

# A geochemical and lead isotopic record from a small pond in a remote equatorial island, Fernando de Noronha, Brazil

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**Abstract:** A 72 cm long core was collected from Lagoa da Viração (LV), a small pond in the Fernando de Noronha island, northern Brazil. Sediments from the lower section of the core (20–72 cm depth) contain essentially mineral matter, while in the upper section (0–20 cm depth) mineral matter is mixed with organic matter. Lithogenic conservative elements – Si, Al, Fe, Ti, Co, Cr, Cu, Ba, Ga, Hf, Nb, Ni, Y, V, Zn, Zr and REE – exhibit remarkably constant values throughout the core, with concentrations similar to those of the bedrock. The vertical distribution of soluble elements – Ca, Mg, Na, K, P, Mn and Sr – is also homogeneous, but these elements are systematically depleted in relation to the bedrock. LOI, TOC, Br, Se, Hg and Pb, although showing nearly constant values in the lower section of the core, are significantly enriched in the upper section. The concentration profiles of Br and Se suggest that they may be accounted for by natural processes, related to the slight affinity of these elements for organic matter. On the other hand, the elevated levels of Hg and Pb in recent sediments may be explained by their long-range atmospheric transport and deposition. Furthermore, the isotopic composition of Pb clearly indicates that anthropogenic sources contributed to the Pb burden in the uppermost pond sediments.

**Key words:** Geochemistry, lake sediments, Fernando de Noronha, mercury, lead isotopes.

## Introduction

Chemostratigraphy of lake sediments has been used in a number of studies as a tool to reconstruct natural environmental changes, and to assess the extent of human activities in trace metal deposition. However, the interpretation of the palaeoenvironmental record provided by sediment geochemistry is often ambiguous. As pointed out by earlier authors, the surface enrichment of metals in lake sediments may be attributed not only to anthropogenic activities, but also to natural processes such as postdepositional remobilization caused, for instance, by different degrees of metal affinity for organic matter (Ramussen, 1998; El Bilali *et al.*, 2002; Yang *et al.*, 2002a; Outridge *et al.*, 2005; Sanei and Goodarzi, 2006). Thus, tracing the sources of trace elements in lake sediments

is not always an easy task. However, for certain elements that have stable isotopes, such as Pb, it is more feasible because anthropogenic and natural sources often exhibit different isotopic compositions, and Pb isotopes are not fractionated by industrial processes or biological recycling, retaining the isotopic fingerprint of their source (Shirahata *et al.*, 1980; Véron *et al.*, 1994; Chiaradia *et al.*, 1997; Monna *et al.*, 2000; Bindler *et al.*, 2001a; Brännvall *et al.*, 2001; Renberg *et al.*, 2001, 2002; Bindler, 2006; Soto-Jimenez *et al.*, 2006; Yang *et al.*, 2007).

While many studies on elemental and lead isotopic geochemistry of lake sediments have been undertaken in the Northern Hemisphere (Carignan and Nriagu, 1985; Hermanson, 1993; Graney *et al.*, 1995; Farmer *et al.*, 1996; Branvaall *et al.*, 1997; Von Gunten *et al.*, 1997; Schettler and Romer, 1998; Rasmussen *et al.*, 1998; Kober *et al.*, 1999; Outridge, 2000; Eades *et al.*, 2002; Outridge *et al.*, 2002; Renberg *et al.*, 2002; Yang *et al.*, 2002a; Ng and King, 2004; Schettler and Romer, 2006; Grahn *et al.*, 2006;

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Mahler *et al.*, 2006), there are few equivalent studies in the Southern Hemisphere (Osborne *et al.*, 1993; Nriagu *et al.*, 1996; Chiaradia *et al.*, 1997; Mogollon and Bifano, 2000; Biester *et al.*, 2002; Abbot and Wolfe, 2003; Cooke *et al.*, 2008). In Brazil, the majority of studies on lake sediments involve mainly palaeoecological and palaeoclimatic reconstructions based on palynological and sedimentological data (Bertaux *et al.*, 1996; Siffedine *et al.*, 2001, 2003; Ledru *et al.*, 2006), but far less attention has been given to the environmental record provided by lake sediment geochemistry (Silva and Resende, 2002; Costa *et al.*, 2005; Gioia *et al.*, 2006; Irion *et al.*, 2006).

The present paper examines the record provided by a small pond – Lagoa da Viração (LV) – situated in a remote oceanic island, Fernando de Noronha, aiming (1) to quantify the vertical distribution of major and trace elements in order to establish the background concentrations in this environment, and (2) to determine the variations in Pb isotopic composition of the sediments in order to investigate the possible contribution of anthropogenic Pb to the total Pb content.

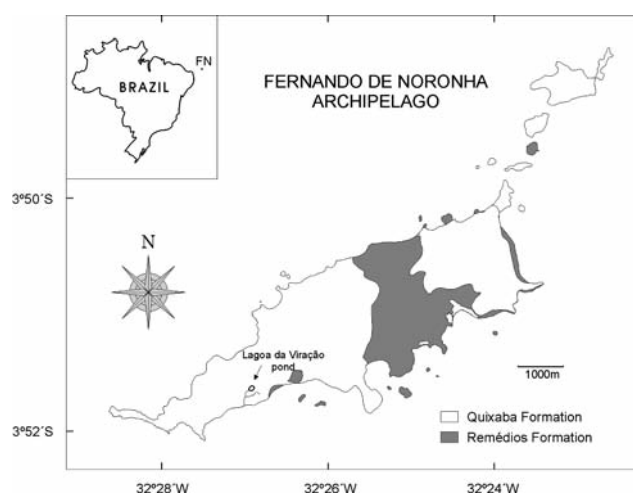
LV is especially suited for this kind of study because it is a relatively pristine ecosystem, not directly affected by urban and industrial activities, but probably affected by atmospheric influxes mainly from the dominant southeasterly trade wind system. Aeolian inputs from the Northern Hemisphere are limited by the formation of an air-mass barrier at the Intertropical Convergence Zone (ITCZ) (Alleman *et al.*, 2001). However, because of the seasonal southward movement of the ITCZ, mineral dust originating from northern Africa can be transported into the tropical South Atlantic. Saharan dust has been detected, for instance, in the lower troposphere over the Balbina meteorological station, in the Amazon basin (1°55'S, 59°24'W) (Formenti *et al.*, 2001). Therefore, the LV pond sediments may be indicative of atmospheric deposition from remote sources and provide evidence of possible anthropogenic Pb pollution in the archipelago.

