bertrand and Fagel, 2008). Several active volcanoes surround the
146 lake: the Antillanca and Puyehue-Cordón de Caulle volcanic complexes eastward, and
147 the Osorno volcano to the South (Fig. 1). The eastern part of the lake watershed belongs
148 to a natural park (the *Parque Nacional Puyehue*) that is virtually free of anthropogenic
149 influence. The population is concentrated in small lowly-populated villages along the
150 southern shore of the lake. The whole region is dominated by westerly winds and the
151 lake is fed by Rio Golgol to the East and by several smaller rivers (Fig. 1). Its outlet,
152 i.e., Rio Pilmaiquen, merges with Rio Bueno and flows into the Pacific westward. Since
153 1944, Rio Pilmaiquen has been dammed by a hydro-electric station 6 km downstream of
154 Lago Puyehue (Laugenie, 1982). The lake is monomictic, with stratification in summer
155 and mixing during the winter months (Campos *et al.*, 1989).

156

157 2.2. Coring and core processing

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

168 In Lago Puyehue, the selection of the coring site is based on high-resolution seismic
169 profiles obtained in February 2002 (Charlet *et al.*, 2008). Site PU-II is located on a sub-
170 aquatic moraine ridge at 48.4 m depth in the southern part of the lake (Fig. 1). The site
171 is under the influence of interflows from the Golgol river. At PU-II site, five short cores
172 were taken using a Uwitec short gravity coring device. For this paper, core PU-II-P4
173 has been opened described and sampled every 1 cm. Organic geochemistry was

174 measured on parallel core PU-II-P5. Macroscopically, sediment core PU-II-P4 is
175 composed of homogeneous to finely laminated silty sediments, and contains a few
176 tephra layers. The core contains two fine green layers representing the in-situ alteration
177 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
178 cm and 42.0–42.2 cm (Bertrand *et al.*, 2005, 2008). Microscopic observations reveal
179 the occurrence of annually laminated sediments composed of an alternation of
180 terrigenous clays and diatomaceous clays, except for a massive layer between 3.5 and 6
181 cm (Boës and Fagel, 2008).

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

191

192 2.3 Chronology

193 The age-depth model of LCSP sediment core (Fig. 2) is based on ^{210}Pb
194 concentrations (Chirinos *et al.*, 2005a). Ages have been estimated using the constant
195 rate of supply model (CRS) and are listed in Table 2a (online supporting information).
196 The oldest available ^{210}Pb date corresponds to AD 1880 ± 26 years, at a depth of 18 cm.
197 Here, we focus on the upper 20 cm of the sediment core, which represents the last ~150
198 years. Low sedimentation rates have been calculated between 14 and 18 cm (as low as
199 0.04 mm/yr), and the highest sedimentation rates occur at 9–10 cm (1.5 mm/yr, AD
200 1976–1977).

201 For the sediments of PU-II coring site, the age-depth model (Fig. 2) is based on
202 varve-counting results obtained on parallel core PU-II-P5 (Boës and Fagel, 2008). They
203 are in agreement with radionuclide profiles (^{210}Pb and ^{137}Cs ; Arnaud *et al.*, 2006) and
204 with the recognition of historically-documented event deposits (Boës and Fagel, 2008,
205 Bertrand *et al.*, 2008). In particular, the massive layer microscopically described at 3.5–
206 6 cm has been attributed to the 1960 Valdivia earthquake and used as a time-marker
207 (Boës and Fagel, 2008). In this paper, we focus on the upper 22 cm of PU-II-P4

208 sediment core, which covers the last ~150 years (1833–1842 AD at 21.5 cm).
209 Sedimentation rates vary from 0.7 to 1.7 mm/year (Table 2b, online supporting
210 information).

211

212 **3. Methods**

213 3.1 Bulk organic geochemistry

214 Stable isotope ratios of carbon and nitrogen were measured by
215 continuous flow isotope ratio mass spectrometry after sample combustion to CO₂ and
216 N₂ at 1000°C in an on-line elemental analyzer. For PU-II-P5 sediments, approx 25 mg
217 of sediment was oven-dried, ground and homogenized in an agate mortar, and analyzed
218 on a FISOONS NA 1500 NC elemental analyser in line with an Optima mass
219 spectrometer (GV Instrument, Lab. Océanologie, ULg, Belgium). The other samples
220 (LCSP, river and soils samples) were freeze-dried, ground and homogenized in an agate
221 mortar, decarbonated using 1N sulphurous acid and analyzed at the UCDavis Stable
222 Isotope Facility, USA, on an Europa Hydra 20/20 mass spectrometer in line with an
223 ANCA-GSL elemental analyzer. Before introduction to the IRMS the gases were
224 separated on a Carbosieve G column. Isotopic measurements are presented as δ values
225 (‰) expressed relative to VPDB ($\delta^{13}\text{C}$) or AIR ($\delta^{15}\text{N}$) standards. The precision is
226 calculated by replicate analysis of internal standards, i.e., sucrose (ULg, $\delta^{13}\text{C} = -10.3 \pm$
227 0.2 ‰) or a mixture of ammonium sulfate and sucrose (UCDavis, $\delta^{13}\text{C} = -23.83$ ‰,
228 $\delta^{15}\text{N} = 1.33$ ‰). For $\delta^{13}\text{C}$, the precision is 0.04 ‰ (UCDavis) or 0.20 ‰ (ULg), and
229 the precision for $\delta^{15}\text{N}$ is 0.18 ‰ (UCDavis).

230

231 3.2. Inorganic geochemistry and Pb isotopes

232 Total Pb and Ti concentrations of LCSP sediments were determined by ICP-OES
233 with an accuracy of 16% for Pb and 1.5% for Ti (2 RSD, Chirinos *et al.*, 2005b). For
234 sediment core PU-II-P4, total Ti concentrations were determined by XRF on fused glass
235 beads, with an accuracy of 3 % (Bertrand *et al.*, 2005) and total Pb was estimated by
236 MC-ICP-MS (accuracy: 10%).

237 For Pb isotopes, ~500 mg of sediment was heated at 550°C overnight to volatilize
238 organic matter. The weight loss-on-ignition at 550°C ranges between 13 to 16% for
239 LCSP sediments (Chirinos, 2005) and vary between 1.5 and 11% for PU-II-P4
240 sediments (Bertrand *et al.*, 2005). The samples (~50 mg for LCSP and 100 mg for PU-

