

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.,  $^{210}\text{Pb}$ ,  $^{14}\text{C}$ ) 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 km<sup>2</sup> and a small  
122 drainage basin of 4.5 km<sup>2</sup> (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 19<sup>th</sup>  
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 km<sup>2</sup> 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 km<sup>2</sup> 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  $\mu\text{m}$  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  $^{210}\text{Pb}$   
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  $^{210}\text{Pb}$  date corresponds to  $\text{AD } 1880 \pm 26$  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 ( $^{210}\text{Pb}$  and  $^{137}\text{Cs}$ ; 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 CO<sub>2</sub> and  
216 N<sub>2</sub> 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  $\delta$  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-HNO<sub>3</sub> 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 (<sup>204</sup>Pb) 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  $36.7158 \pm 0.027$  (2SD) for <sup>208</sup>Pb/<sup>204</sup>Pb,  $15.4969 \pm$   
258  $0.011$  for <sup>207</sup>Pb/<sup>204</sup>Pb,  $16.9399 \pm 0.0011$  for <sup>206</sup>Pb/<sup>204</sup>Pb,  $0.9148 \pm 0.0001$  for <sup>207</sup>Pb/<sup>206</sup>Pb,  
259 and  $2.1674 \pm 0.0007$  for <sup>208</sup>Pb/<sup>206</sup>Pb, which are in good agreement with long term  
260 laboratory values (n = 1000, <sup>208</sup>Pb/<sup>204</sup>Pb =  $36.7130 \pm 0.012$  (2SD), <sup>207</sup>Pb/<sup>204</sup>Pb =  
261  $15.4950 \pm 0.004$  (2SD), <sup>206</sup>Pb/<sup>204</sup>Pb =  $16.9393 \pm 0.0044$  (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  $16.5 \pm 1.0$ ;  $\delta^{13}\text{C}$ :  $-25.8 \pm 0.9$ ;  $\delta^{15}\text{N}$ :  $7.6 \pm 2.5$ ), 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  $18.533 \pm 0.022$  (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  $18.257 \pm 0.022$  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  $18.5644 \pm 0.0018$ . 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:  $13.1 \pm 1.0$  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  $18.5069 \pm 0.0007$  and  $18.6097 \pm 0.0008$   
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:  $16.5 \pm 1.0$ ) 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 19<sup>th</sup> century, it only  
372 became intensive in the mid 20<sup>th</sup> 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 ( $Pb_{\text{sample}}$ ) 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  $Pb/Ti_{\text{natural}}$  is the Pb/Ti ratio measured in pre-anthropogenic sediments.

439 The assumption that the  $Pb/Ti_{\text{natural}}$  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 ( $F_{\text{bulk}}$ ) and anthropogenic ( $F_{\text{anthropogenic}}$ ) lead using the concentration data,  
447 the dry density  $D$  ( $\text{g}/\text{cm}^3$ ) and the sediment accumulation rate SAR ( $\text{cm}/\text{yr}$ ) 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/m<sup>2</sup>/yr) is still 2–3  
480 times lower than in the French Alps and in Canada (30 mg/m<sup>2</sup>/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 <sup>206</sup>Pb/<sup>204</sup>Pb 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 <sup>206</sup>Pb/<sup>207</sup>Pb and <sup>208</sup>Pb/<sup>206</sup>Pb results are illustrated in Fig. 6.  
491 At both sites, we note a decrease of the <sup>206</sup>Pb/<sup>207</sup>Pb and an increase of <sup>208</sup>Pb/<sup>206</sup>Pb 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 (<sup>206</sup>Pb/<sup>207</sup>Pb –  
498 <sup>208</sup>Pb/<sup>206</sup>Pb) 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 <sup>206</sup>Pb/<sup>207</sup>Pb and higher <sup>208</sup>Pb/<sup>206</sup>Pb 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 (<sup>206</sup>Pb/<sup>207</sup>Pb ~1.191; <sup>208</sup>Pb/<sup>206</sup>Pb ~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  $^{210}\text{Pb}$  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 20<sup>th</sup> 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

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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  $^{210}\text{Pb}$   
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).

