Science of the Total Environment 553 (2016) 541–550

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Historical records of mercury in southern latitudes over 1600 years: Lake Futalaufquen, Northern Patagonia

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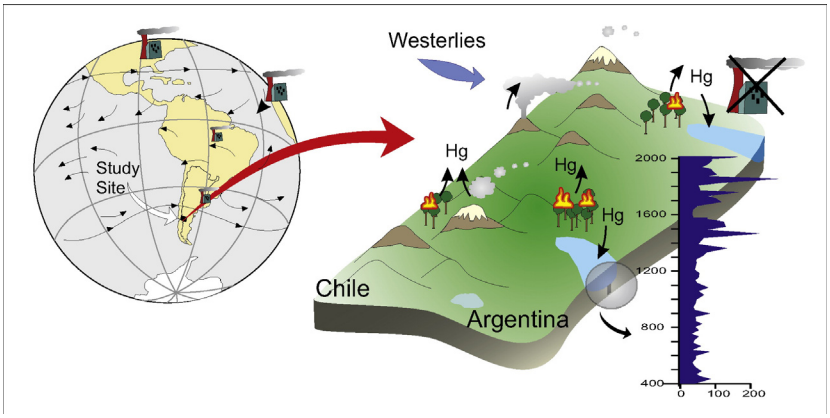
HIGHLIGHTS

- Mercury is a natural element globally distributed affecting remote areas.
- A short core from L. Futalaufquen, Patagonia, was analyzed for Hg time evolution.
- High natural baselines and relative low post-industrial increase were measured.
- Natural/anthropogenic fires and volcanism were the main sources of Hg peaks.
- Lakes from southern latitudes provide valuable records for atmospheric processes.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 30 October 2015
Received in revised form 16 February 2016
Accepted 17 February 2016
Available online xxxx

Editor: D. Barcelo

Keywords:
Global pollutant
Lakes
Atmospheric deposition
Fires
Volcanism
Argentina

ABSTRACT

Mercury is released to the environment from natural and anthropogenic sources, and through atmospheric transport is distributed globally. Lake Futalaufquen (42.8°S) is an oligotrophic lake located in Los Alerces National Park (Northern Patagonia), providing a remote and unpolluted study system. A lacustrine sedimentary sequence revealed 1600 years of Hg deposition, identifying natural baselines and marked peaks not correlated with long-range atmospheric transport. Organic matter and catchment erosion were discarded as Hg drivers. Natural background, pre-1300 CE Hg concentrations, ranged between 27 and 47 ng g^{-1} (accumulation rates from 8 to 15 μg m^{-2} y^{-1}). From 1300 CE on, the Hg background profile did not follow the generally increasing Hg pattern observed in both Southern and Northern Hemisphere since pre-industrial times. It was not until the last century that a 1.6-fold increase is observed in the Hg accumulation rate, considered among the lowest increments in southern South America. Noteworthy local/regional sources of Hg for this area, along with global transport, are forest fires and volcanic activity. Between approx. 1340 and 1510 CE, sharp increase in Hg concentration and accumulation rate (up to 204 ng g^{-1} and 51 μg m^{-2} y^{-1}, respectively) were clearly associated with extended fire episodes. Furthermore, high Hg peaks during the last 300 years were associated with volcanic eruptions in

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http://dx.doi.org/10.1016/j.scitotenv.2016.02.114

northernmost Patagonia together with fairly irregular fire episodes, caused by anthropogenic burning by settling population in the Andes.

1. Introduction

Mercury (Hg) is a heavy metal dispersed in the atmosphere by natural processes (volcanoes, geothermal vents, forest fires, geologically Hg-enriched soil), as well as by human activities (mining, coal-fired power plants, landfills, sewage sludge treatment plants) (Bagnato et al., 2014; Driscoll et al., 2013; Lindqvist et al., 1991; Nriagu, 1989; Schroeder and Munthe, 1998). As global pollutant, Hg travels long distances from sources via atmospheric transport, impacting terrestrial, lacustrine, and marine ecosystems (Fitzgerald et al., 1998; Pirrone and Mahaffey, 2005), even in remote regions like the Arctic and Antarctic (Durnford et al., 2010; Sun et al., 2006).

Mercury deposition from the atmosphere increase the global pool of Hg in surface sinks. This depends on deposition mechanisms and meteorological conditions. After deposition, anthropogenic or natural processes result in sequestration or emission back to the atmosphere. Continental water bodies and aquatic sediments are reservoirs of deposited Hg, recording Hg impact in the watersheds (Driscoll et al., 2013; Sprovieri et al., 2010). Thereupon, lake and peat bog sediments can be used as archives of Hg accumulation, integrating local, regional, and global environmental signals (Fitzgerald et al., 1998). Mercury determinations in lake, peat bog, and ice sequences have shown significant changes in prehistoric deposition rates due to climate forcing, i.e. changes in precipitation, air circulation patterns and temperature regimens, extended fires, and volcanic activity (Hermanns and Biester, 2013a; Lacerda et al., 1999; Martínez-Cortizas et al., 1999; Roos-Barraclough et al., 2002). In historical times, increase in Hg deposition with respect to prehistoric rates has been reported associated with anthropogenic activities (Allan et al., 2013; Muir et al., 2009; Perry et al., 2005; among others), with a significant change in the temporal trend due to industrialization (Fitzgerald et al., 1998; Lacerda et al., 1999).