241 II-P4) were subsequently dissolved in closed Teflon beakers in an HF-HNO₃ mixture,
242 and placed on a hot plate (110°C) for 3 days. The solution was then evaporated to
243 dryness, re-dissolved in HCl, re-evaporated and finally dissolved in 0.8N HBr. Lead
244 (Pb) was chemically extracted using an AG1-X8 anionic resin loaded in a 2 ml column
245 in an HBr environment (Manhès *et al.*, 1978). Pb isotopes were measured using a Nu-
246 Plasma Multi Collector-Inductively Coupled Plasma-Mass Spectrometer (MC-ICP-MS)
247 at the 'Département des Sciences de la Terre et de l'Environnement' (DSTE - Université
248 Libre de Bruxelles). As an internal isotopic standard, a thallium solution was added to
249 each sample and standard to monitor and correct for mass dependent isotopic
250 fractionation. Whilst the samples were characterized by a large variability in Pb
251 concentrations, the sample solutions were prepared to obtain a beam intensity in the
252 Axial collector (²⁰⁴Pb) of minimum 100 mV, and a Tl/Pb ratio of ~ 0.2, matching the Pb
253 and Tl concentrations of the NBS981 standard (200 ppb in Pb, added with 50 ppb in Tl).
254 Tl/Pb ratio was relatively stable from one day of analysis to another. For PU-II-P4
255 sediments, Tl/Pb ranges between 0.14 and 0.23. For LCSP, this ratio is usually less than
256 0.5, except for one sample (0.58). In the course of the study, measurements of NBS981
257 yielded weighted average values of 36.7158 ± 0.027 (2SD) for ²⁰⁸Pb/²⁰⁴Pb, $15.4969 \pm$
258 0.011 for ²⁰⁷Pb/²⁰⁴Pb, 16.9399 ± 0.0011 for ²⁰⁶Pb/²⁰⁴Pb, 0.9148 ± 0.0001 for ²⁰⁷Pb/²⁰⁶Pb,
259 and 2.1674 ± 0.0007 for ²⁰⁸Pb/²⁰⁶Pb, which are in good agreement with long term
260 laboratory values (n = 1000, ²⁰⁸Pb/²⁰⁴Pb = 36.7130 ± 0.012 (2SD), ²⁰⁷Pb/²⁰⁴Pb =
261 15.4950 ± 0.004 (2SD), ²⁰⁶Pb/²⁰⁴Pb = 16.9393 ± 0.0044 (2SD)), with the TIMS values
262 published by Galer and Abouchami (1998), and with the MC-ICP-MS values of Weis *et*
263 *al.* (2006). These values are also in agreement with TIMS triple-spike values previously
264 published by Galer and Abouchami (1998). Although the NBS981 standard results were
265 within error of the triple-spike values after online correction for instrumental mass bias
266 by Tl addition, the results were further corrected by the sample-standard bracketing
267 method (as described by White *et al.* (2000) and Weis *et al.* (2006)) to circumvent any
268 instrumental drift during the analytical session. Duplicates of the entire analytical
269 procedure (n = 7) are reported in Table 3 (online supporting information), and all fall
270 within error bars.

271

272 **4. Results**

273 4.1. Laguna Chica de San Pedro

274 The TOC and TON profiles of LCSP are roughly parallel, with the TOC and TON
275 values ranging from 3.1 to 5.0 % and 0.3 to 0.5 %, respectively (Fig. 3a). The C/N
276 atomic ratio varies from 11.2 to 15.2. The carbon and nitrogen isotopic values range
277 from -22.8 to -27.6 ‰ and 2.7 to 4.6 ‰, respectively. Two significant changes are
278 observed in all the variables at around 5 cm and 14 cm depth (Fig. 3a). The samples
279 collected in the lake watershed show values typical for terrestrial organic matter (C/N:
280 16.5 ± 1.0 ; $\delta^{13}\text{C}$: -25.8 ± 0.9 ; $\delta^{15}\text{N}$: 7.6 ± 2.5), with no significant difference between
281 the river sediment sample and the soil samples (Table 1a, online supporting
282 information).

283 Lead concentration and isotopic composition has been determined in thirteen
284 samples from LCSP sediment core and on a few samples from the catchment (soil
285 profiles and river sediments, see location on Figure 1) (Figs. 4-6; Tables 2a and 3a,
286 online supporting information). The Pb composition of LCSP sediments remains
287 relatively stable in the lower core section, i.e., in the interval between 11 and 20 cm
288 corresponding to sediments older than 1972 A.D (Fig. 5). For instance the mean
289 $^{206}\text{Pb}/^{204}\text{Pb}$ ranges around 18.533 ± 0.022 (2 SD). Then a shift to lower $^{206}\text{Pb}/^{204}\text{Pb}$,
290 $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios is observed in the upper 10 cm (Figs. 5 and 6). It is
291 especially pronounced in the last 3 cm, i.e., in sediments younger than 1992 (Fig. 5).
292 The $^{206}\text{Pb}/^{204}\text{Pb}$ ratio decreases down to 18.257 ± 0.022 in the upper 0–1 cm sample.
293 The range of variation in $^{206}\text{Pb}/^{204}\text{Pb}$ ratio (standard deviation = 0.079) reached in the
294 upper section is 4-fold higher than in the lower section. Note that the general trend in
295 the Pb isotopic profile, in particular the uppermost sharp shift, is confirmed by the three
296 duplicate analyses reported on Fig. 5. The signature of the soil and river samples is
297 more scattered, with $^{206}\text{Pb}/^{204}\text{Pb}$ ranging between 18.481 and 18.768 (mean = 18.628;
298 standard deviation = 0.11, online supporting information table 3a). The river sediments
299 and the lower soil sample of site 2 display the highest isotopic ratios. The lowest
300 isotopic ratios (e.g., $^{206}\text{Pb}/^{204}\text{Pb} = 18.4807 \pm 0.0010$) are recorded in the upper soil
301 sample at site 2 (see Fig. 1 for location). At site 1 the two soil samples collected from
302 the upper brown to black and lower red to brown horizons give similar Pb composition
303 (e.g., $18.5847 \pm 0.0009 < ^{206}\text{Pb}/^{204}\text{Pb} < 18.5869 \pm 0.0009$, online supporting information
304 table 3a). Those Pb ratios are more radiogenic than the lacustrine sediments values. For
305 instance, all the $^{206}\text{Pb}/^{204}\text{Pb}$ values for LCSP are lower than 18.5644 ± 0.0018 . The
306 mean soil signature displays slightly more radiogenic $^{206}\text{Pb}/^{204}\text{Pb}$ ratios (18.593) than
307 the lower core section (Fig. 5).

308

309 4.2 Lago Puyehue

310 The TOC and TON profiles of the upper 22 cm of PU-II-P5 sediment core are
311 roughly parallel (Fig. 3b), with particularly low values at 13.5 cm, which are due to
312 the occurrence of a tephra layer (Bertrand *et al.*, 2005). The lake sediments
313 (excluding the tephra layer) are characterized by TOC and TON values ranging from
314 1.9 to 3.6 %, and 0.3 to 0.2 %, respectively, and slightly decreasing towards the
315 bottom of the core. The C/N ratio and the $\delta^{13}\text{C}$ values do not show any particular
316 trend, and the values range between 12.8 and 14.7 for C/N and -27.8 to -28.8 ‰ for
317 $\delta^{13}\text{C}$. The river sediment samples are characterized by more terrestrial values that do
318 not vary significantly between the different rivers (C/N: 13.1 ± 1.0 and $\delta^{13}\text{C}$: $-27.2 \pm$
319 0.5). Details regarding each particular river are given in Bertrand *et al* (in press).

320 The Pb elemental and isotopic composition of 10 bulk sediment samples from
321 sediment core PU-II-P4 are reported in figures 4, 5 and 6, and the data are presented
322 in tables 2b and 3b (online supporting information). The Pb isotopic ratios vary
323 within a narrow range in most of the studied core section. For instance, the
324 $^{206}\text{Pb}/^{204}\text{Pb}$ values are comprised between 18.5069 ± 0.0007 and 18.6097 ± 0.0008
325 (Fig. 5). Similarly to the LCSP record, a slight excursion to lower $^{206}\text{Pb}/^{204}\text{Pb}$,
326 $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios occur in the upper sediment section. The change is
327 gradual. It appears within the upper 3 cm, i.e., since at least 1976 AD (Fig. 5). Again,
328 duplicates (n=5, online supporting information table 3a) confirmed the observed
329 isotopic trend.

