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GEOCHEMICAL AND Pb ISOTOPIC SIGNATURE OF PEATY SEDIMENTS FROM CENTRAL-SOUTH CHILE: IDENTIFICATION OF PARTICLE SUPPLIES OVER THE HOLOCENE

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ABSTRACT

Two cores from tephra rich peat soils of the Chilean Lake District were investigated for mineral source and potential anthropogenic impact using elemental geochemistry, including rare earth elements, and lead isotopes. The dominant particle source to the area are the *Trumaos* which are the local ando soils derived from the weathering of volcanic deposits. In Galletué, although short term events of enhanced particle inputs occur, elemental and isotopic signatures show that the *Trumaos* are the only particle source to the area. In San Pablo de Tregua, punctual events of crustal particle inputs are recorded in Pb enrichment factors and isotopic profiles, reflecting a long range crustal involvement. This site also records the inception of the anthropogenic in the area in recent samples of which Pb enrichment factors and lead isotopic signatures shift drastically.

Keywords: Peat soil, Trace elements, Pb isotopes, Ando soils, Lake District, Chile, Holocene

INTRODUCTION

During the last decade, many researches have been focused on peat cores as archives of atmospheric deposition, providing important data on palaeoclimatic and anthropogenic history¹⁻⁵. Recent studies have for example demonstrated that ombrotrophic peat (*i.e.* exclusively fed by atmospheric deposition) is an excellent archive to record Pb atmospheric history throughout the Holocene^{4,6}.

Studies of past atmospheric deposition are more rare in minerotrophic peat despite a common occurrence relative to ombrotrophic bogs. This is principally due to possible mobilization of elements linked to the fluctuation of watertable, or leaching by groundwater^{7,8}. However other authors⁹⁻¹³ have demonstrated the potential of minerotrophic peat to record past climatic or anthropogenic changes.

In Southern Hemisphere, very few articles have investigated Holocene or anthropocene reconstruction derived from peat bog geochemistry¹⁴⁻¹⁷. There are however numerous geochemical data from several sites of the Antarctic ice cap¹⁸⁻²⁰ are available and could be useful to decipher sources of particles and/or periods of pollution.

In this study, we focus on minerotrophic peat soils from the Chilean Lake District (Meridional Chile, 38-40°S). In an attempt to identify the main particle source (average Upper Continental Crust, mean Chilean Southern Volcanic Zone, and *Trumaos*, anthropogenic source), this study aims to decipher between local and global influence on peat records, using the depth evolution

of geochemical and Pb isotopic compositions of peat soils.

MATERIAL AND METHODS

Site description

Two vertical cores (PB2 : 38°40'47''S – 71°12'60''W - 2.80 m; PB4 : 39°35'20''S – 71°03'78''W - 4.00 m) were drilled in peat soils from the Chilean Lake District (Fig. 1). The cores were retrieved using a Belorussian-type stainless steel D-corer^{21,22}. Semi-cylindrical core are 50 cm long and 4.5 cm in diameter were sampled and bagged into PVC tubes and then wrapped in plastic. A pre-coring was performed to locate the thickest sediment accumulation.

The Chilean Lake District is located at the feet of the Andes, between 38° S and 42° S. The lakes are the results of the retreat of the Andean glaciers during the Late Glacial-Holocene transition²³⁻²⁶. This glacial landscape provides several peat infillings. This region, part of the Chilean Southern Volcanic Zone (SVZ), has been repeatedly under volcanic activity during the Holocene. Tephra were deposited from surrounding complex active volcanoes such as the Llaima, Lonquimay, Villarrica or Mocho-Choschuenco volcanoes²⁷. The entire area is covered by 4 to 6m thick andosols formed by volcanic ash accumulation and weathering^{28,29}, locally called *Trumaos* (Fig. 1). These *Trumaos* provide a large amount of local mineral particles that could be transported by wind action and trapped by peat soils.

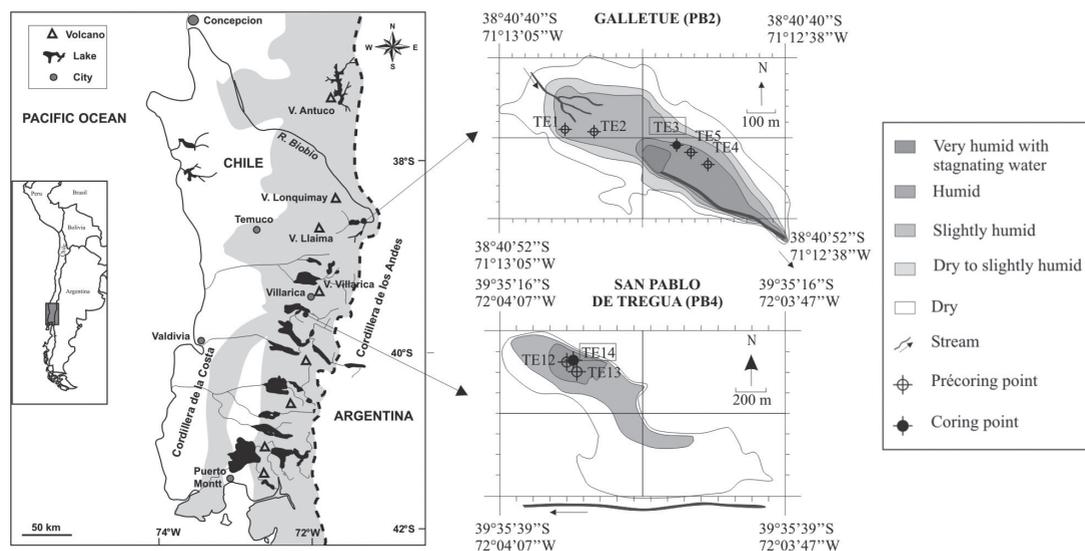


Figure 1. Locations of the two sites in the lake district map²⁹, and surface humidity zones. Grey shaded zone on the left map shows the extension of Andosols, locally called *Trumaos* (reported from FAO-UNESCO).

In Galletué peat soil (PB2), vegetation is mainly composed of *Juncus sp.*, *Carex spp.*, a few *Sphagnum spp.*, and several species of *Gramineae*³⁰. In San Pablo de Tregua (PB4), *Sphagnum spp.* becomes abundant in the uppermost peat layers (20 cm). The actual vegetation of this mire presents an important cover of *Carex spp.* and *Gramineae spp.* Shrubs species like *Escallonia alpina*, *Baccharis sp.*³¹ and *Chusquea spp.* are also present, indicating a drying of the area. Both sites are fed by several little streams providing a non-atmospheric contribution to the peat soils.

¹⁴C dating

Two samples from PB2 and four from PB4 have been dated either by AMS at Poznan Radiocarbon Institute (Poland), and by conventional (*i.e.* β -counting) technique at Centre for Isotope Research, University of Groningen (The Netherlands). Results are reported in Table 1. Sediment accumulation covers more than 8500 years in PB2 and more than 11000 years in PB4.

Table 1. AMS (Poz samples) and conventional (GR samples) dating and associated *Oxcal 3.8*³² calibrated ages from samples from PB2 and PB4. * depth dated by tephra correlation of a dated sample in a neighboring outcrop.

Site	Sample number	Depth (cm)	Age yr B.P.	Error	Age ranges yr cal B.P.
PB2	Poz-252	*120.5	2900	± 45	2920 - 3170
	GrN-27083	282.5	7350	± 200	7750 - 8550
PB4	Poz-6863	45	645	± 30	550 - 670
	Poz-1320	90	3970	± 50	4250 - 4540
	Poz-1319	190	7490	± 40	8180 - 8380
	GrN-27085	340	9480	± 160	10250 - 11200

Sediment characterization

High resolution magnetic susceptibility (HRSM), bulk density and total organic carbon (Fig. 2) were measured in both peat cores to detect specific lithologies that could induce geochemical fluctuations. HR-magnetic susceptibility was measured every 5 mm using an MS2 Magnetic Susceptibility System equipped with a MS2E spot-reading sensor (Bartington Instruments). Measurements were duplicated to assess reproducibility. HRSM exhibits sharp peaks when fine tephra are present. When tephra are coarser, their porosity prevents good contact between the sensor and the core. Recorded values represent in this case an underestimation of the real magnetic field. Additional HRSM fluctuations are rather due to other lithological variations. Bulk density is estimated by weighting a 1 cm thick semi-cylinder of sediment preliminary dried at 105°C for 12h. Total organic carbon was measured with a CS-200 Leco analyzer (CBR Harmignies, Belgium) on dried (105°C, 12h) and milled samples. Errors on C_{org} measurements range from 5 to 10%.

Preparation and acid digestion of peat samples

Samples were taken out from the core using 5 ml acid cleaned plastic tools. Only the central part of the semi-cylinder sampled. Samples were dried (105°C for 12h) and milled using an agate mortar. The sampling was constrained by the numerous tephra falls along the profiles and remained therefore irregular and quite large (sampling resolution up to 1 sample/40 cm).