## Study area

Fernando de Noronha archipelago is a group of 21 remote volcanic islands situated in the South Atlantic Ocean at 03°51' south and 32°25' west, approximately 400 km offshore from the Brazilian coast (Figure 1). The main island, Fernando de Noronha (FN), is 10 km long and 3.5 km at its maximum width, comprising 91% of the total area of the archipelago. The climate is tropical, with two well-defined seasons: the rainy season from January to August and the dry season for the remaining of the year. The average annual temperature is 25°C and the rainfall averages 1300 mm/yr. Although first settled around 1770, FN was barely inhabited until World War II. In 1988 approximately 70% of the archipelago was declared an environmentally protected area.

Nowadays, with a permanent population of about 2100 inhabitants, the island has some facilities for touristic activities, which are restricted to protect its delicate ecosystem. Most human activities are concentrated on the northern side of the island where the main village, Remédios, is situated.

Fernando de Noronha forms part of a chain of seamounts extending eastwards from the Brazilian coast. The archipelago was mapped by de Almeida (1955) who distinguished two main volcanic and subvolcanic units of highly alkaline and silica-undersaturated rocks: Remédios and Quixaba Formations, separated by an erosional hiatus (Figure 1). The Remédios Formation comprises phonolitic and trachytic pyroclastic deposits intruded by lamprophyre and alkali-basalt dikes, and trachyte and phonolite plugs and domes. The Quixaba Formation is predominantly formed by alternating highly mafic lava (nepheline-basalts or ankaratrites) and pyroclasts, with minor nephelinite dikes, tuffs



**Figure 1** Simplified geological map of the Fernando de Noronha (FN) archipelago, and location of the Lagoa da Viração (LV) pond

and breccias. The Remédios Formation ranges in age from 12.3 to 8 Ma and the Quixaba Formation, from 1.7 to 3.8 Ma (Cordani, 1967). A general petrographic account is given in Ulbrich (1993). Gunn and Watkins (1976), Weaver (1990), Ulbrich *et al.* (1994) and Lopes (2002) are the main sources for major and trace geochemical data. Lead isotopic data are given in Gerlach *et al.* (1987) and Lopes (2002).

Lagoa da Viração is the only body of water in the entire archipelago. It is a small (50 m diameter) and shallow (1.5 m maximum depth) pond, located in the southwestern part of the FN island (Figure 1), 20 m a.s.l. and 400 m inland from the shoreline. Confined by steep cliffs of lava flows alternating with pyroclasts on its northern side, the catchment area joins the coastal plain on its southern oceanic side. There is no well-defined inflow channel feeding the pond; yet it is not a closed system since an intermittent small outflow stream drains to the sea during the rainy season. The terrigenous input entering the lake is limited as a result of a diffuse surface runoff that goes through a dense vegetation cover. A floating plant, the macrophyte *Pistia stratiotes*, forms dense mats on the surface of the pond. The local bedrock surrounding and underlying LV pond is the nepheline-basalt from the Quixaba Formation, comprised of Ti-rich clinopyroxene, nepheline, olivine, and hematite, Ti-magnetite, pseudobrookite and ilmenite as accessory minerals (Lopes, 2002).

## Materials and methods

The pond was cored and described as part of a previous study that included <sup>14</sup>C dating, elementary and isotopic C and N determination, and palynological studies (Gouveia *et al.*, 2004). The coring operation was performed in the central and deepest part of the pond. A 72 cm long undisturbed core was collected manually by means of a vibration core and a 7.6 cm diameter aluminum tube. The core was removed from the tube, macroscopically described and sampled in 2 cm sections. About 100 mg of chemically pre-treated (HCl 4%) sediment samples were sent to the Environmental Isotope Laboratory of the University of Waterloo, Canada, for elementary and isotopic C and N determinations that were performed in a Carlo Erba analyser coupled to an Optima mass spectrometer. The results are expressed in percentage of dry weight and in relative  $\delta$  unit, determined in relation to the international standard VPDB for <sup>13</sup>C. For radiocarbon analyses, sediment samples were treated with HCl 4% for 5 h at 80°C. After successive washes with deionized water and drying to 60°C for 48 h,

samples were combusted and the purified CO<sub>2</sub> sent to the Isotrace Laboratory, University of Toronto, Canada, for AMS dating.