330

331 5. Discussion

332 5.1 Sources of organic matter and land-use changes over the last 150 years

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

340

341 5.1.1 Laguna Chica de San Pedro

342 In LCSP, the lake sedimentary organic matter represents a mixture of terrestrial
343 organic matter (C/N: 16.5 ± 1.0) and lake plankton (C/N generally between 6 and 10,
344 Meyers and Terranes, 2001). Shifts towards higher C/N ratios are interpreted as a
345 higher supply of terrestrial organic matter and/or lower lake productivity and *vice*
346 *versa*. At LCSP, the measured C/N atomic ratios and isotopic values display
347 significant and concomitant shifts, evidencing a variable contribution of lake *versus*
348 terrestrial organic matter during the last ~150 years. In the deepest part of the core
349 (20–14 cm, i.e., 1880–1953 AD) the C/N ratios are relatively low (~12), evidencing a
350 high contribution of lake plankton compared to the supply of terrestrial organic
351 matter. Then, around 1950–1955, the C/N ratios and the TOC sharply increase,
352 which probably represents a higher supply of terrestrial organic matter, with approx.
353 ~80% of the organic matter originating from the lake watershed. The C/N values
354 remain high until around 1986, where they gradually decrease towards the present-
355 day conditions, reflecting a decrease in the terrestrial supply of sedimentary organic
356 matter and/or higher lake productivity during the last 2 decades. During the last 17
357 years, the TOC values are generally low, evidencing that the shift in the C/N atomic
358 ratio at around 5 cm is most likely due to a decrease in the supply of terrestrial
359 organic matter. A shift towards less negative $\delta^{13}\text{C}$ and a concomitant decrease of the
360 $\delta^{15}\text{N}$ values (Fig. 3) between in ~1953 AD are in agreement with an increased supply
361 of terrestrially-derived organic carbon during the 1953–1986 AD period.

362 The significant increase in the supply of terrestrial organic matter to LCSP at
363 around 1953 is strikingly consistent with a rapid increase in the total mass
364 accumulation rate of sediment in the same core (Chirinos *et al.*, 2005a) and in
365 another core from the same lake (Cisternas and Araneda, 2001; Cisternas *et al.*,
366 2001). In addition, Urrutia *et al.* (2000b) observed a significant increase in terrestrial
367 hydrocarbons and fatty acids in ~ 1945 in agreement with our interpretation.

368 The observed changes in the supply of terrestrial organic carbon are most likely
369 linked to anthropogenic activities in the watershed of LCSP, mostly related to
370 deforestation. Although the replacement of the native forest by commercial
371 plantation in the watershed of LCSP began at the end of the 19th century, it only
372 became intensive in the mid 20th century (Debels *et al.*, 1999; Urrutia *et al.*, 2000b,
373 Cisternas *et al.*, 2001). In 1943, the native forest still occupied 70% of the watershed
374 area and no area had been left deforested (Cisternas *et al.*, 2001). Between 1943 and
375 1955, 17% of the forest had been logged and replaced by exotic species. Most of the

376 native species disappeared between 1943 and 1994 (from 70.1% to 12.6 %).
377 Although some of them have been replaced by pine plantations, deforested areas
378 started to occur in 1961, and were covering up to 22% of the lake watershed between
379 1961 and 1981 (Cisternas *et al.*, 2001). In 1994, most of the watershed had been
380 replanted with exotic species. In the watershed of LCSP, human settlement began in
381 1961 and peaked in 1981 (Cisternas *et al.*, 2001).

382 Deforestation and denudation of the soil cover generally result in increased soil
383 erosion and runoff of soil particles (including organic matter), which in turn triggers
384 higher sedimentation rates in lake sediments (e.g., Page and Trustrum, 1997). The
385 increased supply of terrestrial organic matter in the sediments of LCSP between 1953
386 and 1986 is in good agreement with the peak of anthropogenic activities in the lake
387 watershed, especially deforestation, clear-cutting of indigenous species and human
388 settlement. After 1986, our results show a decrease in TOC and C/N, which reflects a
389 decrease in the supply of terrestrial organic matter into the lake. This change is very
390 likely related to the stabilization of the soils in the lake watershed in response to
391 reforestation after 1981. It is noteworthy that the anthropogenic introduction of the
392 macrophyte *Egeria densa* in LCSP in the mid-eighties (Urrutia *et al.*, 2000b) is not
393 directly recorded in the lake sediments (i.e., no increase in C/N), although it acted a
394 sink for nutrients, resulting in the actual apparent oligotrophication of the lake.

395

396 5.1.2 Lago Puyehue

397 The sedimentary organic matter of core PU-II-P4 is composed of a mixture of
398 terrestrial and aquatic end-members that are characterized by average C/N atomic
399 ratios of 13.7 (river sediment), 14.6 (soils and paleosoils), and 8.5 (lake plankton),
400 respectively (Bertrand *et al.*, in press). By contrast with the sediments of LCSP, the
401 sediments of Lago Puyehue show rather stable C/N and $\delta^{13}\text{C}$ values during the last
402 150 years (Fig. 3), ranging around 13.4 and 28.4 ‰, respectively. No significant
403 trend is observed and the only excursions of the C/N ratio occur at 8–9 and 13–14
404 cm, in relation with a clay layer (weathered pumices) and a sandy tephra layer,
405 respectively. Because of the remote location of Lago Puyehue and its situation within
406 a national park, anthropogenic impacts in the lake watershed are very minor, and do
407 not affect the soil erosion and the terrestrial runoff. Neither can they modify the lake
408 trophic conditions. Therefore, the composition of the bulk sedimentary organic
409 matter in Lago Puyehue reflects the natural supply and export production of

410 terrestrial and aquatic organic matter. Changes in its composition over longer time-
411 scales are driven by natural variations in lake productivity, resulting from natural
412 changes in the supply of nutrients to the lake (Bertrand *et al.*, 2005). The sediments
413 of Lago Puyehue are therefore a good archive of paleoclimate changes over the last
414 millennia (Bertrand *et al.*, 2005) and even since the Last Glacial Maximum (Bertrand
415 *et al.*, in press), but do not contain any evidence of anthropogenic impact.

416

417 5.2. Sedimentary Pb isotopes: a record of human activities over the last 150 years

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

425

426 5.2.1 Estimation of anthropogenic lead using Pb concentrations

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

$$437 \quad Pb_{\text{anthropogenic}} = Pb_{\text{sample}} - [(Ti_{\text{sample}} * Pb/Ti_{\text{natural}})] \quad (1)$$

438 where Pb/Ti_{natural} is the Pb/Ti ratio measured in pre-anthropogenic sediments.

439 The assumption that the Pb/Ti_{natural} ratio of pre-anthropogenic sediments is
440 constant in the whole core is usually valid for lakes with catchments characterized by
441 a relatively small size (like for LCSP) and/or by a simple and homogeneous geology
442 (like for both lakes: metamorphic rocks in LCSP, dominant volcanic andesitic or
443 basaltic rocks in Puyehue).

444 In order to compare distant records, anthropogenic Pb fluxes are generally more
445 appropriate than concentrations (Arnaud *et al.*, 2004). Therefore, we calculated the
446 flux of bulk (F_{bulk}) and anthropogenic ($F_{\text{anthropogenic}}$) lead using the concentration data,
447 the dry density D (g/cm^3) and the sediment accumulation rate SAR (cm/yr) estimated
448 from the respective age models:

$$449 \quad F_{\text{bulk}} = D * \text{SAR} * \text{Pb}_{\text{sample}} \quad (2)$$

$$450 \quad F_{\text{anthropogenic}} = F_{\text{bulk}} * \% \text{Pb}_{\text{anthropogenic}} \quad (3)$$

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

458 In LCSP sediments, the total lead concentration increases from 40 ppm in the
459 pre-industrial samples (before 1965) up to a maximum of 58 ppm in the sample
460 corresponding to year 1974 (Fig. 4). It corresponds to 18 ppm of $\text{Pb}_{\text{anthropogenic}}$ and an
461 anthropogenic flux of $10 \text{ mg}/\text{m}^2/\text{yr}$. The flux of $\text{Pb}_{\text{anthropogenic}}$ is the highest in 1985
462 ($16.1 \text{ mg}/\text{m}^2/\text{yr}$) but is generally well above $10 \text{ mg}/\text{m}^2/\text{yr}$ between 1974 and 1991,
463 where it represents up to 30% of the total Pb.