All the samples were processed in clean air cabinets (ULB, Belgium). Digestion consisted in a two-step acid dissolution in closed Savilex® beakers: (1) organic matter is digested by repeated addition of H₂O₂ 30% *p.a.* and HNO₃ 65% *cc. sub.* in a proportion of 3:1; (2) mineral matrix is then digested by addition of HF *suprapur* (Merck) + HNO₃ 65% *cc. sub.* ± HClO₄ in a proportion of 1:6:0.5. The beakers were placed on a hot plate at 130°C for 4 days. After drying, 6N HCl was added and slowly evaporated.

Elemental geochemistry

Elemental geochemistry was measured using ICP-AES (IRIS Advantage) for major and transition elements and ICP-MS (VG PlasmaQuad PQ2) for trace elements at MRAC-Tervuren (Belgium). Si could not be analysed because of SiF₄ volatilisation during the HF-HNO₃ digestion procedure. Calibrations were made with In-Ru-Re-Bi internal standards (10 and 20 ppb), and two international reference materials: BCR CRM-100 beech leaves (EU certificated) and granite GA³³, chosen to be representative of the current soil and volcanic samples. Accuracy varied between 1-11% for major elements, 1-2% for transition metals and 1-5% for other trace elements. Detection limits (*i.e.* mean + 3 σ) were lower than 1 ppm for major elements excepted Na (2.7 ppm), K (1.1 ppm) and P (7.9 ppm). Detection limits for trace metals and other trace elements were lower than 1 and 10 ppb, respectively. To assess sample heterogeneity, replicates from both cores were analysed (PB2 – 108 cm, PB4 – 310 cm). Results for replicates are comparable within errors to the original analyses.

Lead isotope signatures

Lead fraction was separated using a one step ion-exchange chromatography on AG1-X8 resin following previously reported chemical procedures³⁴. To monitor instrumental mass bias, Tl was added to each sample to achieve a Pb/Tl of = 5 and thus match the Pb/Tl ratio of the standard. During the analysis sessions, measurement of NBS 981 Pb standard was systematically performed after every two samples. It gave average individual error (2 σ , 95% confidence) on Pb isotopic analyses for Galletué (PB2) and rock samples of 0.0200 for ²⁰⁸Pb/²⁰⁴Pb, 0.0150 for ²⁰⁷Pb/²⁰⁴Pb and 0.0180 for ²⁰⁶Pb/²⁰⁴Pb (for more details see Table 4). Acids were distilled (HNO₃) or sub-boiled (HF, HCl, HBr). Pb total blanks for the whole procedure range between 40pg and 200pg. This is negligible relative to Pb contents in the samples (150ng < PB2 content < 900ng, 25ng < PB4 content < 8.3 μ g).

Lead isotopic ratios were measured on Nu-Plasma MC-ICP-MS (ULB, Belgium) during three analysis sessions. All the standard values of this study fall in these ranges. Internal laboratory reproducibility are 0.027 for ²⁰⁶Pb/²⁰⁴Pb, 0.026 for ²⁰⁷Pb/²⁰⁴Pb, 0.003 for ²⁰⁸Pb/²⁰⁴Pb, 0.1 for ²⁰⁷Pb/²⁰⁶Pb and 0.15 for ²⁰⁸Pb/²⁰⁶Pb (n~600, 2 σ level, 95% confidence) after several years of analyses. The total Pb beam intensities varied from 4 to 10V. Intensities during analyses of San Pablo de Tregua were sometimes lower (<1V), explaining the larger average individual errors for those samples. A duplicate of the whole procedure (*i.e.* including dissolution, column exchange and analysis) on a PB2 sample (108 cm depth) was also analysed. The sample and the replicate results show differences of 13x10⁻³ for ²⁰⁶Pb/²⁰⁴Pb, 36x10⁻⁵ for ²⁰⁷Pb/²⁰⁶Pb and 87x10⁻⁷ for ²⁰⁸Pb/²⁰⁶Pb.

Selection of the reference element

Comparable profiles of major element concentrations variations as a function of depth suggest an important imprint of the soil lithology. To compensate for the influence of the lithology or matrix effect, trace and major element concentration values have been normalized. The peat soils of this study are located in a volcanic environment. Therefore the regional non-crustal geology of the Chilean Lake District has to be taken into account. Ti, Al, Zr, or Y are lithophile elements, well known for their resistance against weathering^{35,36}. They are common in several minerals found in volcanic falls, such as, for example, glass shards (Al, Ti), plagioclase (Al), titanite (Ti), ilmenite (Ti), titanomagnetite (Ti), zircon (Zr). Zr and Y have been often used in literature¹⁰ as reference elements, but they are in this study sometimes under detection limit. In contrast Al appears to be the most abundant element the samples. A slight fluctuation in [Al] will therefore strongly influence the fluctuation in the corresponding [trace element]/[Al] ratio. Consequently, Ti, a conservative element³⁵ moderately abundant in several resistant volcanic mineral phases, is chosen as the reference element. We assume in the studied area an almost entire Ti supply provided by weathering products of the SVZ volcanism (*i.e.* *Trumaos*). Because such a soft material is easily transported by wind, it is the most suitable source of particles in this area. Ti flux is obtained using the following formula¹⁰:

$$\text{Ti Flux} = [\text{Ti}]_{\text{sample}} \times (\text{density}) \times (\text{accumulation rate}),$$

Total particle flux is calculated as follows :

$$\text{TPF} = \text{Ti Flux} \times 100 / [\text{Ti} (\%)]_{\text{Trumaos}}$$

Pb enrichment factors are calculated using the formula³⁷:

$$\text{E.F. (Pb)} = ([\text{Pb}]_{\text{sample}} / [\text{Ti}]_{\text{sample}}) / ([\text{Pb}]_{\text{Trumaos}} / [\text{Ti}]_{\text{Trumaos}})$$

RESULTS

Lithology

The lithology of both cores is strongly influenced by weathering products from SVZ as the mineral residue of the samples is exclusively composed of volcanic minerals (e.g. plagioclase, pyroxene, olivine) and glass shards. Both peat soils were repeatedly blanketed by tephra falls up to 10 cm thick. These observations are consistent with the minerotrophic character of the two sites.

PB2 shows a low organic carbon content (mean $C_{org} = 5.4\%$) and high density values (mean $\delta = 0.6$). A peak in density ($\delta = 0.91$) at 90 cm is correlated with a rapid decrease of the total organic carbon content ($C_{org} = 2.73\%$) and a slight positive shift in HRSM. This shift is not due to a tephra layer (as the nearest tephra is at 95 cm depth), but to a strong clayey and mineral-rich layer (Fig. 2). Below total organic carbon is very low and density is high, reflecting the strong minerogenic character of the sediment. This mineral character becomes more important under 250 cm depth as HRSM increases significantly.

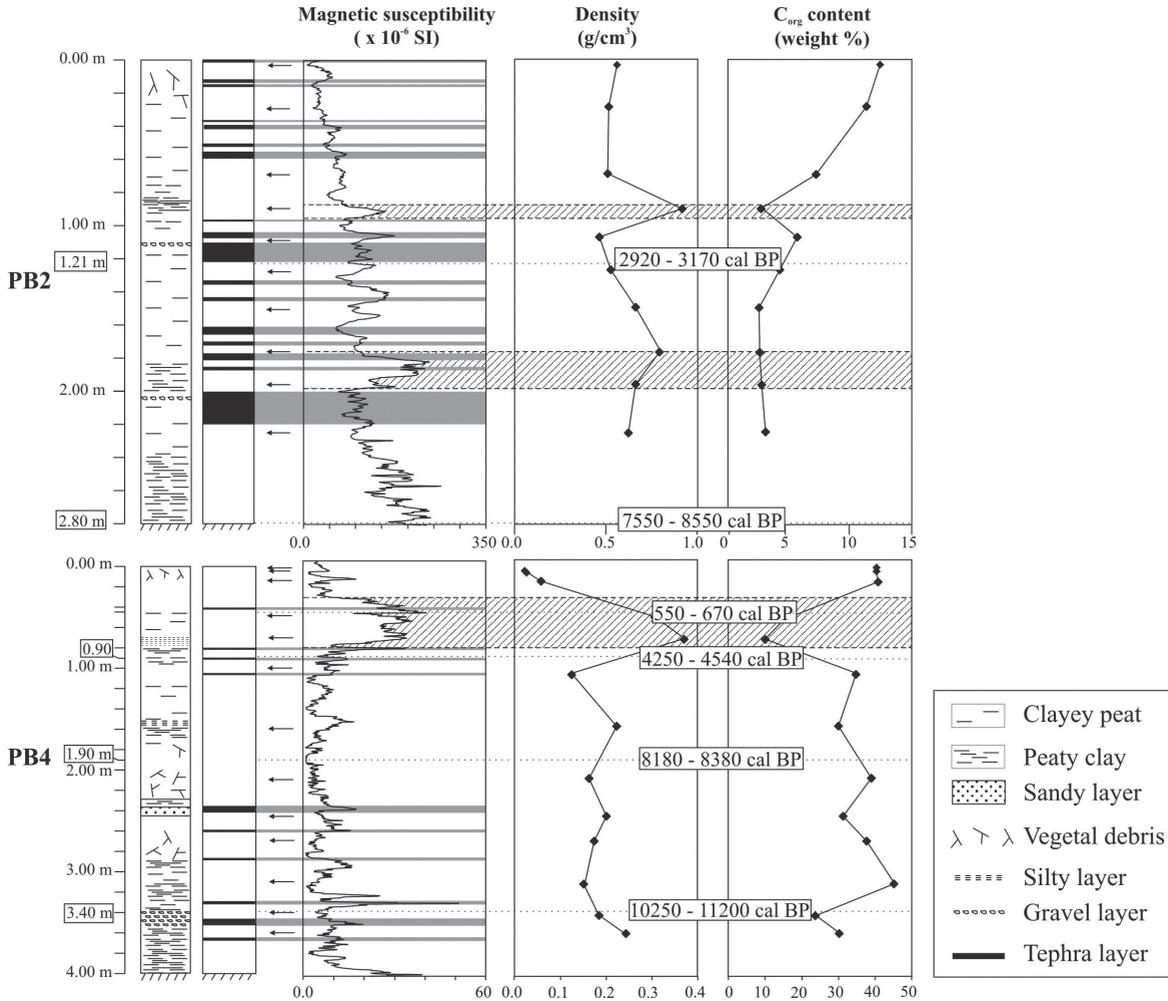


Figure 2. Lithological (left log) and tepthrostratigraphical (right log) columns. In parallel are shown high resolution magnetic susceptibility dry bulk density and organic carbon content curves. Arrows indicate samples depth. ^{14}C calibrated³² ages are also reported.