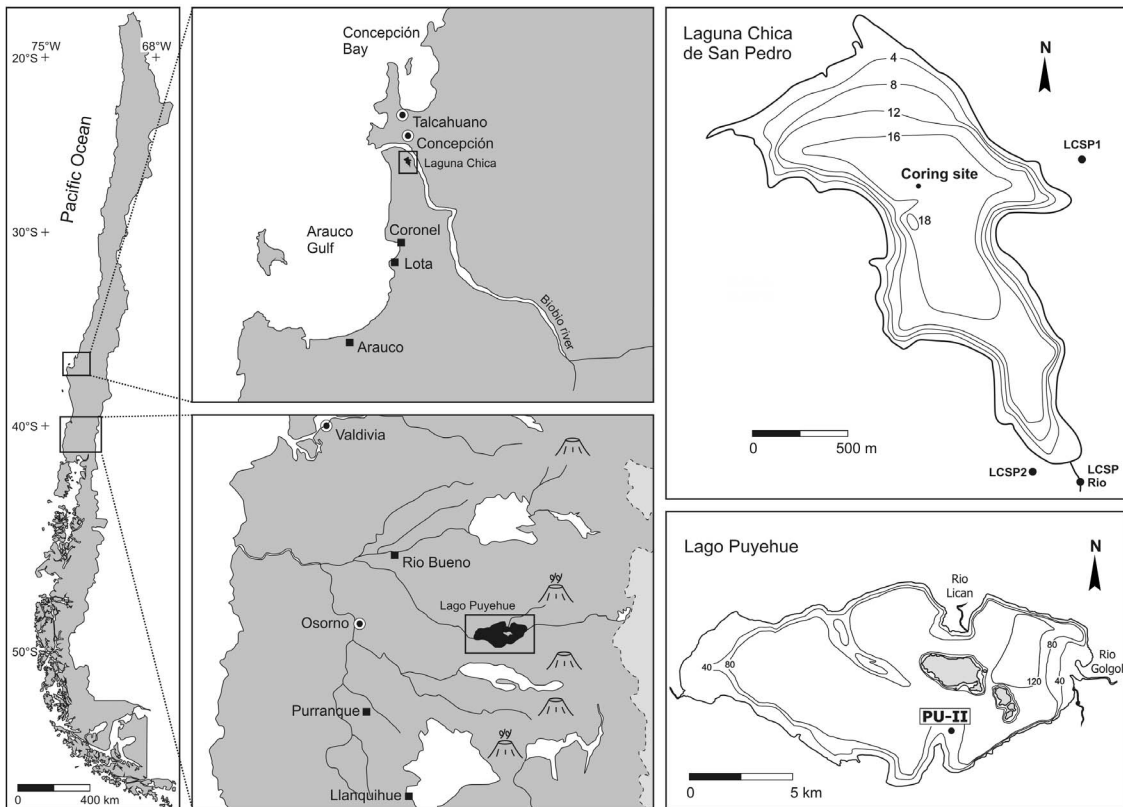
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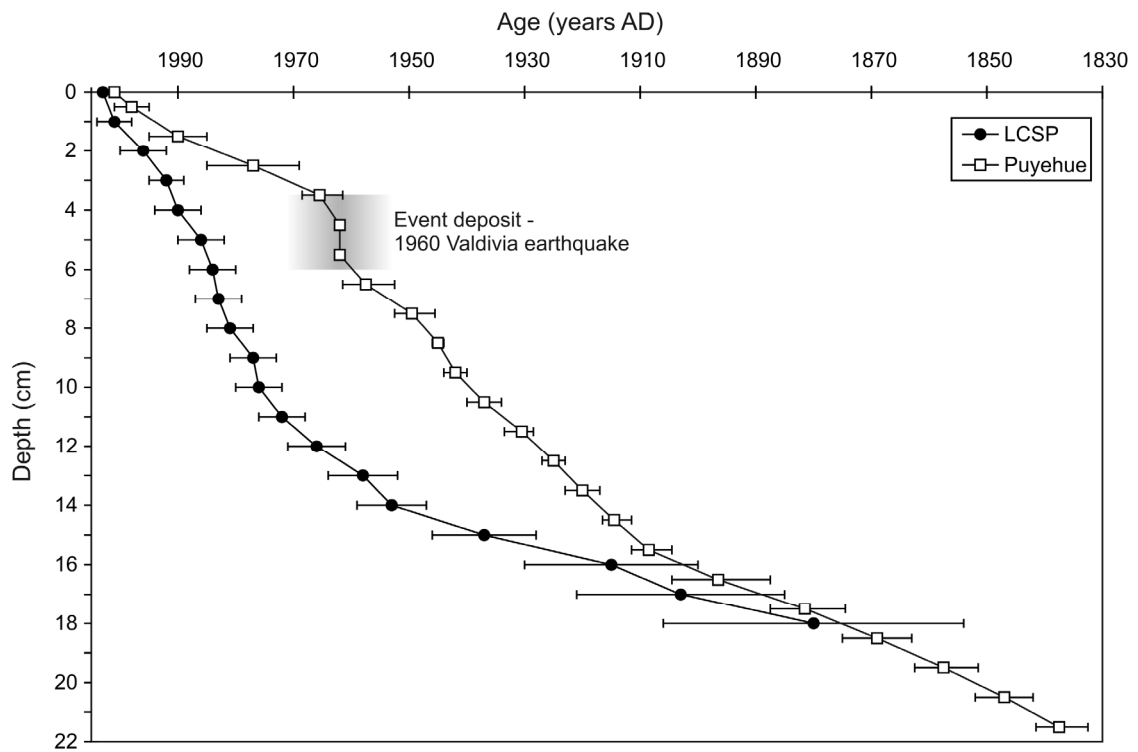