464 In both lakes, we evidence a peak in Pb concentration in 1974–1976 (Fig. 4).
465 Taking into account the error in age model and the sampling resolution, it
466 corresponds to a synchronous change despite the contrasted environments of the two
467 lake settings. Such change underlines the global character of the Pb contamination in
468 Chile. The contamination by industrial airborne particles is approximately 10 times
469 greater in LCSP than in Lago Puyehue, reflecting the natural setting characterizing
470 the region of Puyehue. Interestingly, the inception of airborne pollution in LCSP is
471 consistent with the detection of spheroidal carbonaceous particles, i.e., residue of
472 fossil fuel combustion, in LCSP sediments. Indeed, using the same sediment core,
473 Chirinos *et al.* (2005a) have detected the occurrence of SCP only in sediments
474 younger than 1976 (first 11 cm of the sediment core). Detection of contamination in
475 newly industrialized countries and in areas remote from industry can be difficult and
476 it is important to pay attention to estimation of the natural concentrations, especially
477 in region where atmospheric contamination is minor (Boyle, 2001), as it is the case

478 in Chile. Even if Concepción is one of the most industrialized cities in Chile, the flux
479 of anthropogenic Pb recorded in the sediments of LCSP (10–15 mg/m²/yr) is still 2–3
480 times lower than in the French Alps and in Canada (30 mg/m²/yr, Arnaud *et al.*,
481 2004; Ndzangou *et al.*, 2005).

482

483 5.2.2 Estimation of anthropogenic lead using Pb stable isotopes

484 The anthropogenic lead content can similarly be calculated using lead stable
485 isotopes, with the main advantage that we can now discuss the possible sources of
486 anthropogenic lead. The downcore records of the ²⁰⁶Pb/²⁰⁴Pb ratio are illustrated in Fig.
487 5. They show that the Pb isotopic composition of the two sedimentary environments
488 depicts a similar trend through the last ~150 years, with less radiogenic values in the
489 most recent sediments. The isotopic sedimentary Pb signatures are relatively constant in
490 older sediments (Fig. 5). The ²⁰⁶Pb/²⁰⁷Pb and ²⁰⁸Pb/²⁰⁶Pb results are illustrated in Fig. 6.
491 At both sites, we note a decrease of the ²⁰⁶Pb/²⁰⁷Pb and an increase of ²⁰⁸Pb/²⁰⁶Pb ratios
492 towards the surface (Fig. 6b). The shift seems to start earlier in the sediments of LCSP
493 than in those of Lago Puyehue, (i.e., between 1969 and 1976 and between 1976 and
494 1990, respectively), although this might be affected by the relatively low sampling
495 resolution. These trends evidence a supply of anthropogenic Pb than can be estimated
496 using Pb isotopes after identification of the isotopic signatures of the natural and
497 anthropogenic sources. In both lakes, the lead isotopic compositions (²⁰⁶Pb/²⁰⁷Pb –
498 ²⁰⁸Pb/²⁰⁶Pb) are distributed along two different trends (Fig. 6), which can be interpreted
499 as mixing lines between two end-members. One end-member represents the regional
500 natural background sedimentation. The other end-member, characterized by lower
501 ²⁰⁶Pb/²⁰⁷Pb and higher ²⁰⁸Pb/²⁰⁶Pb ratios, coincides with the anthropogenic source.

502

503 *a. Identification of the natural sources of lead*

504 In lake sediments the “old” or pre-industrial samples are usually used as
505 representative of the isotopic composition of the sediment matrix (e.g., Arnaud *et al.*,
506 2004). In Lago Puyehue, a long record of the sedimentary Pb composition is
507 available (Deraymaeker, 2003). The range of variation of Pb ratios measured on an
508 11 m-long core (PU-II) is narrow. The Holocene and deglacial sediments are
509 characterized by stable Pb isotopic signatures. Their averaged signature ratios
510 (²⁰⁶Pb/²⁰⁷Pb ~1.191; ²⁰⁸Pb/²⁰⁶Pb ~2.071) are therefore used to characterize the natural
511 end-member. The definition of this natural end-member is consistent with regional

512 soil and volcanic rock data (Fig. 6). The Puyehue catchment is covered by volcanic-
513 derived soils (“Trumaos”, Bertrand and Fagel, 2008), characterized by $^{206}\text{Pb}/^{207}\text{Pb}$
514 and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios of 1.192 and 2.070, respectively. The Trumaos signature is
515 therefore in good agreement with the sedimentary pre-anthropogenic Pb isotopic
516 composition (Deraymaeker, 2003; Fig. 6). The average Pb isotopic composition of
517 the volcanic rocks from the surrounding area also perfectly agrees with the
518 composition of the pre-industrial sediments. For instance the mean $^{206}\text{Pb}/^{204}\text{Pb}$ value
519 calculated for the Southern Volcanic Zone (SVZ) between 36 and 41°S ($18.5984 \pm$
520 0.0619 , online supporting information table 3b) perfectly agrees with the
521 sedimentary $^{206}\text{Pb}/^{204}\text{Pb}$ values of PU-II-P4 below 3 cm (Fig. 5). In the $^{208}\text{Pb}/^{206}\text{Pb}$ -
522 $^{206}\text{Pb}/^{207}\text{Pb}$ biplot (Fig. 6), the mean SVZ signature ($^{206}\text{Pb}/^{207}\text{Pb}$: 1.192, $^{208}\text{Pb}/^{206}\text{Pb}$:
523 2.068–2.070) is adjacent to the Trumaos-representative signature.

524 According to the ^{210}Pb age model, the sediment core from LCSP can be divided
525 into a pre-industrial period before 1915 (below 16 cm) and an industrial period after
526 1915 (Chirinos *et al.*, 2005b). We can therefore estimate the natural Pb isotopic
527 signature by the averaging the results of the 3 lowest samples, resulting in $^{206}\text{Pb}/^{207}\text{Pb}$
528 and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios of 1.186 and 2.084, respectively (online supporting information
529 table 3a). Unfortunately, there is a lack of data regarding the Pb isotopic composition
530 of rocks in the region of Concepción. However, in January 2007 we collected and
531 analyzed several sediment samples from soils outcropping around the lake and from
532 the only river flowing into LCSP. Although we are aware this sampling is not
533 exhaustive, it gives an estimate of the scattering of the natural Pb isotopic
534 composition of the LCSP watershed. The mean watershed signature ($^{206}\text{Pb}/^{207}\text{Pb}$:
535 1.192, $^{208}\text{Pb}/^{206}\text{Pb}$: 2.079) and the mean soil signature ($^{206}\text{Pb}/^{207}\text{Pb}$: 1.190,
536 $^{208}\text{Pb}/^{206}\text{Pb}$: 2.080) are comparable to the Pb isotopic composition of the pre-
537 industrial LCSP sediment samples (Fig. 6). The only outlier is soil 2A, which has
538 been collected in the upper part of an outcrop in the southern part of the lake
539 watershed, and may therefore contain industrial lead.