In contrast, PB4 displays an average higher total organic carbon content (mean $C_{org} = 31.7\%$) and lower density (mean $\delta = 0.2$) values relative to PB2. HRSM is also very low (always under 50×10^{-6} SI). This could reflect the lower contents of tephra and/or mineral particles in PB4. In this core, the *Sphagnum*-dominated layers become increasingly mineralised from 0 to 70 cm depth. The density therefore increases while the total organic carbon content decreases. At 71 cm depth, the occurrence of a silty layer causes a strong positive shift of density ($\delta = 0.37 \text{ g/cm}^3$) and a negative shift of organic carbon content ($C_{org} = 10.1\%$). Below 71 cm, profiles are relatively linear with small fluctuations between pure peat values (*i.e.* value of the 1 cm depth sample) and silty values (*i.e.* value of the 71 cm depth sample), reflecting the clayey character of the samples. At the lowermost 20 cm, HRSM increases rapidly, indicating a strong lithological change that represents the base of the peat infilling.

Major elements

Major element analysis reveals that Al, Ca and Fe are the most abundant elements in PB2: average $[\text{Al}]_{\text{PB2}} = 6.5 \text{ wt. \%}$, average $[\text{Ca}]_{\text{PB2}} = 3.5 \text{ wt. \%}$ and average $[\text{Fe}]_{\text{PB2}} = 3.5 \text{ wt. \%}$ (Table 2). All the major elements display similar variation with depth: decreasing values from 198 cm depth, then increasing and peaking at 90 cm, finally decreasing again until the surface. Although concentrations are lower, PB4 displays the same trend in elemental abundance: average $[\text{Al}]_{\text{PB4}} = 3.3 \text{ wt. \%}$, average $[\text{Ca}]_{\text{PB4}} = 0.97 \text{ wt. \%}$ and average $[\text{Fe}]_{\text{PB4}} = 0.98 \text{ wt. \%}$. P is often below detection limits. As in PB2, all the major elements show remarkably comparable profiles: concentrations peak slightly at 390, 310 and 160 cm depth, then decrease and peak strongly at 71 cm, to finally sharply decrease until the surface.

Table 2. Weight percentage of major elements in samples from Galletué (PB2) and San Pablo de Tregua (PB4). <DL: under detection limits (*i.e.* < 3 σ); values in italic: quantitative measurements (*i.e.* > 9 σ); underlined values: semi-quantitative measurements (*i.e.* 3 σ - 6 σ).

Depth										
(cm)	Ti	Al	Fe	Mn	Mg	Ca	Na	K	P	
<i>Galletué (PB2)</i>										
3.5	0.35	4.8	4.4	0.06	1.5	3.6	1.2	0.27	0.07	
29	0.20	2.6	1.6	0.02	0.44	1.7	0.64	0.15	0.05	
70	0.35	4.25	2.3	0.04	0.60	2.3	1.0	0.23	<DL	
90	0.63	9.9	4.8	0.09	1.4	6.4	2.4	0.43	0.07	
108	0.55	6.6	4.0	0.07	1.1	3.8	1.9	0.44	0.10	
Replicate 108	0.55	6.7	3.9	0.07	1.2	4.1	2.0	0.48	<DL	
128	0.58	6.3	3.2	0.06	0.80	3.3	1.8	0.41	0.12	
152	0.62	6.6	3.6	0.08	0.84	3.4	2.3	0.47	0.09	
177	0.61	7.7	3.3	0.06	0.94	3.5	2.1	0.42	<DL	
198	0.66	8.4	4.2	0.09	1.1	4.1	2.7	0.62	0.10	
227	0.61	7.5	3.5	0.07	0.84	3.5	2.3	0.48	0.12	
<i>San Pablo de Tregua (PB4)</i>										
1	0.01	0.17	0.09	0.06	0.30	1.2	<u>0.17</u>	0.24	<DL	
3	0.01	0.15	0.08	0.05	0.31	1.2	0.15	0.26	<DL	
16	0.12	1.7	1.6	0.03	0.26	1.3	0.48	0.19	<DL	
47	0.48	5.5	2.1	0.04	0.51	1.5	1.7	0.76	0.15	
71	0.89	7.4	2.4	0.05	0.70	2.1	1.8	0.73	<DL	
105	0.32	4.2	0.71	0.01	0.16	0.68	<u>0.35</u>	0.09	<DL	
160	0.39	5.0	0.92	0.02	0.27	0.98	1.0	0.32	0.19	
210	0.09	2.6	0.51	0.01	0.07	0.28	0.13	0.05	<DL	
246	0.09	2.5	0.38	0.01	0.07	0.25	0.12	<DL	<DL	
270	0.13	2.0	0.41	0.01	0.06	0.25	0.08	<DL	<DL	
310	0.11	1.9	0.57	0.01	0.12	0.41	0.18	0.09	<DL	
Replicate 310	0.12	1.9	0.57	0.01	0.11	0.43	<u>0.16</u>	<DL	<DL	
340	0.39	5.6	1.9	0.02	0.63	1.3	0.59	0.12	<DL	
360	0.19	4.8	1.1	0.02	0.34	1.1	0.89	0.22	<DL	
<i>Alpehué Pumice</i>										
	0.28	7.9	2.5	0.06	0.47	1.7	2.9	1.6	0.05	
<i>Trumaos</i>										
	0.79	6.0	4.2	0.16	1.8	3.7	0.89	0.20	0.07	
Replicate PB2 %-deviation										
	1	2.3	0.3	0.4	6.2	6.6	5.3	9.5	-	
Replicate PB4 %-deviation										
	1	0.0	0.0	0.0	8.3	4.8	11.1	-	-	

Trace elements

In PB2 (Table 3) Light Rare Earth elements (LREE) show a weak variation range relative to Heavy Rare Earth elements (HREE). Chondrite-normalized³⁸ La/Lu ratio (La_{ch}/Lu_{ch}) ranging between 2.78 and 2.84. The range of variation is more important in PB4 ($La_{ch}/Lu_{ch} = 0.95-9.58$). However, La_{ch}/Lu_{ch} averages suggest an enrichment in LREE relative to HREE in the two peat soils. Other trace elements show comparable trends as those of REE, reflecting a strong influence of a *Trumaos*-SVZ particle source. However, Pb values of PB2 and PB4 show a strong negative anomaly. Based on the behavior of Pb, several potential particle sources to the peat soils could therefore be involved: *Trumaos*, SVZ and/or Upper Continental Crust. These potential sources will be detailed later (*see* section 4).

Lead isotopes

Pb Isotopic compositions in PB2 and PB4 cores are shown in Table 4. The Pb isotopic ratios for Galletué (PB2) define relatively constant profiles and small variations: from 18.556 to 18.601 for ²⁰⁶Pb/²⁰⁴Pb, from 15.602 to 15.607 for ²⁰⁷Pb/²⁰⁴Pb and from 38.462 to 38.500 for ²⁰⁸Pb/²⁰⁴Pb. Except for the three uppermost samples, the Pb isotopic compositions of San Pablo de Tregua (PB4) also vary in narrow ranges: between 18.371 and 18.655 for ²⁰⁶Pb/²⁰⁴Pb, between 15.579 and 15.669 for ²⁰⁷Pb/²⁰⁴Pb, and between 38.238 and 38.617 for ²⁰⁸Pb/²⁰⁴Pb. Isotopic ratios of the three surface samples shift strongly towards lower values (0.868 < ²⁰⁷Pb/²⁰⁶Pb < 0.875 and 2.108 < ²⁰⁸Pb/²⁰⁶Pb < 2.118).

Table 3. Elemental content (ppm) of trace elements in samples from Galletué (PB2). <DL: under detection limits; values in italic: quantitative measurements; underlined values: semi-quantitative measurements.