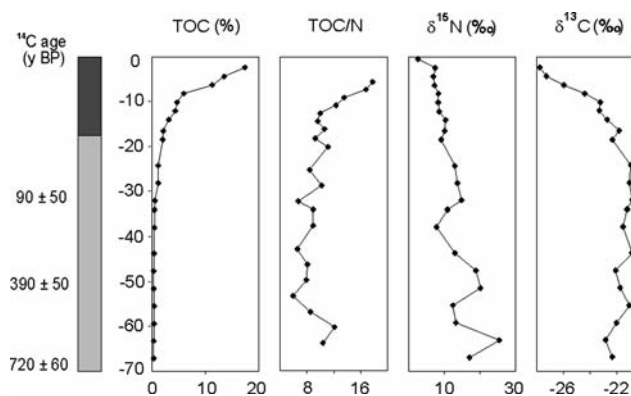
In the present study, 16 samples were selected throughout the core, dried at 90°C for about 24 h, and ground in agate. Separate aliquots of the dried sediments were used to determine mineral and chemical composition, and Pb isotopic ratios. Minerals were identified by x-ray powder diffraction (XRD) with a Philips PW automated powder diffractometer equipped with a graphite monochromator, and Cu K $\alpha$  radiation at 40 kV and 40 mA. The samples were also x-rayed following saturation with ethylene glycol and heat treatment (550°C). Major (Si, Al, Fe, Mn, Mg, Ca, Na, K, Ti and P) and selected trace elements (Ba, Cu, Ga, Nb, Ni, Sr, V, Y and Zr) were determined by conventional wavelength-dispersive x-ray fluorescence spectrometry (XRF), using a Philips PW2400 instrument on glass fusion beads (major) and pressed-powder briquettes (trace). Loss on ignition (LOI) was obtained by calcination of dry samples at 1000°C for 60 min. Analyses of standard reference material showed accuracy and precision to be better than 5% RSD for chemical determinations (Mori *et al.*, 1999). XRD and XRF procedures were carried out at the Institute of Geosciences, University of São Paulo. Selected rare earth metals (REE: La, Ce, Nd, Sm, Eu, Tb, Yb and Lu) and As, Br, Co, Cr, Cs, Hf, Rb, Sb, Sc, Se, Ta, Th, U and Zn were determined using instrument neutron activation analysis (INAA). Samples reference materials and synthetic standards were irradiated for 16 h, in a thermal neutron flux of 10<sup>12</sup> n/cm<sup>2</sup>s in the IEA-R1 nuclear reactor at IPEN, Institute of Nuclear and Energetic Research (São Paulo). Mercury was measured by cold vapour-atomic absorption spectrometry (CV-AAS) technique in a flow injection mercury system (FIMS), after total digestion by a mixture of HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>O<sub>2</sub>, at the same Institute. All Hg determinations were performed in duplicates. Results were consistently within 10% of each other. The INAA methodology validation was performed by measuring the reference materials NIST SRM 2704, IAEA and IWG-GIT, and the AAS methodology, NIST SRM 2704, NIST SRM 1646, and BCR CRM 280. The lower limit detection for the elements determined by XRF, INAA and AAS were well below the lowest measured concentrations in all samples.

For determination of Pb concentrations and isotopic ratios, samples of 50–100 mg of sediments and plant debris were digested with an acid mixture of HF, HNO<sub>3</sub> and HCl for two days. Pb isotope ratios were measured by solid-source thermal ionization mass spectrometry (TIMS) using a multicollector Finnigan MAT 262, at the Center of Geochronological Research, University of São Paulo. A <sup>208</sup>Pb tracer (KU2H: 0.541  $\mu$ g/g) was added for measure of Pb concentrations. Measured ratios of the standard reference material NBS-981 were in close agreement with their certified values.

## Results and discussion

### The core profile: organic matter and chronology

The vertical distribution of total organic carbon (TOC) concentrations throughout the core allowed for distinguishing two sections: a lower one (20–72 cm) with TOC between 0.3 and 1.2%, and an upper one (0–20 cm) where TOC contents increase from 2.0% in the 18–20 cm sample up to 17.2% in the 2–4 cm sample. TOC/N ratios follows the same trend, ranging irregularly from 7.3 to 12.0 below 20 cm depth, and, from this depth upwards, increasing consistently up to 16.3 in the 2–4 cm layer.  $\delta^{13}\text{C}$  values were around –22‰ in the lower section of the core, decreasing upward to –27.6‰ in the 2–4 cm layer.  $\delta^{15}\text{N}$  values also decrease toward the top of the core (Figure 2). The <sup>14</sup>C chronology yielded ages of 720  $\pm$  60 yr BP at 70–72 cm, 390  $\pm$  50 yr BP at 50–52 cm, and 90  $\pm$  50 yr BP at 30–32 cm. These data provide a chronological



**Figure 2** Vertical distribution of total organic carbon TOC (%), TOC/N,  $\delta^{15}\text{N}$  (‰) and  $\delta^{13}\text{C}$  (‰) in the core profile

framework for the upper and lower sections of the core: surface samples (< 20 cm) can be considered as ‘modern’, and the deeper samples (> 20 cm), as ‘pre-industrial’ sediments. Isotopic and palynological data indicated that the composition of ‘modern’ sedimentary organic matter is dominated by a mixture of *P. stratiotes* ( $\delta^{13}\text{C}$  = –28.5‰), algae, and C3 plants belonging to species found presently in the catchment area. In ‘pre-industrial’ sediments, organic matter is scarce, and pollen is nearly absent (Gouveia *et al.*, 2004).