540

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

542 The composition of the anthropogenic end-member is influenced by Pb
543 atmospheric emissions related to alkyl-lead and industrial activities. Bollhöfer and
544 Rosman (2000) have analyzed aerosols collected between 1994 and 1999 at >70 sites
545 widespread in Southern Hemisphere in order to define the modern isotopic signature

546 for atmospheric lead. The isotopic composition in Chile is characterized by low
547 $^{206}\text{Pb}/^{207}\text{Pb}$ ratios (down to 1.06 at the Southern tip of Chile), probably reflecting the
548 supply of alkyl-lead from the UK producer Associated Octel, i.e., the world's
549 primary alkyl-lead producer. Associated Octel has used Pb from different ores (e.g.,
550 Broken Hill in Australia) in variable proportions with time and location (Véron *et al.*,
551 1999). In Chilean airborne samples, the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio, for instance, increases
552 northward, from Punta Arenas (1.063) via Villarica (1.069) and Concepción (1.103)
553 up to a maximum ratio of 1.150–1.182 in Santiago (see online supporting
554 information table 3). This shift can be explained either by different market shares in
555 petrol (different alkyl-lead mixings provided to different cities) or by a change in
556 relative contribution of industrial Pb and leaded petrol. Industrial activities may be a
557 more important source of atmospheric Pb in Santiago than at the Southern tip of the
558 country. Keeping in mind this spatial variability, we selected the lead isotopic
559 signature of airborne particles from the closest city of each lake (Concepción for
560 LCSP, Villarica for Puyehue) to characterize the anthropogenic end-member of each
561 location.

562

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

564 Assuming that the lead isotopic composition of each sample is a mixture of only
565 two sources, i.e., natural lead derived from soil and rocks from the catchment
566 ($\text{IS}_{\text{natural}}$) and anthropogenic lead ($\text{IS}_{\text{anthropogenic}}$), we can estimate the relative
567 contribution of natural and anthropogenic lead using a simple binary mixing model
568 (equation 4 — e.g., Renberg *et al.*, 2002):

569
$$\text{IS}_{\text{sample}} = \alpha * \text{IS}_{\text{anthropogenic}} + \beta * \text{IS}_{\text{natural}}, \text{ with } \alpha + \beta = 1 \quad (4)$$

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

577

578 5.2.3 Anthropogenic lead: general interpretation and comparison of the two
579 estimates

580 Although several studies suggest that the main process of anthropogenic lead
581 incorporation into lake systems is direct atmospheric deposition (Dillon and Evans,
582 1982; Blais and Kalff, 1993), others show that pollutants previously deposited in lake
583 catchments also contribute significantly to the global supply of Pb to lake sediments
584 (Miller and Friedland, 1994). These studies however show that the anthropogenic lead,
585 mainly deposited in lake catchments after 1960, will not be released to upland streams
586 before the middle of the next century (Miller and Friedland, 1994), and has therefore no
587 influence on the lake sedimentary records of Pb pollution. In addition, the recent
588 increase in anthropogenic lead at LCSP can only represent a direct atmospheric supply
589 since the reforestation of the LCSP watershed has stabilized soils and reduced the
590 sediment supply to the lake. Keeping in mind that small variations in concentration may
591 be difficult to interpret (Bränvall *et al.*, 2001), we consider that the anthropogenic
592 estimates using Pb concentrations fit noticeably well with our Pb isotopic approach.
593 Although the estimates using Pb concentrations are constantly higher than the estimates
594 using Pb isotopes, both methods show an increased anthropogenic lead supply for the
595 last 30 years, which is much more distinct in the region of Concepción than around
596 Puyehue.

597

598 **6. Summary and conclusion**

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

604 For the region of Puyehue both methods underline the minimal impact of
605 anthropogenic activities on the natural sedimentation processes. Although the lake
606 receives a small amount of anthropogenic lead from atmospheric deposition, its
607 relative contribution is always lower than 5 %. Since no industrial activity takes
608 place in the watershed of the lake, the anthropogenic lead deposited in Lago Puyehue
609 probably originates from relatively long-distance atmospheric transport. A fraction of
610 the Puyehue anthropogenic lead may also originate from road transport to Argentina,
611 as one of the main routes to cross the Andes runs along the southern shore of the
612 lake.

613 Recent sedimentation in LCSP reflects variable human activities in the region of
614 Concepción during the 20th century. The bulk organic geochemical data provide clear
615 evidence for deforestation episodes in the lake watershed from 1915–1937 to the late
616 80's, with an accentuation between 1943 and 1987, when most of the native forest
617 has been logged and replaced by exotic species. Using two different approaches, we
618 demonstrate that airborne pollution in the region of Concepción started to become
619 significant sometime between 1974 and 1982. We estimate that anthropogenic lead
620 constitutes up to 10 to 20% of total Pb supplies during the last decade. This
621 interpretation is consistent with the detection of spheroidal carbonaceous particles,
622 i.e., residue of fossil fuel combustion, in lake sediments deposited after 1976.

623 Although the contamination levels are much higher around Concepción than in
624 the region of Puyehue (the Pb anthropogenic flux is 10 times lower at Puyehue than
625 at LCSP), the maximum Pb contamination is observed in the mid-seventies (1974–
626 1976) at both sites, suggesting a large-scale Pb pollution.

627

628 **7. Acknowledgements**

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

639

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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

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

847

848 Figure 3 – Bulk organic geochemistry of cores LCSP (a) and PU-II-P4 (b).

849 Total Organic Carbon (TOC) and Total Organic Nitrogen (TON) are in weight
850 %, and $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ are in ‰ relative to VPDB and AIR, respectively. Zones 1, 2
851 and 3 (LCSP) indicate changes in bulk organic geochemistry, resulting from
852 anthropogenic activities in the lake watershed (see text). Data are presented in tables
853 1a and 1b (online supporting information).

854

855 Figure 4 – Total, natural and anthropogenic lead concentrations (a), and flux of
856 anthropogenic Pb (b) in sediment cores LCSP and PU-II-P4.

857 In (a), the error bars cumulate errors associated with the geochemical analysis of Pb
858 ($\pm 10\%$ for PU-II-P4, $\pm 16\%$ for LCSP) and Ti (3% for PU-II-P4 and 1.5% for LCSP).
859 In (b), the error bars cumulate the errors on anthropogenic lead concentrations, sediment
860 accumulation rates and density. See online supporting information for data.

861

862 Figure 5 – Temporal evolution of $^{206}\text{Pb}/^{204}\text{Pb}$ ratios measured on bulk lake
863 sediments from LCSP and Lago Puyehue. The grey symbols correspond to duplicate
864 analyses. “SVZ” (upper dashed arrow and dark grey area) refers to the isotopic
865 composition of rocks from the Southern Volcanic Zone of Chile. “Trumaos” (vertical
866 dashed arrow) refers to the isotopic composition of soils in the vicinity of Puyehue.
867 “LCSP soils” (lower dashed arrow and light grey area) refers to the mean isotopic

868 composition of soils in the watershed of Laguna Chica de San Pedro. Data are
869 presented in tables 3a and 3b (online supporting information).