Depth (cm)	Sr	Y	Zr	Nb	Ba	La	Ce	Pr	Nd	Eu	Sm	Gd	Dy	Ho	Er	Yb	Lu	Hf	Pb	Th	U	
<i>Galletué (PB2)</i>																						
3.5	232	12	44	1.35	115	4.8	11	1.6	7.3	0.62	1.9	2.1	2.1	0.43	1.3	1.2	0.18	1.3	3.7	0.80	0.25	
29	109	7.9	31	0.87	71	3.5	7.8	1.1	5.1	0.4	1.3	1.4	1.4	0.29	0.86	0.81	0.13	0.85	2.7	0.62	0.20	
70	154	11	40	1.22	95	4.4	10	1.4	6.5	0.55	1.7	2.0	1.9	0.38	1.1	1.1	0.17	1.1	3.7	0.62	0.26	
90	425	18	69	1.84	166	6.5	15	2.3	10	1.0	2.8	3.2	3.2	0.66	1.9	1.8	0.27	1.8	5.8	0.90	0.33	
108	285	20	81	2.14	172	8.2	19	2.8	13	1.1	3.3	3.8	3.6	0.74	2.2	2.1	0.32	2.2	6.5	1.4	0.46	
Replicate 108	305	22	89	2.36	189	9.1	21	3.1	14	1.2	3.7	4.1	4.0	0.84	2.4	2.3	0.35	2.4	7.2	1.5	0.51	
128	282	22	92	2.44	186	9.2	22	3.1	14	1.2	3.6	4.1	3.9	0.78	2.3	2.2	0.33	2.4	7.3	1.5	0.50	
152	318	21	85	2.17	214	8.9	21	3.0	14	1.3	3.6	4.1	3.8	0.76	2.2	2.1	0.32	2.3	7.8	1.5	0.51	
177	316	21	82	2.31	187	8.7	20	2.9	13	1.1	3.3	3.7	3.6	0.74	2.1	2.1	0.33	2.2	6.8	1.3	0.42	
198	385	26	106	2.93	253	11	26	3.7	17	1.4	4.2	4.5	4.5	0.89	2.7	2.6	0.40	2.7	8.6	2.1	0.67	
227	337	24	95	2.78	221	11	25	3.6	16	1.3	3.9	4.3	4.0	0.80	2.4	2.3	0.35	2.4	8.2	1.8	0.59	
<i>San Pablo de Tregua (PB4)</i>																						
1	70	0.85	<DL	<DL	29	0.46	0.65	0.10	0.44	<DL	<DL	<DL	0.1	<DL	0.07	<DL	<DL	<DL	83	<DL	0.03	
3	80	0.66	<DL	<DL	48	0.37	0.45	0.08	0.35	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	70	<DL		
16	113	4.3	<DL	0.51	83	1.6	2.8	0.42	2.0	0.18	0.53	0.60	0.62	0.13	0.39	0.38	0.06	<DL	16	<DL	0.10	
47	152	34	132	4.9	121	16	24	4.2	18	1.1	4.0	4.54	4.5	0.92	2.7	2.5	0.39	3.0	13	3.5	1.1	
71	204	33	155	6.5	124	15	25	4.2	18	1.5	4.2	4.73	4.6	0.91	2.7	2.5	0.37	3.4	19	3.9	1.3	
105	67	41	106	2.9	114	25	27	5.0	21	1.3	4.5	5.46	5.6	1.1	3.2	2.8	0.40	2.4	12	<DL	0.88	
160	129	4.2	<DL	0.34	16	3.4	3.1	0.64	2.5	0.13	0.47	0.57	0.54	0.12	0.33	0.26	0.04	<DL	0.78	<DL	0.08	
210	24	88	<DL	0.66	37	48	34	10	44	1.6	7.2	10.11	8.4	1.8	4.8	3.5	0.52	<DL	2.3	<DL	0.38	
246	20	86	<DL	0.67	34	44	25	7.9	33	1.2	5.3	7.45	6.9	1.5	4.4	3.3	0.50	<DL	2.3	<DL	0.46	
270	21	40	22	0.91	31	19	11	2.8	11	0.4	1.7	2.34	2.4	0.6	1.9	1.6	0.25	0.45	2.3	<DL	0.22	
310	37	57	48	1.9	90	23	20	4.1	17	0.85	3.2	4.08	4.1	0.97	3.1	2.8	0.45	<DL	4.8	<DL	0.52	
Replicate 310	41	66	56	2.2	107	27	24	4.9	20	1.0	3.9	4.76	4.8	1.1	3.6	3.2	0.52	<DL	5.6	<DL	0.59	
360	146	5.0	<DL	<DL	12	2.4	3.6	0.59	2.6	0.16	0.55	0.61	0.61	0.13	0.41	0.39	0.06	<DL	0.50	<DL	0.03	
390	99	46	96	2.2	61	15	17	4.1	19	1.7	4.2	4.78	4.8	1.0	3.2	3.2	0.52	2.0	5.4	1.8	0.58	
<i>Alpehué Pumice</i>																						
229	26.2	238	7.71	569	25.7	51.5	6.36	23.4	1.04	4.6	4.37	3.85	0.9	2.55	2.81	0.44	6.1	21.3	9	2.55		
<i>Trumaos</i>																						
166	26.1	127	4.11	143	14.2	31.3	4.28	19.1	1.44	4.59	5.29	4.87	0.96	2.88	2.81	0.41	3.22	10	3.74	0.91		
Replicate PB2 %-deviation	6.9	10.2	10.2	10.2	10.2	10.2	10.2	10.2	10.2	10.2	10.2	10.2	10.2	10.2	10.2	10.2	10.2	10.2	10.2	10.2	10.2	10.2
Replicate PB4 %-deviation	11	15.4	15.3	15.8	18.1	18.0	18.7	18.2	16.7	17.9	18.2	16.5	16.8	15.9	17.4	15.5	14.9	-	16.4	-	13.3	

Depth	²⁰⁶ Pb/ ²⁰⁴ Pb	2σ	²⁰⁷ Pb/ ²⁰⁴ Pb	2σ	²⁰⁸ Pb/ ²⁰⁴ Pb	2σ	²⁰⁸ Pb/ ²⁰⁶ Pb	2σ	²⁰⁷ Pb/ ²⁰⁶ Pb	2σ
(cm)		x 10 ⁻⁴		x 10 ⁻⁴		x 10 ⁻⁴		x 10 ⁻⁵		x 10 ⁻⁵
<i>Galletué (PB2)</i>										
3.5	18.5564	14	15.6053	12	38.4622	31	2.0727	5	0.8409	2
29	18.5820	17	15.6072	16	38.4916	40	2.0714	3	0.8399	1
70	18.5727	13	15.6020	11	38.4761	30	2.0716	4	0.8400	1
90	18.5722	16	15.6037	13	38.4771	32	2.0718	5	0.8402	2
108	18.5710	9	15.6039	7	38.4737	17	2.0717	3	0.8402	1
128	18.5956	10	15.6064	12	38.4974	30	2.0703	4	0.8393	1
152	18.5927	10	15.6045	9	38.4950	25	2.0705	4	0.8393	1
177	18.6014	14	15.6070	11	38.5002	28	2.0699	4	0.8391	1
Replicate 177	18.8800	9	15.6026	9	38.4756	27	2.0699	5	0.8394	1
198	18.5855	10	15.6057	9	38.4881	26	2.0709	5	0.8397	1
227	18.5820	12	15.6032	13	38.4850	32	2.0711	4	0.8397	1

San Pablo de Tregua (PB4)

Table 4. Analyses of lead isotopes in samples from Galletué (PB2) and San Pablo de Tregua (PB4). Italic value (when $2\sigma < 100 \times 10^{-4}$) have to be considered as qualitative data.

1	17.7952	7	15.5737	6	37.6848	19	2.1176	5	0.8751	1
3	17.7799	8	15.5710	8	37.6660	23	2.1184	6	0.8758	2
16	17.9551	64	15.5879	54	37.8373	139	2.1077	80	0.8682	4
47	<i>18.5892</i>	<i>169</i>	<i>15.6408</i>	<i>146</i>	<i>38.5411</i>	<i>356</i>	2.0732	13	0.8413	7
71	18.5136	47	15.6088	42	38.4114	101	2.0745	8	0.8429	4
105	18.5856	64	15.6246	55	38.5147	131	2.0719	9	0.8406	4
160	<i>18.5469</i>	<i>148</i>	<i>15.5888</i>	<i>122</i>	<i>38.4206</i>	<i>304</i>	2.0715	19	0.8405	7
210	<i>18.5435</i>	<i>100</i>	15.6338	83	<i>38.4684</i>	<i>200</i>	2.0747	14	0.8431	6
246	18.6546	17	15.6689	15	38.6174	37	2.0701	5	0.8399	24
270	<i>18.4576</i>	<i>116</i>	<i>15.6145</i>	<i>100</i>	<i>38.3621</i>	<i>250</i>	2.0785	18	0.8459	9
310	<i>18.5601</i>	<i>153</i>	<i>15.5792</i>	<i>131</i>	<i>38.4197</i>	<i>324</i>	2.0701	20	0.8394	10
340	18.5605	46	15.6028	41	<i>38.4549</i>	<i>102</i>	2.0715	9	0.8407	3
360	18.3714	20	15.5913	20	38.2376	53	2.0814	4	0.8486	3
<i>Trumaos</i>	18.6049	7	15.9079	7	<i>38.5087</i>	<i>220</i>	2.0698	1	0.8390	8
<i>Alpehué pumice</i>	18.5454	9	15.6021	8	38.4541	25	2.0735	6	0.8413	8

DISCUSSION

Natural vs. anthropogenic sources

Trace element concentrations normalized to chondrite values³⁸ are reported as spider diagrams (Fig. 3). Profiles of average concentrations for the two peat soils are compared to average compositions of the *Trumaos*, the Chilean Southern Volcanic Zone (SVZ) soils and the average Upper Continental Crust (UCC). Trends suggest a dominant particle sources comparable to the SVZ products and *Trumaos*. Galletué area (PB2) is closer to the SVZ profile than PB4. It is consistent with the influence made by the numerous tephra layers found in the core. This is also consistent with the lithology: PB2 is rather a peaty sediment rich in volcanic particles, than a pure (*i.e.* organic) peat. San Pablo de Tregua (PB4) core as a whole has a comparable lithology to PB2 although it displays less abundant volcanic layers.