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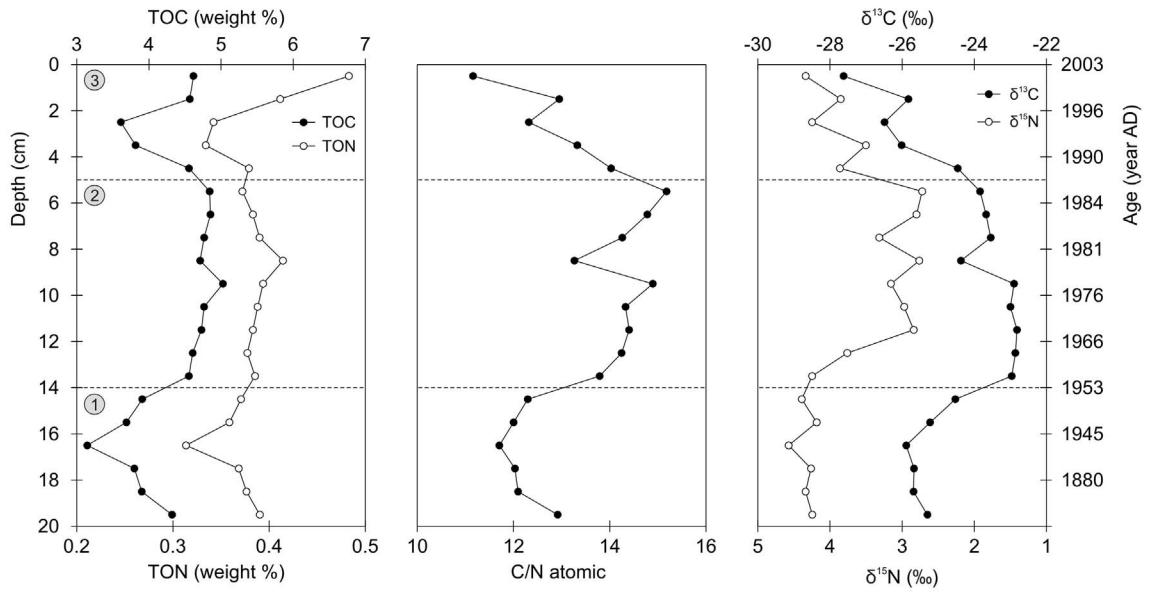