870

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

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

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

877 For data and/or references see tables 3a and 3b (online supporting information).

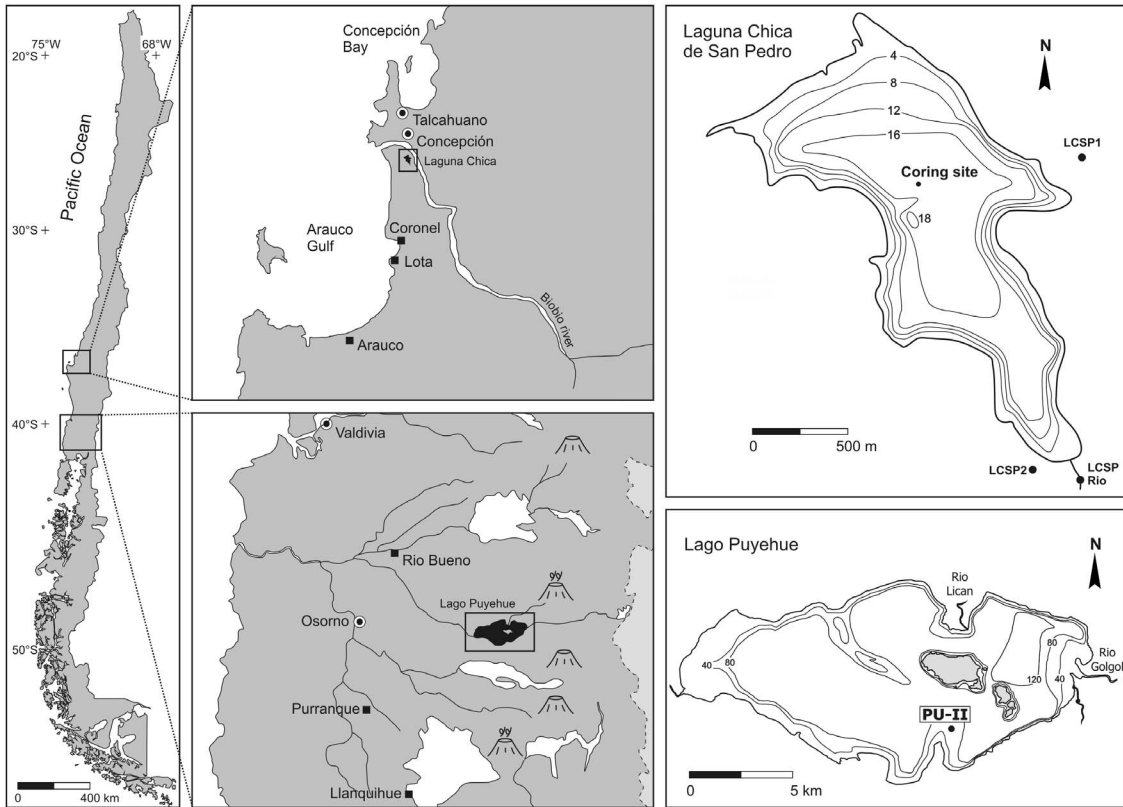
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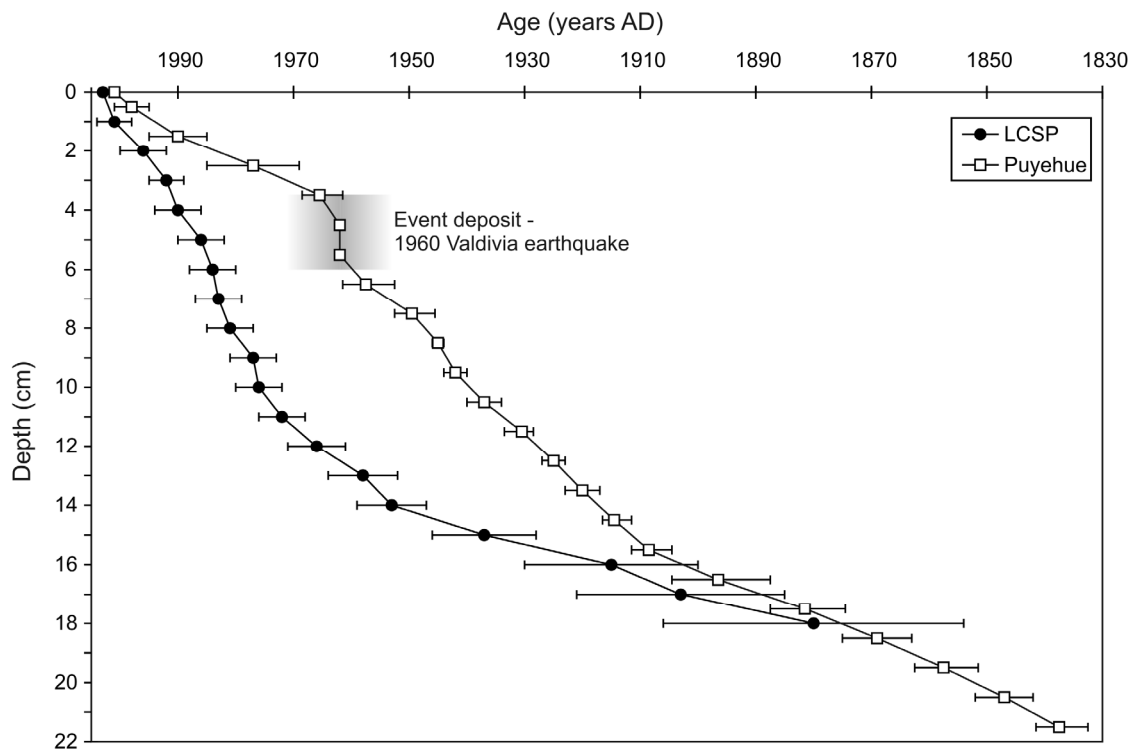
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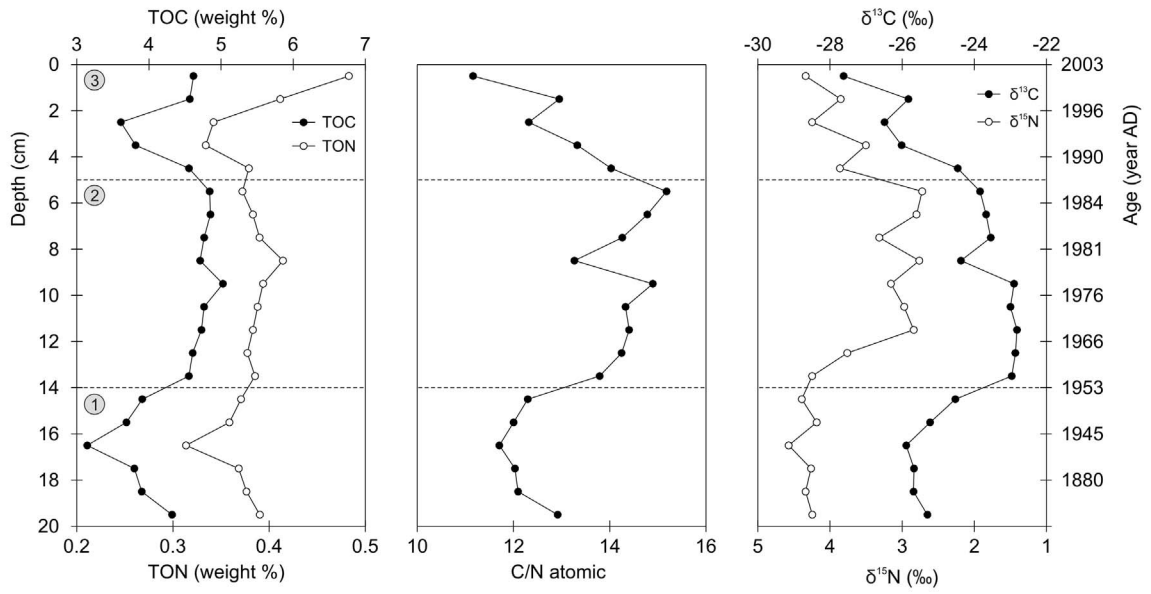