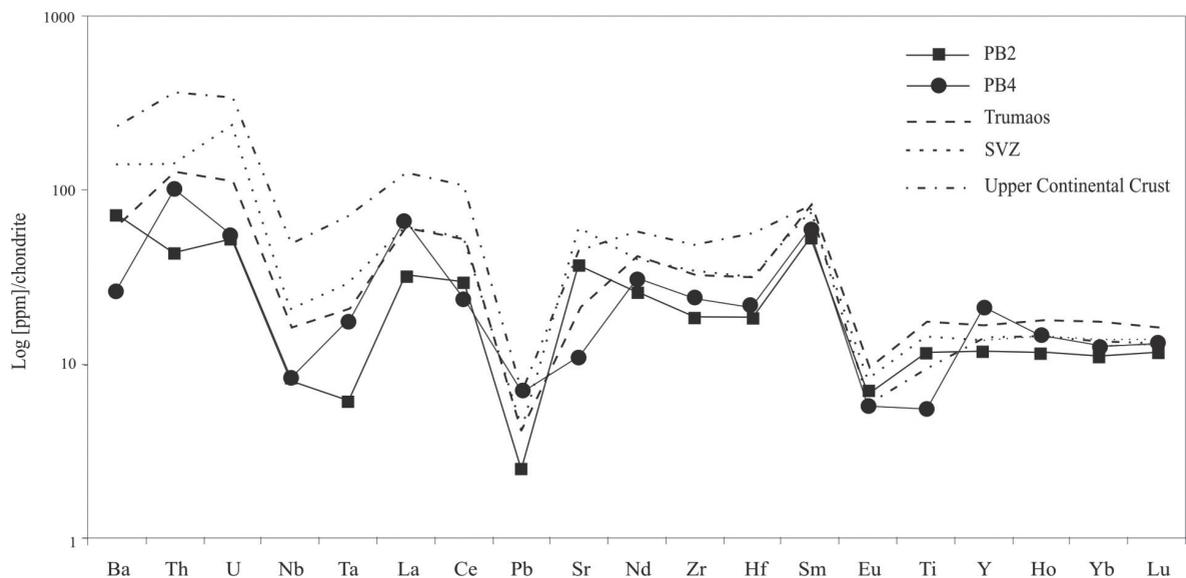


Figure 3. Spider diagrams³⁹ normalized to chondrites³⁸ for the two sites and *Trumaos* compared with SVZ⁴⁰⁻⁵⁷ and Upper continental crust⁵⁸.

Pb isotopic data for Galletué (PB2) show a narrow range of variation and are included within the *Trumaos*-SVZ isotopic data field (Fig. 4.A.). A significant shift in $^{206}\text{Pb}/^{207}\text{Pb}$ is recorded between the two samples taken below (127.75 cm) and above (108.25 cm) the *Alpehué Pumice*, a well known rhyodacitic volcanic layer erupted from Caldera Sollipulli at 3000 yr cal BP⁵⁹. The measured isotopic ratios are shifted from the *Trumaos* trend to the *Alpehué Pumice* isotopic composition (Fig. 4. B and C). This is due to contamination by grains from *Alpehué Pumice* dispersed in nearby upper layers, providing a pumiceous contribution to the isotopic signature of the peaty sediment. The shift shown by the sub-surface sample (3 cm depth) is too small (e.g. $^{206}\text{Pb}/^{204}\text{Pb} = 18.564 \pm 0.0014$) regarding to Pb isotopic ratios in actual Chilean cities aerosols⁶⁰ ($^{206}\text{Pb}/^{204}\text{Pb} = 17.00 \pm 0.02$) to invoke any anthropogenic contribution to the Pb isotopic composition for the

subsurface sample of Galletué core. The shallowest sample has probably been taken under the anthropogenically contaminated layers. Note that it was not possible to sample the subsurface layers due to contamination by sparse tephra grains. Moreover, in cores from Lake Galletué, no anthropogenic influence is recorded in terms of fossil fuel pollution⁶¹. Anthropogenic particles originating from a long distance source are negligible⁶¹.

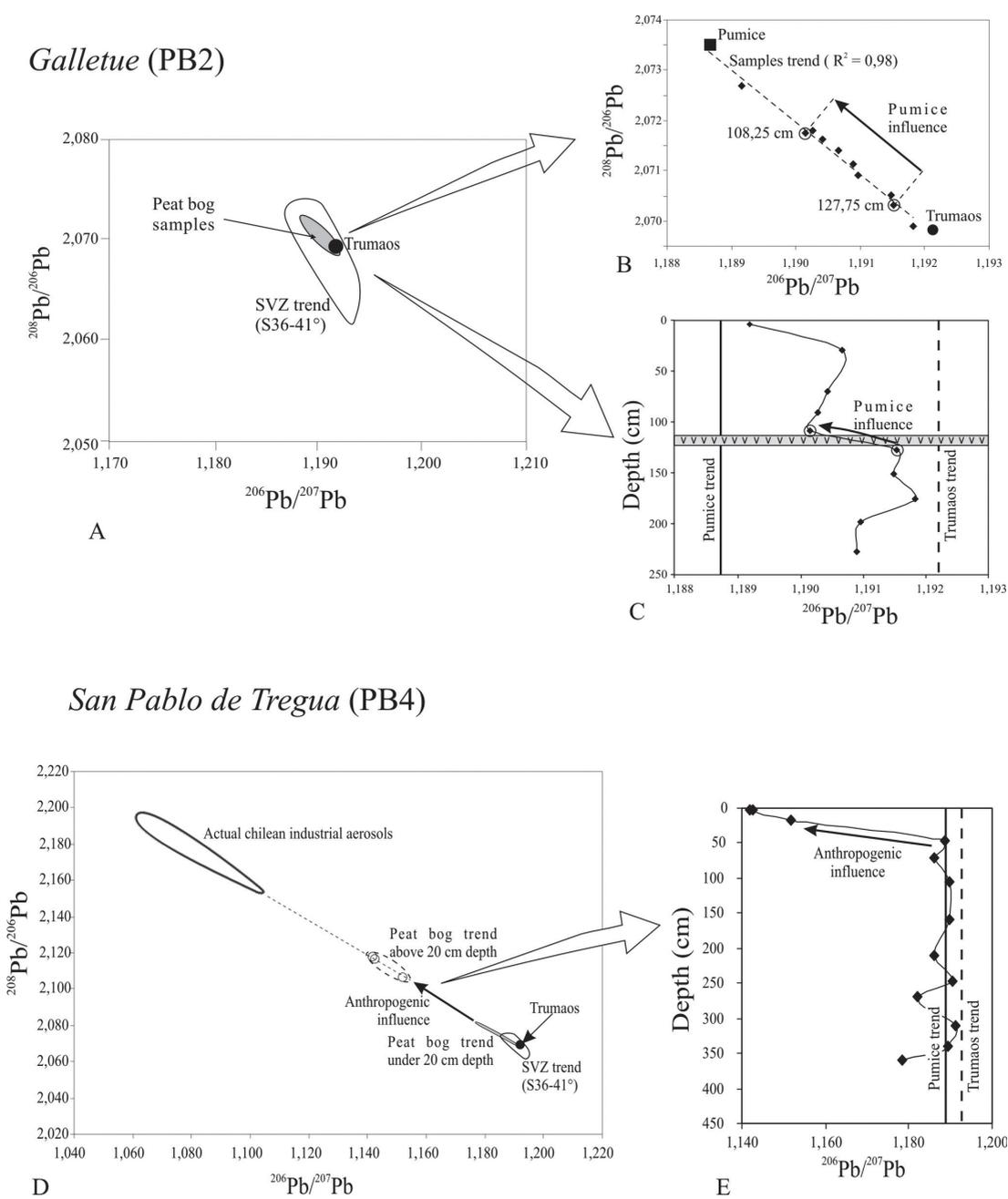


Figure 4. $^{206}\text{Pb}/^{207}\text{Pb}$ vs. $^{208}\text{Pb}/^{206}\text{Pb}$ isotopic biplot of PB2 (A.) and PB4 (D.) SVZ: field of SVZ ratios (95% confidence)^{41, 42, 46-48, 50-52, 55, 56, 62, 63}. SVZ*: possible extension to higher $^{207}\text{Pb}/^{206}\text{Pb}$ values^{43, 49, 65}. Average Upper Continental Crust from literature⁵⁸. Actual Chilean industrial aerosols (younger than 1994) from the cities of Concepción, Villarrica and Punta Arenas⁵⁹. B. and C. Influence of the pumice layer on the isotopic biplot and the $^{206}\text{Pb}/^{207}\text{Pb}$ vs. depth profile, respectively. E. Depth evolution of $^{206}\text{Pb}/^{207}\text{Pb}$ in San Pablo de Tregua (PB4).