Fagel et al – Figure 1

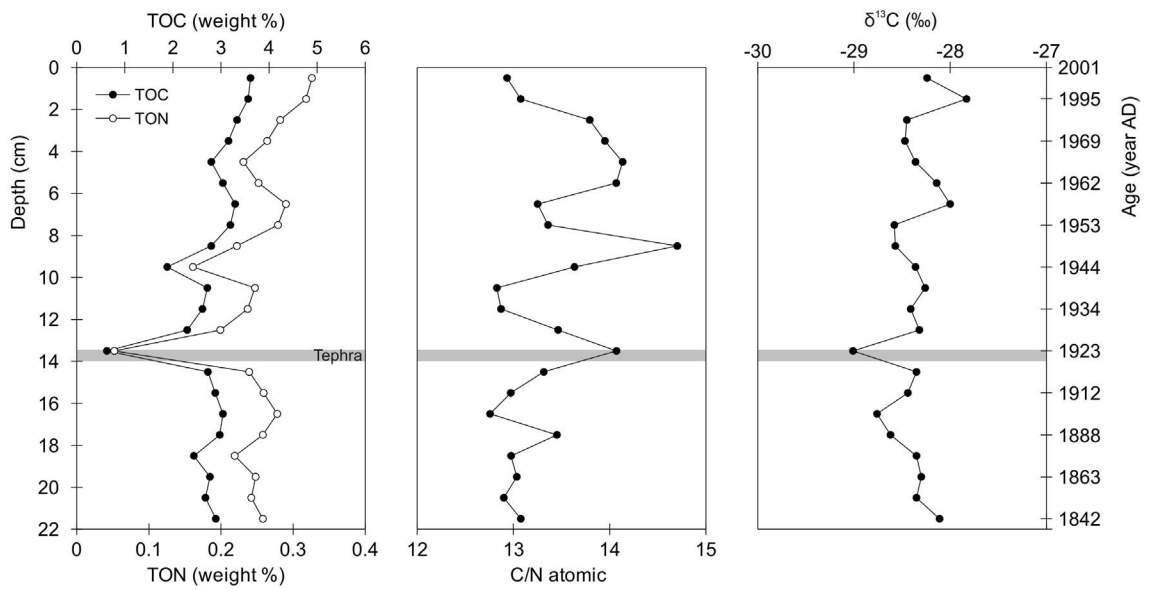


Fagel et al – Figure 2