Fagel et al – Figure 1

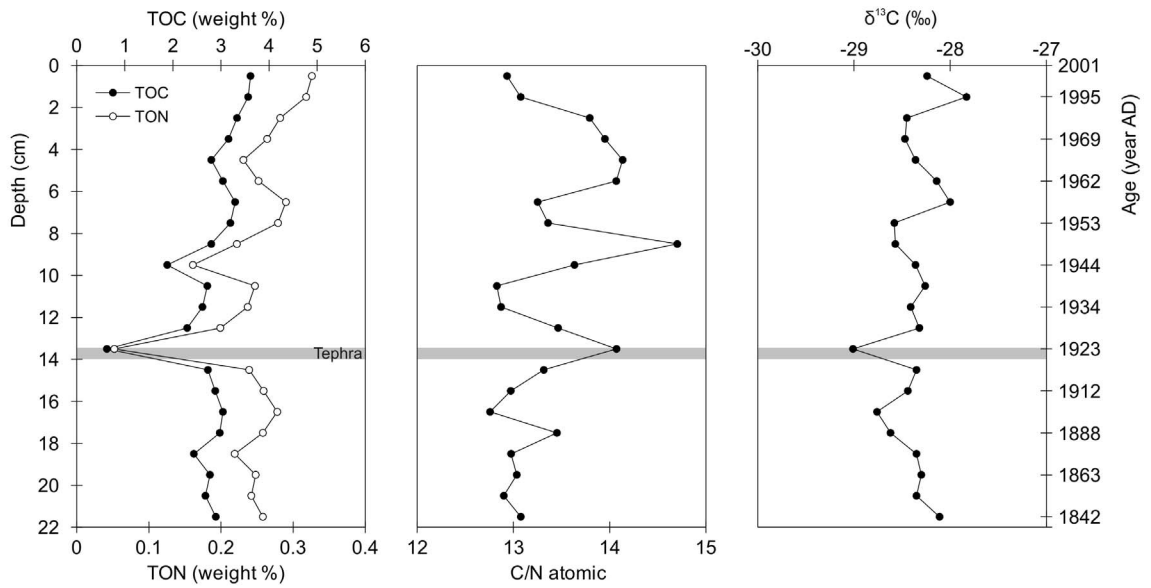


Fagel et al – Figure 2

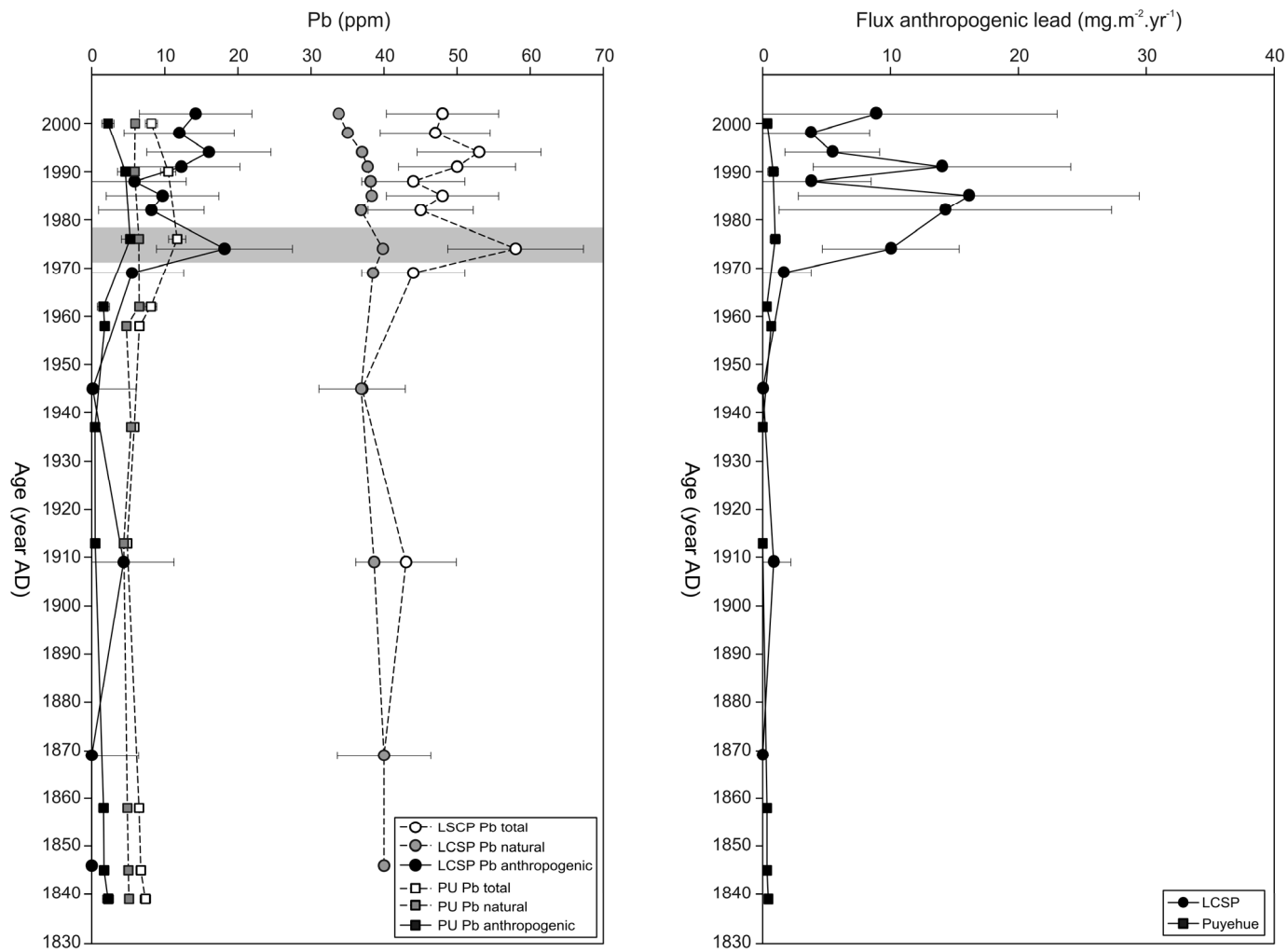
A. Laguna Chica de San Pedro



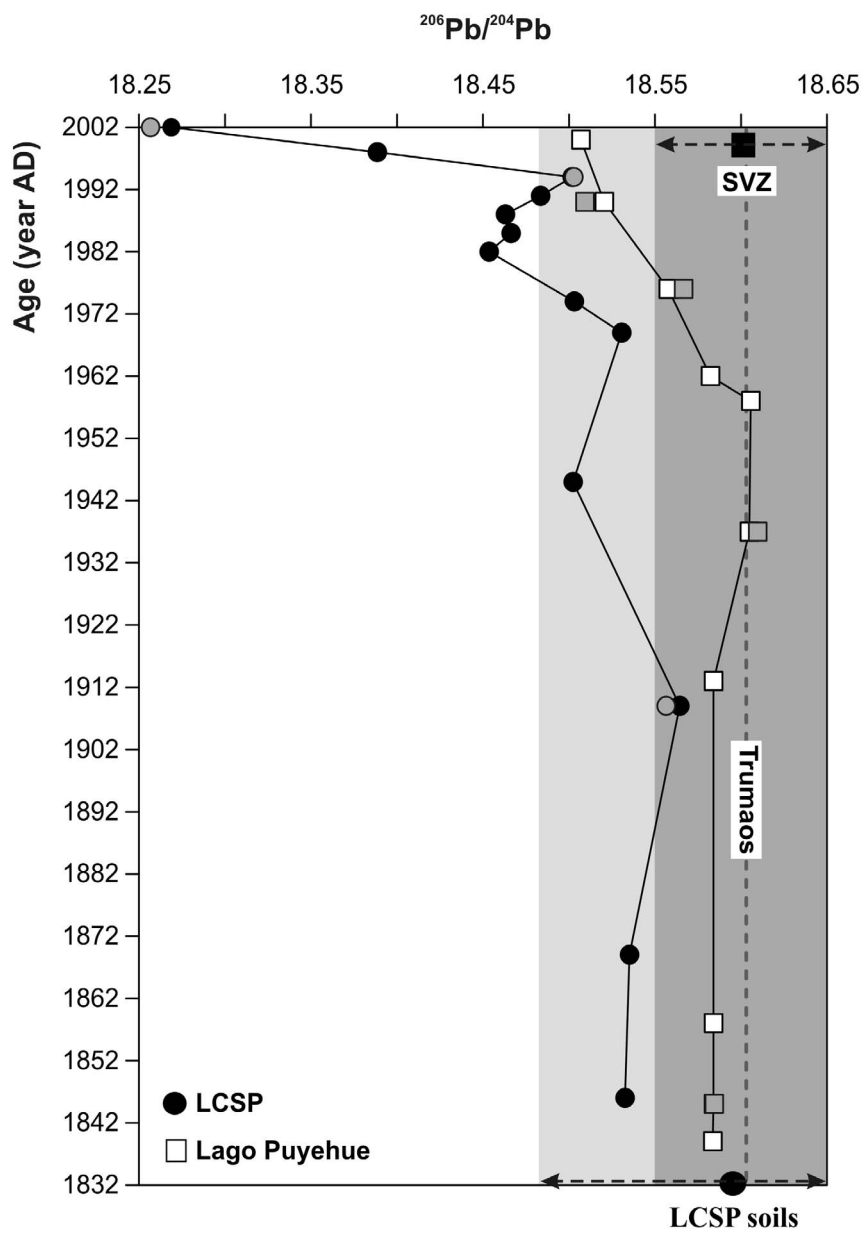