Variation in Pb isotopic ratios ranges are ten times wider for San Pablo de Tregua (PB4) relative to PB2. Sediments sampled above 20 cm depth display isotopic ratios ($^{206}\text{Pb}/^{207}\text{Pb} < 1.16$, $^{208}\text{Pb}/^{206}\text{Pb} > 2.10$) strongly shifted towards anthropogenic field (Fig. 4. D. and E) here reported by Actual Chilean industrial aerosols⁵⁹. As it was already suggested by the high Pb E.F., Pb isotopic signatures of the three uppermost samples (1, 3, and 20 cm) reflect conjugated inputs of both SVZ volcanic particles and actual industrial aerosols. $^{206}\text{Pb}/^{207}\text{Pb}$ ratios were reported to vary between 1.12 and 1.14 associated Pb E.F. higher than 60 in Antarctic ice core samples^{19,20} aging from 1950 A.D. to 1987 A.D. Moreover, ice samples dating from the early 1900's A.D. to about 1940 A.D. show preferentially $^{206}\text{Pb}/^{207}\text{Pb}$ varying between 1.15 and 1.18, and lower Pb E.F. Therefore, despite a lack of dating for our samples, we could assume a young age (1940 A.D.-2000

A.D.) for the two uppermost samples of PB4 on the basis of their low $^{206}\text{Pb}/^{207}\text{Pb}$ ratios (1.12- 1.14), strong Pb enrichment and extremely high Pb E.F. With a $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of 1.15 and lower Pb E.F. (13), the third sample (16 cm depth) could be rather older. However, further sampling and dating of PB4 core would have been necessary to specify the exact age of this anthropogenic influence, but tephra grains contaminating surface samples peat make this sampling very tricky.

Changes in particle fluxes and Crustal involvement

PB2 samples show a Al/Ti profile with an opposite trend relative to Nd/Ti and Pb/Ti profiles (Fig. 5). All the normalized profiles are included within the range of *Trumaos* and SVZ values, except for Al/Ti. This latter profile ranges between (1) the *Trumaos* and/or the SVZ and (2) the average Upper Continental Crust Al/Ti values, suggesting a possible crustal contamination. Pb E.F. profile (calculated with *Trumaos* reference) suggests a unique mineral source for PB2. Nd/Ti and Pb/Ti profiles suggest a mineral particle source with a volcanic geochemical signature reflecting the *Trumaos* and/or SVZ compositions, as already shown by spider diagrams. *Trumaos* are easily eroded and carried by wind. It is therefore assumed that the SVZ signature is due to the *Trumaos* inputs rather than particles issued from solid volcanic rocks weathering or direct volcanic supply.

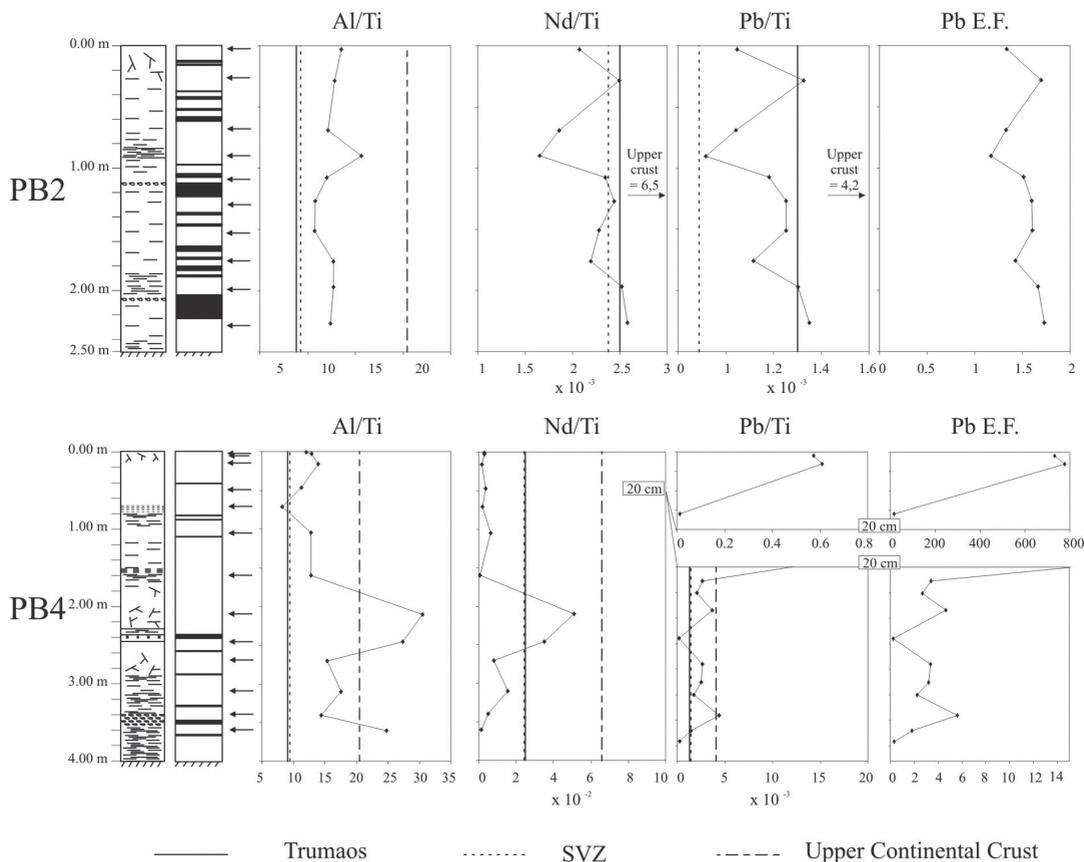


Figure 5. Ratio profiles (Al/Ti, Nd/Ti, Pb/Ti) and Pb enrichment factor (calculated using *Trumaos* values) of the two profiles. SVZ: mean value (for references, see figure 4). Upper continental crust: values from literature⁵⁸.

In PB4, Ti-normalized profiles of Al and Nd are roughly comparable. As a whole, the profiles are included within the composition ranges of SVZ and *Trumaos*. However, three peaks show significantly high ratios exceeding the SVZ and *Trumaos* composition ranges. They correspond to high Al/Ti values between at about 360 cm depth and high Al/Ti and Nd/Ti values between 210 and 246 cm depth (Fig. 5). These compositional shifts suggest a possible crustal particles input. Moreover, Pb/Ti and Pb E.F. profiles show also higher values trending towards crustal composition between 210 and 246 cm depth but not at 360 cm depth. Pb E.F. also shows higher values (approximately 3 and 5.5, respectively) between 210 cm and 246 cm but again not at 360 cm depth. These observations suggest involvement of a crustal particle source. The strong peak clearly observed at 71 cm depth in the Ti, Ti flux, and Pb E.F. profiles, is missing in Ti-normalized profiles. This contrast suggests that the 71 cm depth silty layer is mainly composed of volcanic derived material (*Trumaos*). Pb/Ti and Pb E.F. profiles display natural background (i.e. *Trumaos*) in the lower part of the core, while the uppermost 20 cm of sediments are strongly enriched in Pb.

Figure 6 presents Ti concentrations, Ti fluxes and particulate fluxes for the two peat soils. Galletué (PB2) samples show extremely high fluxes in Ti and particles, averaging $0.93 \text{ g/m}^2/\text{yr}$ and $158 \text{ g/m}^2/\text{yr}$, respectively. For comparison, in Swiss peat bogs¹⁰, the Younger Dryas is recorded by a strong dust peak averaging $11.5 \text{ g/m}^2/\text{yr}$ while the natural background dust flux is less than $0.5 \text{ g/m}^2/\text{yr}$. At 90 cm depth, a shift in [Ti] is correlated with a strong peak in Ti flux and particulate flux. Between 130 and 180 cm, a slight increase in [Ti] is also recorded in the three profiles. However, $^{147}\text{Sm}/^{144}\text{Nd}$ signatures calculated from Sm and Nd concentrations (for more details, see figure 7 caption) of the Galletué (PB2) samples confirm that the dominant source of atmospheric particles to the peat soils is related to the SVZ-*Trumaos* component (Fig. 6). The possible contribution of a crustal sources for the 90 cm depth sample, previously suggested by the Al/Ti ratio, is inconsistent with the $^{147}\text{Sm}/^{144}\text{Nd}$ results. The high values recorded by the PB2 sample reflect abundant inputs of *Trumaos* and other volcanic weathering particles inputs.