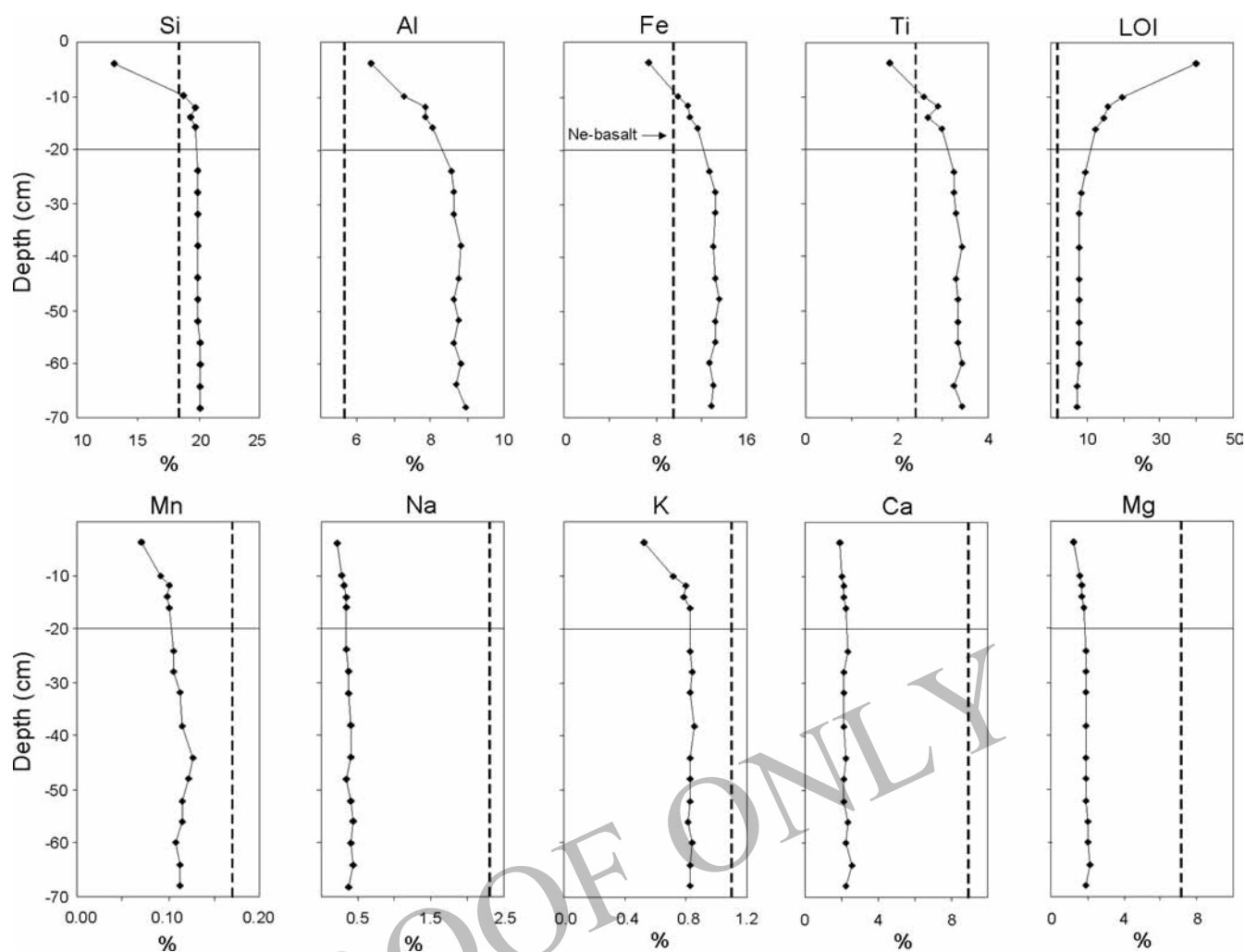
### Mineralogy

Mineralogically, the sediment column is very homogeneous, made up mainly of smectite with lesser amounts of Ti-rich clinopyroxene. Hematite, ilmenite, pseudobrookite and Ti-magnetite were detected in most samples, together with the secondary phases, anatase and goethite. No carbonates, silica or other authigenic minerals were found in the sediments. Such mineralogical composition is consistent with an origin predominantly from the erosion of the surrounding soils. These might be derived mainly from the weathering alteration of the nepheline-basalts found in the catchment area. The secondary clay mineral smectite is the product of weathering of clinopyroxene, olivine and nepheline, while anatase is derived from the primary Ti-bearing oxides. The presence of clinopyroxene, hematite, ilmenite, pseudobrookite and Ti-magnetite as relics of primary minerals, as well as the presence of smectite as the main clay mineral in the sediments, point to a rather moderate degree of weathering in the source area.

### Geochemistry

Herein, the major and trace compositions of the sediments are compared with the average composition of the catchment bedrock – the nepheline-basalts of the Quixaba Formation. The vertical distribution of all major elements shows the same pattern: fairly constant concentrations in the lower section of the core (20–72 cm) and declining concentrations from 20 cm depth up to the surface (Figure 3). Among them, Si, Al, Fe and Ti show concentrations above those of the catchment bedrock throughout the profile, except for the uppermost sample. These elements are quite insoluble in aqueous solutions, behaving as conservative elements during weathering. On the other hand, Ca, Mg, Na, K and Mn are mobile elements, with lower concentrations in the profile as compared with those of the bedrock.

Most of the trace elements analysed follow the same pattern outlined for the lithogenic conservative elements (Figure 4): deeper in the profile, between 20 and 72 cm depth, concentrations remain approximately constant, and decrease gradually from 20 cm depth up to the surface. Throughout the profile, all elements show concentrations in general slightly higher than those of the catchment bedrock within a maximum factor of 2.5.



**Figure 3** Vertical distribution of major elements in the core profile

The only exception is Sr, which behaves similarly to lithogenic mobile elements, being less abundant in the core profile than in the bedrock.

In contrast with the lithogenic elements, loss on ignition (LOI), which measures both organic matter and water in mineral lattices ( $\text{H}_2\text{O}^+$ ), shows minor variation in the 20–72 cm interval (7.1 to 9.3%), and increasing values from 20 cm depth upwards (12.6% in the 14–16 cm sample to 40.2% in the 2–4 cm sample) (Figure 3). The Br, Se and Hg vertical profiles (Figure 4) resemble those of LOI and TOC and contrast with those of lithogenic elements: concentrations are lower and less variable below 20 cm depth and gradually increase to the surface, attaining values of 15  $\mu\text{g/g}$  Br, 6.5  $\mu\text{g/g}$  Se and 97.3 ng/g Hg in the uppermost sample analysed (8–10 cm). Lead concentrations follow the same pattern: approximately constant values below 20 cm, between 8.98 and 9.81  $\mu\text{g/g}$ , and increasing values from 20 cm upwards, attaining 17.28  $\mu\text{g/g}$  in the 2–4 cm sample (see Table 2).

Throughout the core, the lithogenic elements Fe, Al, Ba, Co, Cr, Ga, Nb, Ni, Sr, V, Y and REE showed strong positive correlations ( $r > 0.76$ ,  $n = 15$ ,  $P < 0.001$ ) with the most conservative elements, Zr, Ti and Sc. Zn, Cu and Hf were also positively correlated with this group, but the correlation coefficients are lower ( $r > 0.44$ ,  $n = 15$ ,  $P < 0.1$ ). On the other hand, Br, Hg, Pb, Se, LOI and TOC exhibited strong positive correlations between them ( $r > 0.76$ ,  $n = 15$ ,  $P < 0.001$ ), and strong and negative correlations ( $r < -0.76$ ,  $n = 15$ ,  $P < 0.001$ ) with Zr, Ti and Sc.

### Enrichment factors using Sc-normalized concentrations

The enrichment factor (EF) for each element is estimated by the ratio between the Sc-normalized concentration of the element in the sample and the Sc-normalized concentration of the element in a reference sample:

$$EF = (\text{Me}/\text{Sc})_{\text{sample}} / (\text{Me}/\text{Sc})_{\text{reference}} \quad (1)$$

The bedrock composition (nepheline-basalt) was taken as a reference for all elements analysed, except for Br, Se and Hg, for which data are lacking. For these elements, the average Me/Sc ratios of the four deepest samples (54–56 cm, 58–60 cm, 62–64 cm and 66–68 cm) were taken as reference values.