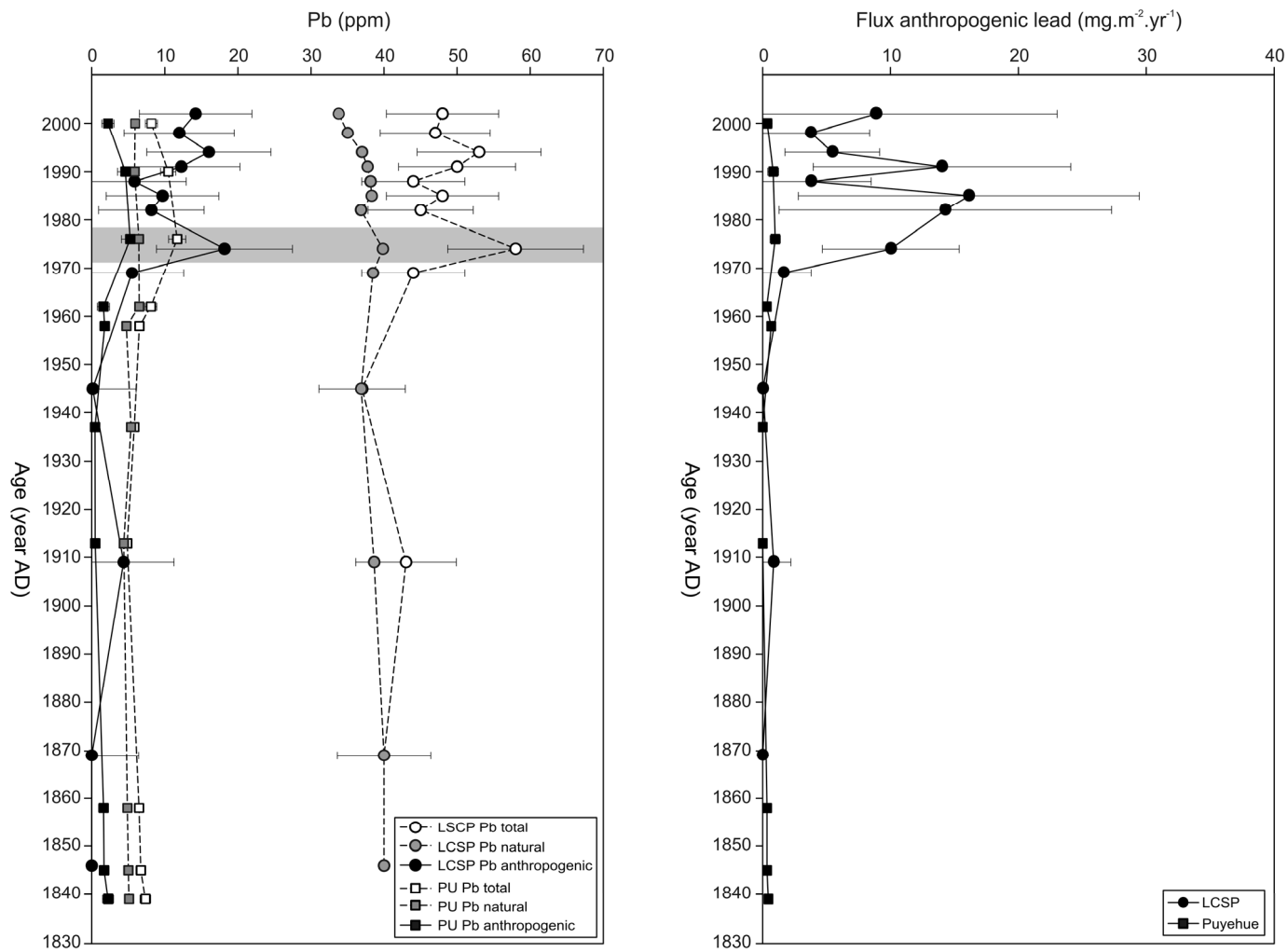
**A. Laguna Chica de San Pedro**



**B. Lago Puyehue**