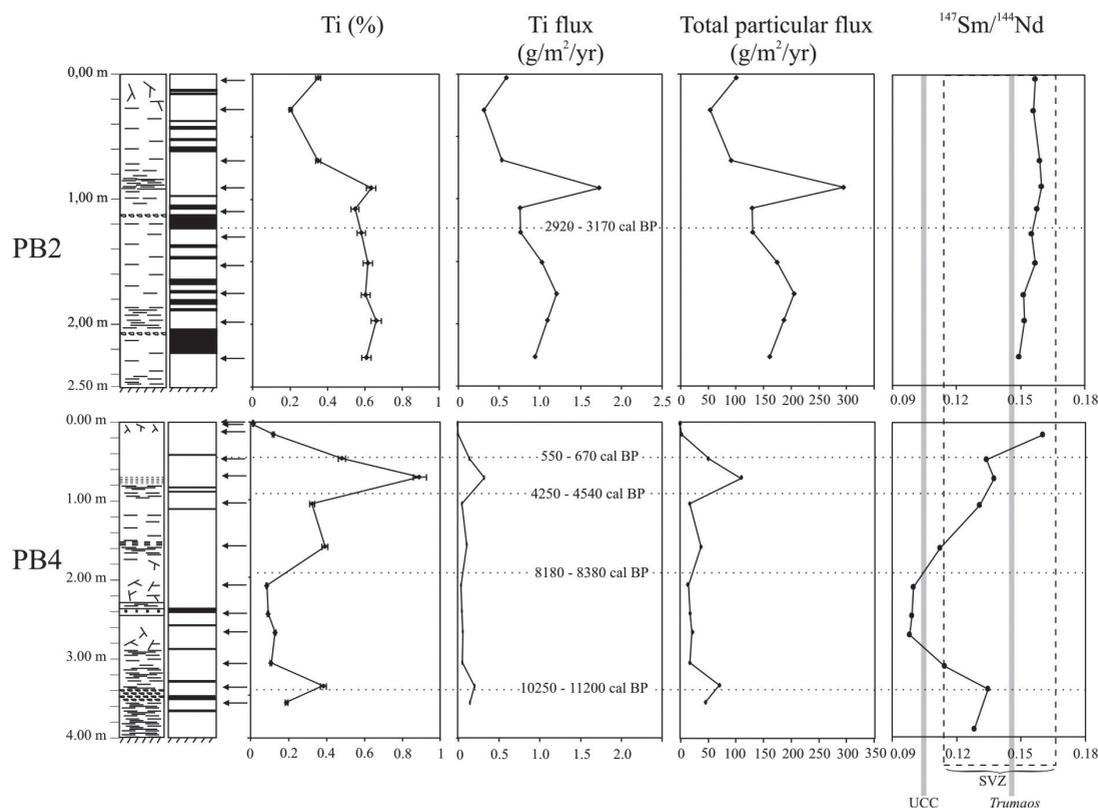


Figure 6. Ti concentration, Ti flux, total particle flux and $^{147}\text{Sm}/^{144}\text{Nd}$ profiles. Arrows indicate samples depth. SVZ: mean value from literature⁴⁰⁻⁵⁷, so as Upper continental crust values⁵⁸. $^{147}\text{Sm}/^{144}\text{Nd}$ is calculated using $[\text{Sm}]/[\text{Nd}]$ in sample multiplied by the ratio between natural abundance of ^{147}Sm in Sm and natural abundance of ^{144}Nd in Nd (i.e. 0.60847). $^{147}\text{Sm}/^{144}\text{Nd}$ results for 1 cm and 3 cm depth samples in PB4 are not represented, because Sm and Nd concentration measurements are under detection limits.

In San Pablo de Tregua (PB4), flux values are globally lower relative to PB2. [Ti] flux and total particular flux average $0.18 \text{ g/m}^2/\text{yr}$ and $31 \text{ g/m}^2/\text{yr}$, respectively. In the three profiles of PB4, a peak is located at 71 cm depth (Fig. 6). $^{147}\text{Sm}/^{144}\text{Nd}$ data mainly plot in the SVZ isotopic field (Fig. 6) except for five samples (130 cm, 210 cm, 246 cm, 270 cm and 310 cm). Samples 160 cm and 310 cm depth may reflect contamination by a crustal input as they are at the limit of the SVZ and Upper Continental Crust isotopic fields (Fig. 6). In addition they display opposite trends in Pb/Ti and Pb E.F. profiles. However, sample at 160 cm depth shows negative shifts ($\text{Pb}/\text{Ti} = 2 \times 10^{-3}$, $\text{Pb E.F.} = 1.6$) while sample at 310 cm shows positive ones ($\text{Pb}/\text{Ti} = 7 \times 10^{-3}$, $\text{Pb E.F.} = 5.6$). Therefore, it is doubtful to interpret them as contaminated by crustal particles. Samples from 210 cm, 246 cm and 270 cm depth are distinguishable from the others by significant lower $^{147}\text{Sm}/^{144}\text{Nd}$ values, reflecting potential contribution of a crustal source. This is especially consistent for the 210 and 246 cm samples because they present strong peaks in Al/Ti, Nd/Ti, Pb/Ti and Pb E.F. Those observations suggest a possible involvement of a long range crustal dust source during corresponding deposition period, strongly influencing $^{147}\text{Sm}/^{144}\text{Nd}$ signatures of these layers.

Summary and conclusions

We investigated peat cores from Chilean lake district. In this region, continental archives are frequently affected by volcanic falls. The availability of soft ash-derived Andosols (i.e. Trumaos) material provides a continuous particle rain input in the Lake District. Short-term high fluxes of particles from various origins appeared to reflect punctual events. Cores from Galletué and San Pablo de Tregua peat soils (Chilean Lake District, South Chile) record ca 6000 and 10000 years of atmospheric particle deposition. Those peat soils are characterized by a minerotrophic matrix rich in volcanic dust with variable organic content. The use of major and trace elements data as well as Pb isotopes allow to decipher between three the particles categories supplied to the peat soils: a) SVZ weathering products (Trumaos) ($0 < \text{Pb E.F.} < 2$ and $1.185 < ^{206}\text{Pb}/^{207}\text{Pb} < 1.195$) providing a great amount of erodible material easily

transported by wind, and constituting the local and main particles source; b) a mix of SVZ weathering products and long range crustal particles ($2 < \text{Pb E.F.} < 6$ and $^{147}\text{Sm}/^{144}\text{Nd} < 0.105$ to 0.115), only recorded in San Pablo de Tregua; c) an anthropogenic undifferentiated source ($\text{Pb E.F.} > 6$ and $^{207}\text{Pb}/^{206}\text{Pb} > 0.865$) only recorded in the uppermost 20 cm of San Pablo de Tregua (PB4).

In Galletué (PB2) core, a clayey layer induces a peak in several elemental profiles at 90 cm depth. Particularly, the total particle flux reaches $158 \text{ g/m}^2/\text{yr}$, which is extremely high. This particular clayey level could suggest a climatic change corresponding to a warmer period with a main volcanic atmospheric dust supply. Since this period, no crustal aerosol input is detected.

In San Pablo de Tregua (PB4) core, the particle source below 20 cm depth is the SVZ-Trumaos source. Above this depth, the signature is a mix between SVZ-Trumaos and the industrial sources, reflecting the inception of the anthropogenic influence. In PB4, two periods of Pb pollution could be distinguished by comparison with isotopic values from the Antarctic ice cap^{19,20}. The sample at 16 cm could be related to the beginning of the 20th century while the two uppermost ones reflect more likely the isotopic signature of the period between 1950 and 1987. Moreover the isotopic signatures between 210 cm and 246 cm suggest punctual crustal involvement, possibly linked to a long range particle transport.