EFs were calculated for two separate core sections:  $EF_{0-20}$  for the upper TOC-enriched core section and  $EF_{20-72}$  for the lower TOC-depleted core section (Table 1). Lithogenic elements show EFs within a factor of less than 2.5 of the bedrock values in both sections, and  $EF_{0-20}/EF_{20-72}$  ratios between 0.84 and 1.14. On the other hand, Pb, Se, Hg and Br show EFs above 2.8 in the upper section of the core, and  $EF_{0-20}/EF_{20-72}$  ratios greater than 1.5, meaning that these elements are consistently enriched in the upper section of the core. Since Br and Se have a binding affinity for organic matter (Ramussen *et al.*, 1998; Boyle, 2004; Ng and King, 2004; Biester *et al.*, 2007; Li *et al.*, 2007), their higher concentration in the upper, TOC-enriched, layers could be related to natural

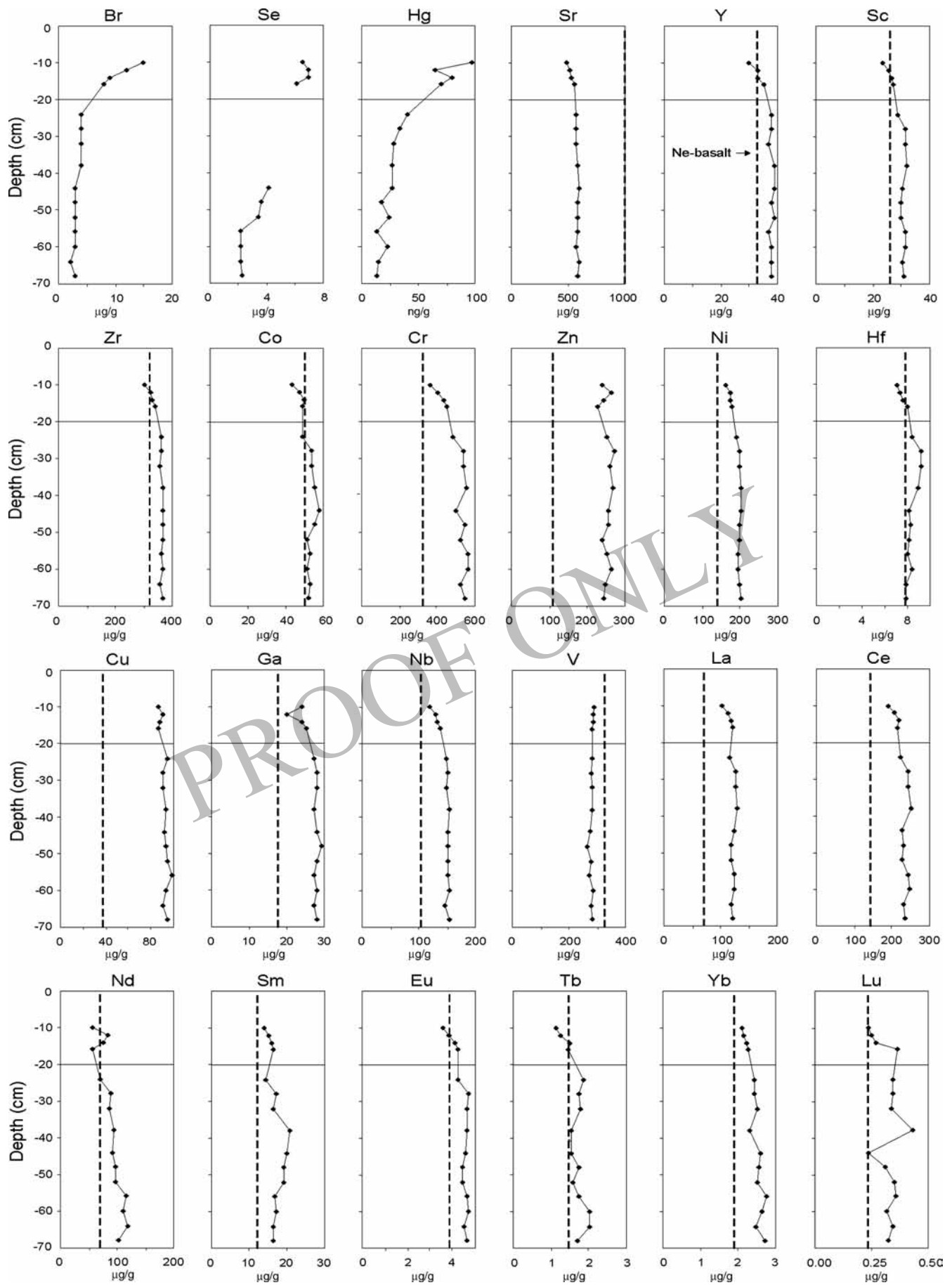


Figure 4 Vertical distribution of trace elements in the core profile

**Table 1** Enrichment factors (EF) using Sc-normalized concentrations

	EF <sub>0–20 cm</sub>	EF <sub>20–72 cm</sub>	EF <sub>0–20</sub> /EF <sub>20–72</sub>
Nd	0.97	1.16	0.84
Tb	0.91	1.01	0.90
Cr	1.27	1.38	0.92
Lu	1.27	1.29	0.99
Ga	1.31	1.32	0.99
Ti	1.15	1.14	1.00
Y	0.96	0.93	1.03
Nb	1.27	1.23	1.03
Eu	0.97	0.94	1.03
Yb	1.24	1.20	1.03
Ba	1.14	1.10	1.04
Ni	1.20	1.15	1.04
Ce	1.40	1.34	1.05
Sm	1.19	1.13	1.05
Zr	0.94	0.88	1.06
Co	1.03	0.96	1.07
Hf	0.95	0.89	1.07
V	0.98	0.91	1.08
La	1.56	1.42	1.10
Cu	2.25	1.99	1.13
Zn	2.51	2.20	1.14
Pb	3.33	2.02	1.65
Se	2.87	1.04	2.76
Hg	3.40	0.87	3.89
Br	3.74	0.87	4.28

postdepositional processes, such as upward migration of pore solutions containing these elements followed by sorption by humic material.