B. Lago Puyehue



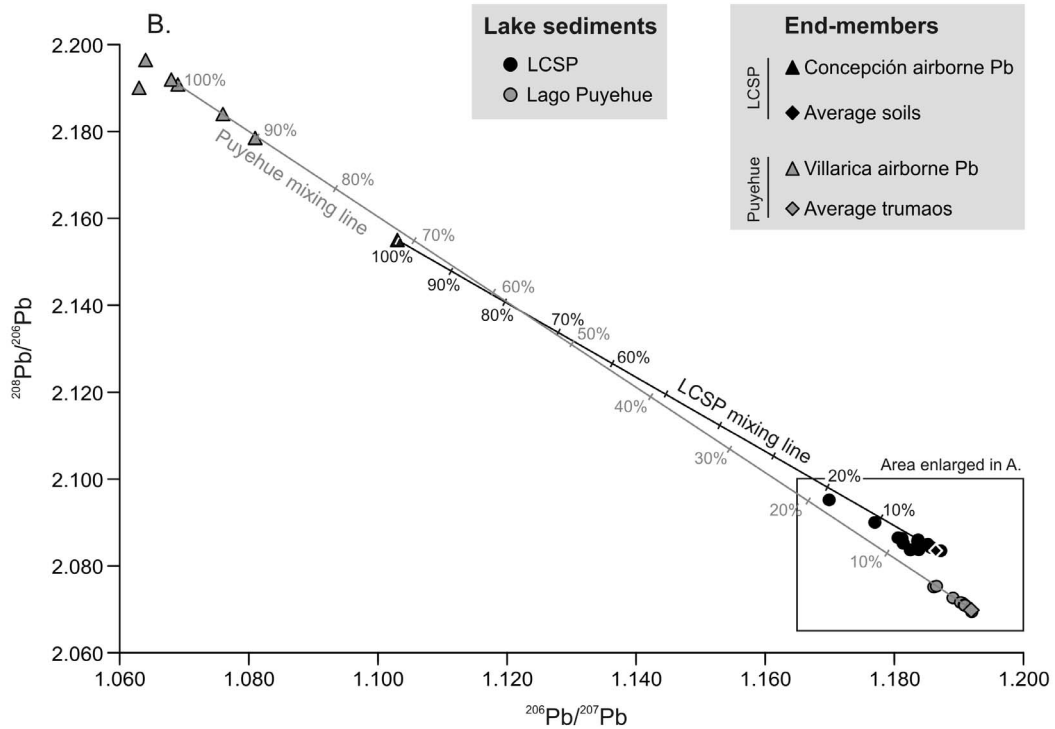
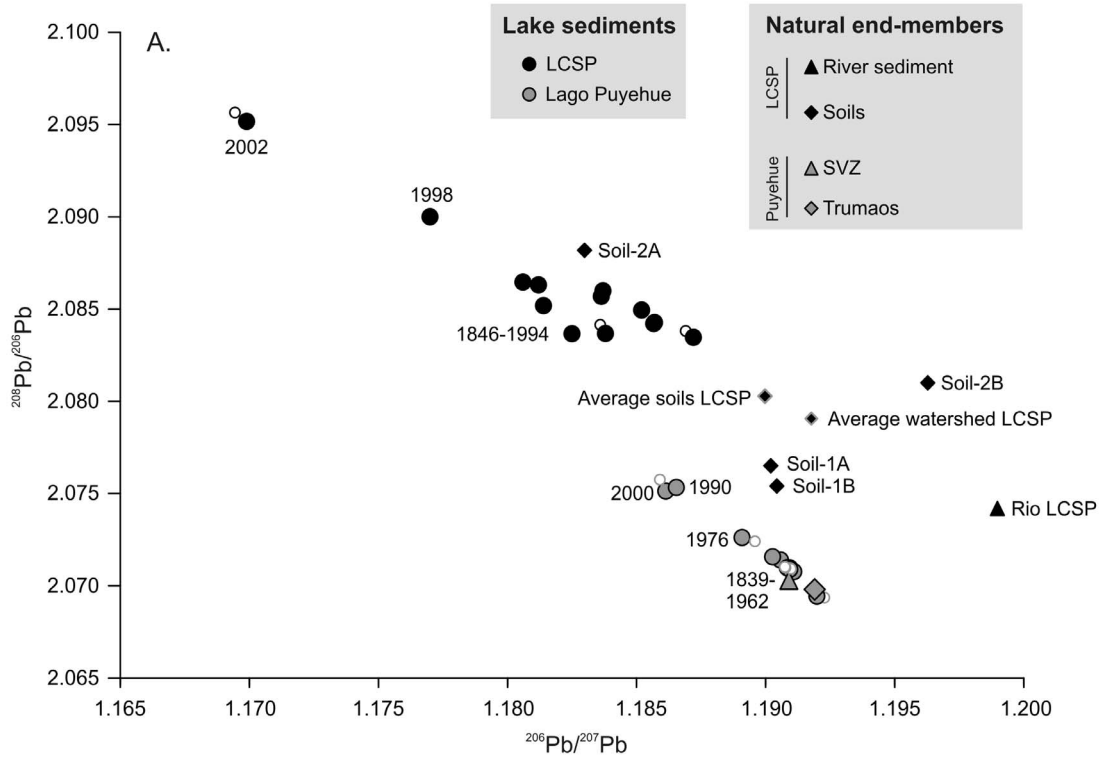
Fagel et al – Figure 3



Fagel et al – Figure 4



Fagel et al – Figure 5



Fagel et al – Figure 6