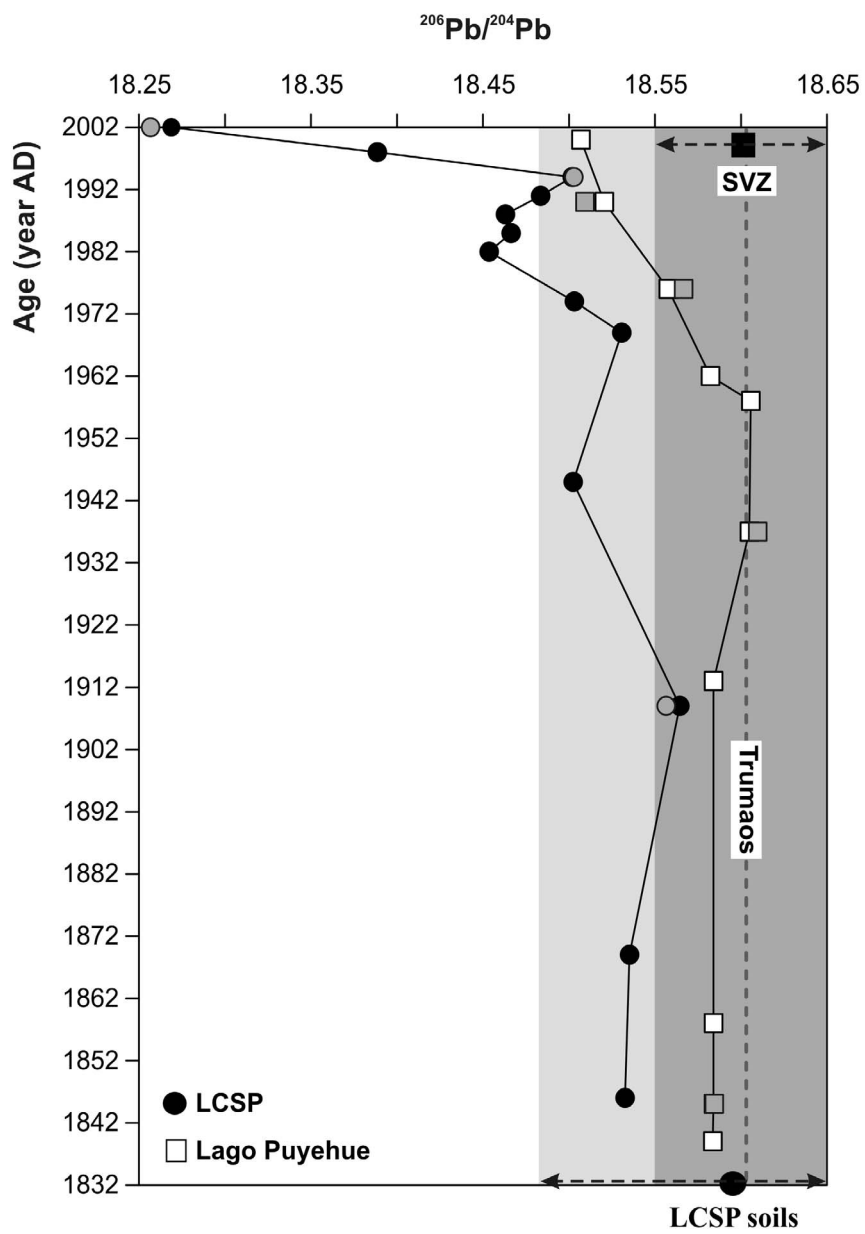


Fagel et al – Figure 3

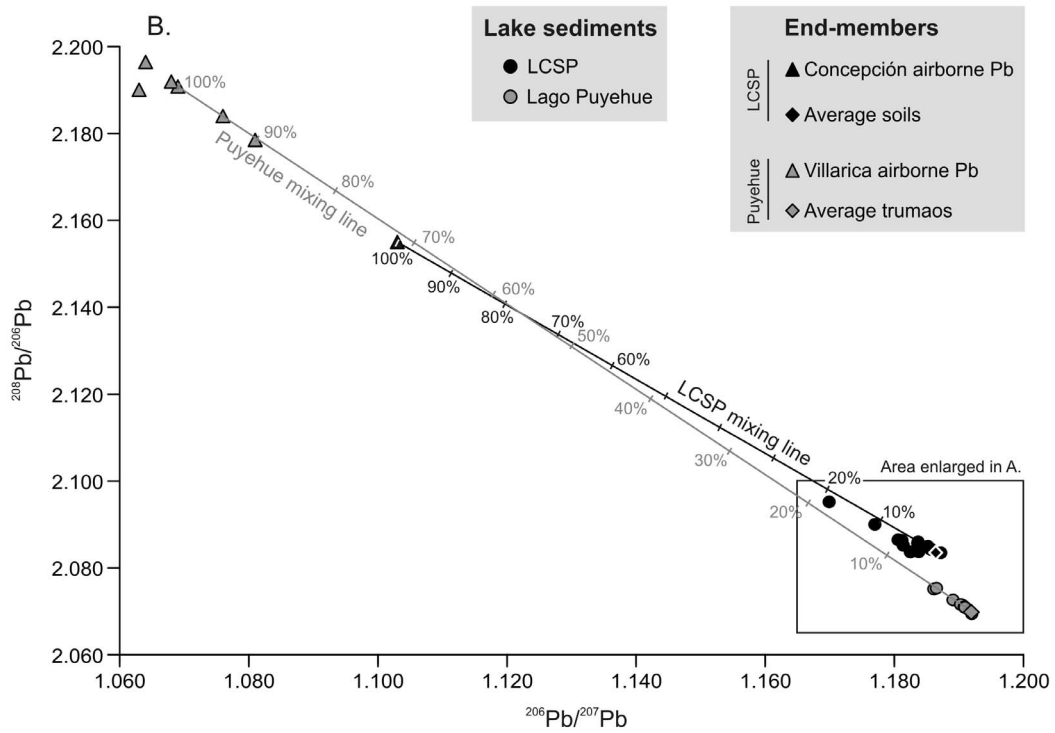