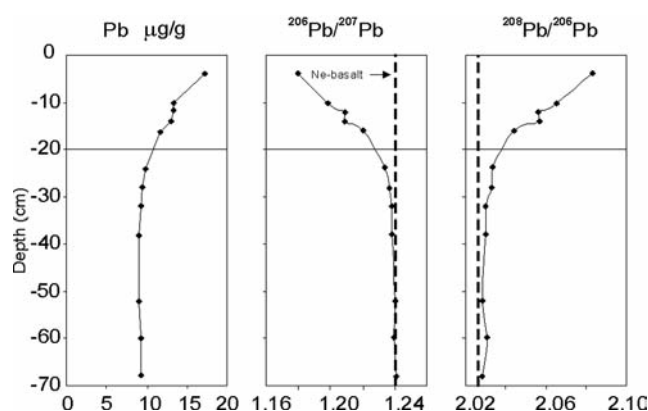
### Mercury

Empirical and experimental studies demonstrated that diagenetic processes cannot explain the increasing concentrations of Hg compared with background values in recent lake sediments (Fitzgerald *et al.*, 1998). Such increasing concentrations have been attributed to long-range atmospheric transport and deposition of Hg emitted mainly from anthropogenic sources (Mason *et al.*, 1994). Because of its high volatility and an atmospheric half-life of about one year, the atmosphere is the main pathway for the distribution of Hg at the Earth's surface. In fact, a signal of Hg pollution has been detected worldwide in sediments, peats and glaciers over the last century, even in pristine regions (Nriagu, 1989; Hermanson, 1998; Lacerda *et al.*, 1999; Bindler *et al.*, 2001b; Lamborg *et al.*, 2002; Roos-Barraclough *et al.*, 2002; Schuster *et al.*, 2002; Yang *et al.*, 2002b; Biester *et al.*, 2002, 2007; Yang and Rose, 2003; Paulson and Norton, 2008). A growing number of these records indicates an approximately threefold increase (2× to 4×) in Hg deposition since pre-industrial times in both Northern and Southern Hemispheres (Lindberg *et al.*, 2007).

In the LV pond concentrations of Hg vary between 65.2 and 97.3 µg/g (average 78.2 µg/g) in the upper 20 cm of the core, and between 12.7 and 39.8 µg/g (average 23.8 µg/g) in the 20–72 cm interval (Figure 4). Such a strong increase of Hg concentrations in the 'modern' sediments cannot be accounted for by natural sources or processes. Because of the remote location of the archipelago, and in the absence of local pollution sources, we suggest that long-distance atmospheric transport and deposition are the main mechanisms responsible for the increase in Hg concentrations.

### Lead

The downcore profile of Pb, with increasing concentrations in the 'modern' sediments, mirrored by changes in Pb isotopic composition, is also strongly suggestive of the presence of long-range anthropogenic sources.



**Figure 5** Pb concentrations (µg/g) and Pb isotopic ratios ( $^{206}\text{Pb}/^{207}\text{Pb}$  and  $^{208}\text{Pb}/^{206}\text{Pb}$ ) versus depth

The  $^{206}\text{Pb}/^{207}\text{Pb}$  and  $^{208}\text{Pb}/^{206}\text{Pb}$  ratios present fairly constant baseline values in the depth range 50–68 cm (mean values are 1.240 and 2.029, respectively). From 36–38 cm to the 22–24 cm depth, the  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio declines slightly down to 1.234, and the  $^{208}\text{Pb}/^{206}\text{Pb}$  ratio increases to 2.034. From 22–24 cm depth towards the surface the  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio declines rapid and consistently, mirroring the increasing  $^{208}\text{Pb}/^{206}\text{Pb}$  ratios. The maximum and minimum values for these ratios were observed for the surface sample (2–4 cm): 1.180 and 2.083 (Figure 5).

Taking the  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio, the approximately constant values for the isotopic ratios found in the basal pond sediments (1.239–1.241) are very close to those of the nepheline-basalts (1.242–1.243), slightly above those of trachytes (1.236) and slightly below those of phonolites (1.251–1.256) and basanites (1.241–1.250). This means that this Pb is predominantly lithogenic, derived basically from the catchment rock (nepheline-basalt), but with possible minor contribution of other lithologies found in the island. Saharan dust, with a less radiogenic  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio, in the range of 1.174–1.199 (Alleman *et al.*, 2001), cannot be excluded as an additional minor source of natural Pb.

From 36 to 38 cm depth up, and particularly from 22 to 24 cm up, the simultaneous increase in Pb contents and the evolution of the isotopic compositions suggest an increasing contribution to the sediment Pb burden of one or more additional sources of Pb with a less radiogenic isotopic signature, probably of anthropogenic origin (Figure 5).

### Quantifying lithogenic and anthropogenic lead

Mass balance calculations using conservative elements allow estimation of the anthropogenic component of lead from the total lead content of sediments. Ti, Zr and Sc, the most conservative elements during chemical weathering, and generally strongly correlated between them, could be used interchangeably for normalization of Pb concentrations. Ti was chosen for the quantification of lithogenic and anthropogenic Pb in the LV sediments because Zr and Sc were not measured in the uppermost sample analysed (2–4 cm). It should be emphasized that use of Sc or Zr would not significantly affect the results and interpretation we arrived at.

Assuming that the concentration of Pb in the deepest samples (50–68 cm) represents the lithogenic background, it is possible to estimate the lithogenic Pb throughout the core as follows:

$$[\text{Pb}]_{\text{lithogenic}} = [\text{TiO}_2]_{\text{sample}} \times [\text{Pb}/\text{TiO}_2]_{\text{background}} \quad (2)$$

where  $[\text{Pb}/\text{TiO}_2]_{\text{background}}$  is taken from the average composition of the deepest sediments (50–68 cm):  $9.23 \mu\text{g/g}/5.59\% = 1.651 \mu\text{g/g}/\%$ .