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REFERENCES

- 1.- H. Kempter, B. Frenzel, *Sci Tot. Environ.* **241**, 117, (1999).
- 2.- A. Martínez-Cortizas, X. Pontevedra-Pombal, E. García-Rodeja, J. C. Nóvoa Muñoz, W. Shotyk, *Science* **284**, 939, (1999).
- 3.- A. Martínez -Cortizas, E. García-Rodeja, X. Pontevedra-Pombal, J. Nóvoa Muñoz, D. Weiss, A. K. Cheburkin *Sci Tot. Environ.* **292**, 33, (2002).
- 4.- W. Shotyk, D. Weiss, P. G. Appleby, A. K. Cheburkin, R. Frei, M. Gloor, J. D. Kramers, S. Reese, V. D. Knaap, *Science* **281**, 1635, (1998).
- 5.- W. Shotyk, M. Krachler, A. Martínez-Cortizas, A. K. Cheburkin, H. Emons, *Earth planet. Sci. Lett.* **199**, 21 (2002)
- 6.- D. Weiss, W. Shotyk, J. D. Kramers, M. Gloor, *Atm. Environ.* **33**, 3751, (1999).
- 7.- W. Shotyk. *Earth Sci. Rev.* **25**, 95, (1988).
- 8.- W. Shotyk, *Environ. Rev.* **4**, 149, (1996).
- 9.- S. West, D.J. Charman, J.P. Grattan, A.K. Cheburkin, *Wat. Air. Soil. Poll.* **100**, 343, (1997).
- 10.- W. Shotyk, D. Weiss, J. D. Kramers, R. Frei, A. K. Cheburkin, M. Gloor, S. Reese, *Geoch. Cosm. Acta* **65**, 2337, (2001).
- 11.- W. Shotyk, *Sci. Tot. Environ.* **292**, 19, (2002).
- 12.- T. M. Mighall, P. W. Abrahams, J. P. Grattan, D. Hayes, S. Timberlake, S. Forsyth, *Sci. Tot. Environ.* **292**, 69, (2002).
- 13.- S. Baron, M. Lavoie, A. Ploquin, J. Carignan, M. Pulido, J.-L. De Beaulieu, *Environ. Sci. Technol.* **39**, 5131, (2005).
- 14.- W. Shotyk, A. Sapkota, A.K. Cheburkin, B. Kober, Submitted to *Geoch. Cosm. Acta*.
- 15.- A. Sapotka, Mineralogical, chemical, and isotopic (Sr, Pb) Composition of atmospheric mineral dusts in an ombrotrophic peat bog, Southern South America. PhD Thesis, Ruprecht-Karls-Universität, Heidelberg, Germany, 2006.
- 16.- H. Biester, A. Martínez-Cortizas, S. Birkenstock, R. Killian, *Environ. Sci. & Technol.* **37**, 32, (2003).
- 17.- D. Weiss, W. Shotyk, J. Rieley, S. Page, M. Gloor, S. Reese, A. Martínez-Cortizas, *Geoch. Cosm. Acta* **66**, 2307, (2002).
- 18.- I. Basile, F. E. Grousset, M. Revel, J. R. Petit, P. E. Biscaye, N. I. Barkov, Earth planet. *Sci. Lett.* **146**, 573, (1997).
- 19.- P. Vallelonga, K. van de Velde, J.-P. Candelone, V.I. Morgan, C.F. Boutroun, K.J.R. Rosman, *Earth planet. Sci. Lett.* **204**, 291, (2002).
- 20.- F.A.M. Planchon, K. van de Velde, K.J.R. Rosman, E.W. Wolff, C.P. Ferrari, C.F. Boutroun *Geoch. Cosm. Acta* **67**, 693 (2003).
- 21.- I.E. Belokopytov, V.V. Beresnevich, *Torf. Prom.* **8**, 9, (1955).
- 22.- P. C. Jowsey, *New Phyt.* **65**, 245, (1965).
- 23.- B.G. Andersen, G.H. Denton, T.V. *Geogr. Ann.* **81A**, 155, (1999)
- 24.- G.H. Denton, C.J. Heusser, T.V. Lowell, P.I. Moreno, B.G. Andersen, L.E. Heusser, C. Schlüchter, D.R. Marchant, *Geogr. Ann.* **81A**, 107, (1999a).
- 25.- G.H. Denton, T.V. Lowell, C.J. Heusser, C. Schlüchter, B.G. Andersen, L.E. Heusser, P.I. Moreno, D.R. Marchant, *Geogr. Ann.* **81A**, 167, (1999b).
- 26.- R.D. McCulloch, M.J. Bentley, R.S. Purves, N.R.J. Hulton, D.E. Sugden, C.M. Clapperton, *J. Quat. Sci.* **15**, 409, (2000).
- 27.- O. González-Ferrán Volcanes de Chile. Instituto Geográfico militar, Santiago de Chile, 1995.
- 28.- E. Besoain in Suelos volcánicos de Chile. J. Tosso ed., Instituto de Investigaciones Agropecuarias (INIA), Santiago de Chile, 1985; pp. 23-106.
- 29.- S. Bertrand, N. Fagel, *Catena* **73**, 10, (2008).
- 30.- L. V. Vargas-Ramírez, Investigación paleopalínológica en el Sur de Chile (38°S a 41°S). Proceedings the XIV Simposio de Palinología (A.P.L.E.). Salamanca, 2002.
- 31.- O. Martínez-Miranda, *Bosque* **4**, 3, (1981).
- 32.- C. Bronk Ramsey, *Radiocarbon* **43**, 355, (2001).
- 33.- K. Govindaraju, H. de la Roche, *Geost. Newsl.* **1**, 67, (1977).
- 34.- D. Weis, B. Kieffer, C. Maerschalk, W. Pretorius, J. Barling, *Geoch. Geoph.*, Geos. 6, paper number 10.1029/2004GC000852, (2005).
- 35.- K. H. Wedepohl, C. W. Correns, D. M. Shaw, K. K. Turekian, J. Zeman Handbook of geochemistry, 13E1-13L2, 21A1-21L1, 22A3-22L2, 40A1-40L2, 72A1-72L1. Springer-Verlag. Berlin, 1978.
- 36.- H. W. Nesbitt, G. Markovics, *Geoch. Cosm. Acta* **61**, 1653, (1997).
- 37.- W. Shotyk, Peat bog archives of atmospheric Pb deposition. Habilitation Thesis, Geological Institute, University of Berne, 1995.
- 38.- E. Anders, N. Grevesse, *Geoch. Cosm. Acta* **53**, 197, (1989)
- 39.- S.-S. Sun, W.F. McDonough, in Magmatism in the Ocean Basins. A.D. Saunders, M.L. Norry eds, *Geol. Soc. Spec. Publ.* **42**, 313 (1989).
- 40.- F. Costa, B. Singer, *J. Petr.* **43**, 1571, (2002).
- 41.- J. P. Davidson, M. A. Dungan, K. M. Ferguson, M. T. Colucci, *Geol.* **15**, 443, (1987).
- 42.- J. P. Davidson, K. M. Ferguson, M. T. Colucci, M. A. Dungan, *Cont. Min. Petr.* **100**, 429- (1988).
- 43.- T. C. Feeley, M. A. Dungan, F. A. Frey, *Cont. Min. Petr.* **131**, 393, (1998).
- 44.- K.M. Ferguson, M.A. Dungan, J.P. Davidson, M.T. Colucci *J. Petrol.* **33**, 1, (1992)
- 45.- F. A. Frey, D. C. Gerlach, R. L. Hickey, L. López-Escobar, F. Munizaga-Villavicencio, *Cont. Min. Petr.* **88**, 133, (1984).
- 46.- D. C. Gerlach, F. A. Frey, H. Moreno Roa, L. López- Escobar, *J. Petr.* **29-2**, 333, (1988).
- 47.- R. L. Hickey, F. A. Frey, D. C. Gerlach, L. López- Escobar *J. Geophys. Res.* **91**, 5963, (1986).
- 48.- R. Hickey-Vargas, H. Moreno Roa, L. López- Escobar, F. A. Frey *Cont. Min. Petr.* **103**, 361, (1989).
- 49.- W. Hildreth, S. Moorbath, *Cont. Min. Petr.* **98**, 455, (1988).
- 50.- L. López- Escobar, F. A. Frey, M. M. Vergara, *Cont. Min. Petr.* **63**, 199, (1977).
- 51.- L. López- Escobar, M. A. Parada, H. Moreno, F. A. Frey, R. Hickey-Vargas, *Rev. Geol. Chile* **19**, 211, (1992).
- 52.- L. López- Escobar, M. A. Parada, R. Hickey-Vargas, F. A. Frey, P. D. Kempton, H. Moreno Roa, *Cont. Min. Petr.* **119**, 345, (1995).
- 53.- P. D. Jr. Noll, H. E. Newson, W. P. Leeman, J. G. Ryan, *Geoch. Cosm. Acta* **60**, 587, (1996).
- 54.- O. Sigmarrson, M. Condomines, J. Morris, R. S. Harmon, *Nature* **346**, 163, (1990).
- 55.- C. R. Stern, F. A. Frey, K. Futa, R. E. Zartman, Z. X. Peng, T. K. Kyser, *Min. Petr.* **104**, 294, (1990).
- 56.- D. R. Tormey, R. Hickey-Vargas, F. A. Frey, L. López- Escobar, *Geol. Soc. Am. Spec. Pap.* **265**, 57, (1991).
- 57.- M. M. Vergara, J. B. Muñoz *Rev. Geol. Chile* **17**, 31, (1982).
- 58.- S. M. McLennan, *Geoch. Geoph. Geos.* 2, paper number 2000GC000109. (2001)
- 59.- A. Bollhöfer, K. J. R. Rosman, *Geoch. Cosm. Acta* **64**, 3251, (2000).
- 60.- J. A. Naranjo, H. Moreno, C. Emparan, M. Murphy, *Rev. Geol. Chile* **20**, 167, (1993).
- 61.- L. Chirinos, N. L. Rose, R. Urrutia, P. Munoz, F. Torrejon, L. Torres, F. Cruces, A. Araneda, C. Zoror, *Environ. Pol.* **141**, 247, (2006).
- 62.- R. S. Harmon, B. A. Barreiro, S. Moorbath, J. Hoefs, P. W. Francis, S. Thorpe, B. Deruelle, J. McHugh, J. A. Viglino, *J. Geol. Soc. London* **141**, 803 (1984).
- 63.- K. Notsu, L. López- Escobar, N. Onuma, *Geoch. J.* **21**, 307, (1987).
- 64.- W. Siebel, W. B. W. Scnurr, K. Hahne, B. Kraemer, R. B. Trumbull, P. van den Bogaard, R. Emmermann, *Chem. Geol.* **171**, 213, (2000).
- 65.- D. A. Hilton, K. Hammerschmidt, S. Teufel, H. Friedrichsen, *Earth Planet. Sci. Lett.* **120**, 265, (1993).