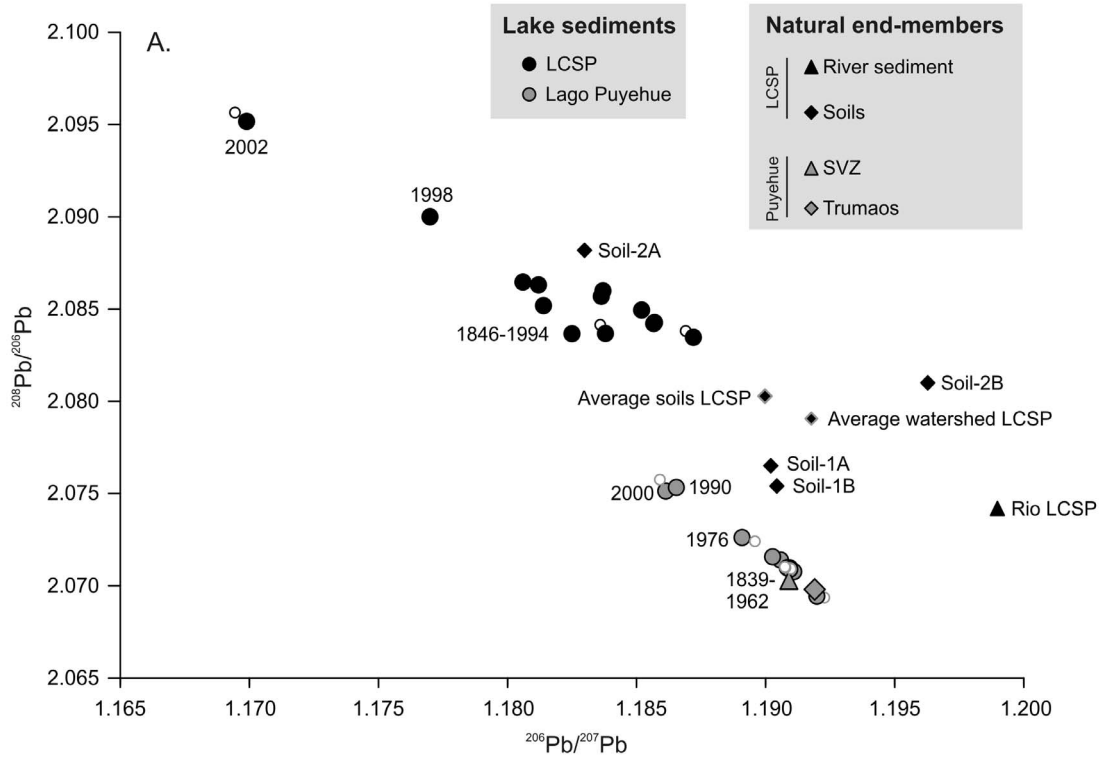


Fagel et al – Figure 4





Fagel et al – Figure 5



Fagel et al – Figure 6