Once the lithogenic component (background) has been estimated, the anthropogenic Pb is calculated by subtracting it from the total Pb:

**Table 2** Total Pb ( $\mu\text{g/g}$ ), Pb isotopic ratios, calculated Pb lithogenic and Pb anthropogenic ( $\mu\text{g/g}$ ), and calculated isotopic ratios of Pb anthropogenic

Depth cm	Total Pb	LV sediments				Anthropogenic Pb	
		$^{206}\text{Pb}/^{207}\text{Pb}$	$^{208}\text{Pb}/^{206}\text{Pb}$	Pb lithog.	Pb anthrop.	$^{206}\text{Pb}/^{207}\text{Pb}$	$^{208}\text{Pb}/^{206}\text{Pb}$
2–4	17.278	1.180	2.083	5.06	12.22	1.155	2.105
8–10	13.300	1.198	2.065	7.17	6.13	1.149	2.107
10–12	13.280	1.209	2.056	7.85	5.43	1.164	2.095
12–14	13.094	1.209	2.056	7.95	5.14	1.161	2.099
14–16	11.727	1.220	2.044	8.30	3.43	1.172	2.080
22–24	9.806	1.234	2.034	8.96	0.85	1.171	2.082
26–28	9.430	1.237	2.033	9.01	0.42	nd	nd
30–32	9.260	1.238	2.030	9.17	0.09	nd	nd
36–38	8.977	1.238	2.030	9.39	-0.41	nd	nd
42–44	nd	nd	nd	nd	nd	nd	nd
46–48	nd	nd	nd	nd	nd	nd	nd
50–52	9.055	1.240	2.028	9.26	-0.20	nd	nd
54–56	nd	nd	nd	nd	nd	nd	nd
58–60	9.349	1.239	2.031	9.34	0.01	nd	nd
62–64	nd	nd	nd	nd	nd	nd	nd
66–68	9.232	1.241	2.028	9.42	-0.19	nd	nd

$$[\text{Pb}]_{\text{anthropogenic}} = [\text{Pb}]_{\text{total}} - [\text{Pb}]_{\text{lithogenic}} \quad (3)$$

Table 2 displays the calculated contents and percentages of lithogenic and anthropogenic Pb. The anthropogenic component of Pb is virtually absent in the lower section of the core ('pre-industrial' sediments), and is present in 'modern sediments', showing increasing values from 13% in the 22–24 cm sample to 71% in the 2–4 cm sample.

The isotopic signatures of the anthropogenic Pb, rather than those of the total Pb, are the values needed in order to constrain Pb sources more accurately (Graney *et al.*, 1995). Assuming that the isotopic signature of lithogenic Pb remained constant throughout the core, the isotopic composition of anthropogenic Pb can be modelled for each sediment sample (0–24 cm) by combining mass and isotopic balance (Renberg *et al.*, 2002). Using the  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio as an example:

$$\frac{(^{206}\text{Pb}/^{207}\text{Pb})_{\text{anthropogenic}}}{(^{206}\text{Pb}/^{207}\text{Pb})_{\text{sample}}} = \frac{F1}{F2} \quad (4)$$

where F1 and F2 are, respectively, the percentages of anthropogenic and lithogenic Pb in the sediments, and the lithogenic isotopic ratios are the baseline values for the basal (50–68 cm) sediments (see above). The results obtained for the anthropogenic component of Pb are much less radiogenic than those of the lithogenic Pb (Table 2).

### Anthropogenic sources of lead

The sources for the anthropogenic Pb in the LV sediments might be related to emissions originating from the Southern Hemisphere, since the interhemispheric advection of industrial lead aerosols seems to be negligible (Flegal *et al.*, 1993; Bollhöffer and Rosman, 2000). Unfortunately, very few Pb isotope data are presently available on potential sources. These include the Pb isotopic composition of marine aerosols and bulk deposition in the South Atlantic Ocean between 0°S and 30°S latitude (Alleman *et al.*, 2001), continental aerosols collected in rural and inner-city environments throughout the hemisphere (Bollhöffer and Rosman, 2000), Antarctic snow, which records Pb anthropogenic emissions in the Southern Hemisphere (Planchon *et al.*, 2003), and some measures of fuel samples used South American cities (Gioia *et al.*, 2006).

Figure 6 displays the Pb isotopic compositions of the calculated anthropogenic component of LV sediments (this study) compared

with representative data from the above-mentioned sources for the Southern Hemisphere. Also shown in the figure are the isotopic data for the LV sediments (this study) and the country rocks.

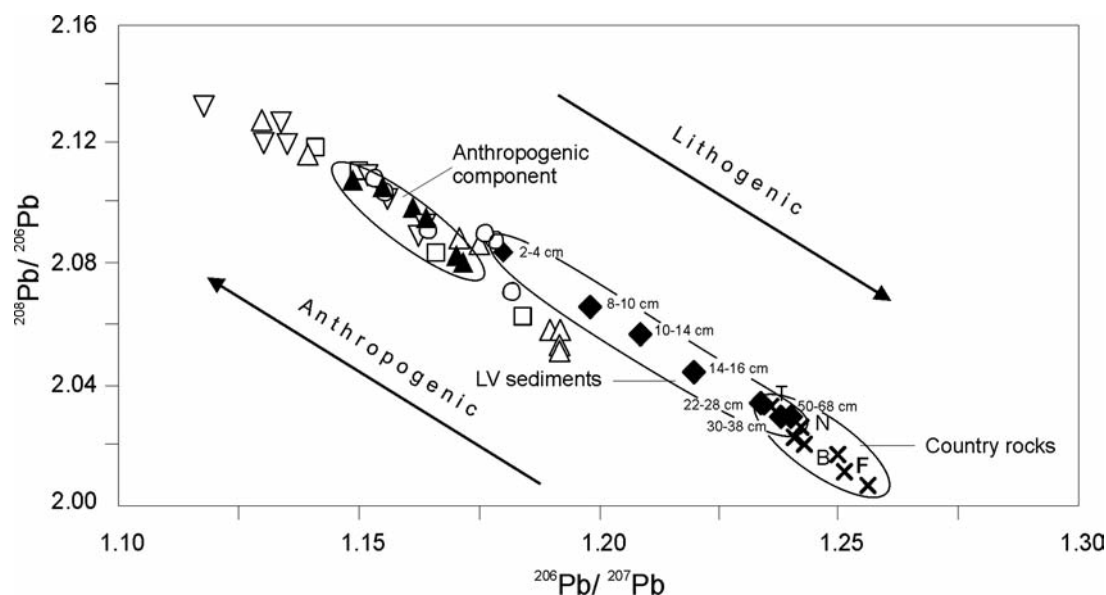
Contrasting with the Pb isotopic composition of the LV 'pre-industrial' sediments, which is close to the field defined by the volcanic rocks found in the island, the isotopic composition of anthropogenic Pb falls well within the field of global emissions in the Southern Hemisphere. Although the data are not sufficient to identify the specific contaminant sources, there is a general consensus that atmospheric lead in the South Atlantic mainly originates from human activities such as industrial processes and the combustion of alkyl-leaded petroleum-derived fuels (Nriagu *et al.*, 1996). Thus, superimposed on a natural Pb component, an unequivocal anthropogenic component derived predominantly from atmospheric long-range emissions can be recognized in the LV 'modern' sediments deposited in the last decennials ( $< 90 \pm 50$  yr). A rather local source, such as fuel combustion, which has increased in the island with the increasing population since World War II, could have contributed to the anthropogenic Pb signal in the 'modern' sediments as well.

The isotopic signature of *P. Stratiotes* ( $^{206}\text{Pb}/^{207}\text{Pb} = 1.170\text{--}1.180$ , and  $^{208}\text{Pb}/^{206}\text{Pb} = 2.080\text{--}2.090$ ), which plots in the field of anthropogenic sources of Pb, shows that the floating plant also records the Pb contamination of the pond.

### Summary and conclusions

Chemostratigraphy of sediments from the LV pond allowed the distinction of two different environments, corresponding to the upper (0–20 cm) and the lower (20–72 cm) section of the core. Based on  $^{14}\text{C}$  dating, the upper section can be considered younger than 90 years, while the lower section comprises the interval from 90 to 700 yr BP. In the older environment, 'pre-industrial' sediments consist essentially of products from the incipient weathering of the surrounding volcanic rocks (mineral fraction). In the 'modern' sediments, the mineral fraction is found mixed with organic matter (organic fraction) which is increasingly abundant toward the top of the section.

The mineral fraction is mineralogically and chemically homogeneous throughout the core. Its composition, marked by the presence of a primary readily weatherable mineral such as clinopyroxene and a neoformed clay mineral such as smectite,



**Figure 6**  $^{206}\text{Pb}/^{207}\text{Pb}$  versus  $^{208}\text{Pb}/^{206}\text{Pb}$  diagram showing the Pb-isotopic composition of: crosses, country rocks: T, trachyte; P, phonolite; N, nepheline-basalts; B, basanites (averages calculated from Gerlach *et al.*, 1987 and Lopes, 2002); solid diamonds, LV sediments (measured); solid triangles, Pb anthropogenic component of the sediments (estimated using mass-balance calculations); open circles, marine aerosols and bulk deposition in the South Atlantic Ocean between  $0^{\circ}\text{S}$  and  $30^{\circ}\text{S}$  latitude (Alleman *et al.*, 2001); open squares, continental aerosols collected in rural and inner city environments throughout the southern hemisphere (Bollhöffer and Rosman, 2000); inverted open triangles, Antarctic snow, which records Pb anthropogenic emissions in the Southern Hemisphere (Planchon *et al.*, 2003); and open triangles, fuel samples used in South American cities (Gioia *et al.*, 2006)

points to a rather incipient degree of bedrock–water interaction in the source area. This is also shown by a moderate enrichment of Si, Al, Fe and Ti, and a rather incomplete depletion of the most soluble elements such as Ca, Mg, Na, K, Mn and Sr in the sediments as compared with the catchment bedrock.

The organic fraction is mainly derived from the accumulation of *P. stratiotes* debris, as suggested by the similar  $\delta^{13}\text{C}$  signature of the most TOC-enriched samples (*c.*  $-27\%$ ) and the aquatic plant ( $-28.5\%$ ). The concentration of organic matter restricted to the upper section of the core can be explained by the fact that the colonization of the pond by *P. stratiotes* occurred quite recently, since the plant was introduced in the island in the second half of the twentieth century.

The vertical distribution of most trace elements – Sr, Sc, Zr, Zn, Cu, Hf, Ga, Co, Y, Ni, Nb, Cr and REE – shows approximately constant values throughout the core, meaning that there are no important changes in the mineral matter composition of the sediments with depth. On the other hand, Br, Se, Pb and Hg are strongly concentrated in the surface (0–20 cm). Enrichment of Br and Se in the TOC-enriched layers is likely related to their binding affinity for organic matter, but this process cannot explain the distributional pattern for Hg and Pb. In the case of Hg, the coherent temporal pattern and the magnitude of its recent enrichment in lakes in remote areas of Europe and North America point to long-range atmospheric transport and deposition as the main mechanism of Hg accumulation. This must be the case for the recent Hg accumulation observed in LV pond, which is situated in a pristine environment, protected from possible local pollution sources. Lead, like mercury, can also be carried into lakes by long-range atmospheric transport. The Pb isotopic record preserved in the sediments of LV pond indicated that the Pb found in the lake is derived both from catchment rocks (lithogenic Pb) and from atmospheric emissions (anthropogenic Pb). A small contribution of aeolian inputs of Saharan dust to the overall Pb burden of the sediments is not excluded. The calculated contributions of lithogenic

and anthropogenic Pb in each sample of sedimentary column demonstrated that, while prior to the deposition of the ‘modern’ sediments all Pb was lithogenic, in recent decades increasing amounts of anthropogenic Pb have been added to the pond. The isotopic signature of this Pb is in general agreement with those of airborne particles derived from burning of leaded gasoline and industrial emissions in the Southern Hemisphere.

Finally, it is important to note that the increase in Pb and Hg in sediments occurred well before the occupation of the islands during World War II, suggesting a significant increase of these two atmospheric pollutants in the Southern Hemisphere since the beginning of the twentieth century.

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