Furthermore, aquatic systems are considered highly sensitive to Hg (Grigal, 2002). In Northern Patagonia, where no relevant Hg releases associated with industrial activities or mining were identified, high Hg concentrations were reported during the last decade. Lichens and mussels were studied as air and water bioindicators; the Hg concentrations measured were compatible with those at locations exposed to moderate contamination (Ribeiro Guevara et al., 2004a, 2004b). High Hg concentrations were measured in lacustrine biota, notably high in plankton, reaching 240 μg g^{-1} dry weight (DW) in Lake Moreno and Lake Nahuel Huapi (Rizzo et al., 2014), and in fish muscle, up to 2–3 μg g^{-1} DW in different lakes including Lake Futalaufquen (Rizzo et al., 2011). Also, high Hg concentrations, up to 3 μg g^{-1}, were measured in Northern Patagonia lake sediments, far above the values determined in non-contaminated fresh water sediments, together with very high Hg fluxes corresponding to 14th and 18-19th century's deposition (Ribeiro Guevara et al., 2010).

Mercury records in lacustrine sedimentary sequences can be associated with the impact of Hg sources in the watershed, both natural and anthropic at local, regional, or global scale. The study of Hg concentration profiles in dated sedimentary sequences provides valuable information on the Hg sources to aquatic ecosystems, and on environmental events and processes that are associated with Hg concentration variations along the profile. In the present work, Hg concentrations were studied in a 1600 years sedimentary sequence extracted from Lake Futalaufquen, close to the Southern Volcanic Zone, located in a remote, protected area with low anthropogenic pressure but high Hg levels in biota. Regional volcanic activity is tested as a Hg source, as well as fires and global transport.

2. Study site

Lake Futalaufquen (42°49′ S, 71°43′ W) is an oligotrophic system, with 168 m max. depth, located in Los Alerces National Park (LANP) at 518 m above sea level (Fig. 1), in the Northern Patagonia Andean Range (40°15′ to 41°25′ S, 71° to 72°45′ W). Lake Futalaufquen extends over 44.6 km^2 of old fluvial valleys deepened by glacial erosion, collecting waters from a 2920 km^2 catchment area characterized by high mountains and several lakes. The main tributary is the river Arrayanes, which drains lakes Rivadavia and Menéndez (Fig. 1). Vegetation is dominated by pure or mixed stands of conifer (*Austrocedrus chilensis*), evergreen (*Nothofagus dombeyi*), and deciduous species (*Nothofagus pumilio* and *Nothofagus antarctica*). Shrub lands dominate between 1000 and 1200 m a.s.l. (Pizzolón, 1995; Vila and Borrelli, 2011).

The Andean Range is located in the Southern Volcanic Zone (SVZ, 33°–46° S) of the Andes, including several active volcanic systems (Stern, 2004). Volcanoes close to the study zone are Huequi, Chaitén, Michinmahuida, and Corcovado (Fig. 1), with partial records available on historical volcanic activity (González-Ferrán, 1995; Petit-Breuilh Sepúlveda, 2004). As it was observed during the last explosive eruption of volcano Chaitén in 2008, volcanic events in the nearby SVZ have frequently affected the Patagonian territory, and the study site in particular (Alfano et al., 2011; Daga et al., 2016).

Climate is cool–temperate humid, with austral fall–winter precipitation, and 8 °C mean annual temperature. The Andes mountains position generate a strong west–east gradient of precipitation across the region, with more than 2000 mm y^{-1} at the eastern base of the Andes decreasing exponentially to under 200 mm y^{-1} on the steppe (Paruelo et al., 1998; Roig and Villalba, 2008).

LANP is a 2600 km^2 protected area, where anthropogenic activity is limited due to low population density and seasonal tourism. Thus there is little anthropic disturbance of the lacustrine sedimentary record. The first inhabitants in the area were settled around 3000 years ago in the river Desaguadero valley. They were hunter–gatherer (http://www.parkswatch.org/parkprofile.php). Nowadays about 2000 people live in the basin, with significant livestock activity in the headwaters. Seasonal tourism is important in the Park (Pizzolón, 1995).

3. Materials and methods

3.1. Coring and sampling

A short sediment core of 79 cm length (5.7 cm diameter) was extracted from Lake Futalaufquen (Fig. 1) with a messenger-activated gravity type corer. The sampling site (42°49′ S, 71°43′ W) was selected in a flat area of the lake bottom, determined after echo sounder survey, at 90 m depth. The sediment core was opened and sectioned into 1 cm slices after visual inspection, or following natural boundaries. Each sediment segment was immediately frozen and then freeze-dried until constant weight was achieved. Tephra layers were visually identified by the colour and the grain size, and confirmed after binocular magnifying glass examination. Five tephra layers were identified in the sedimentary sequence (Daga et al., 2016) (Fig. 1). Physical properties such as water content and dry bulk density (DD) were calculated from weight difference between wet and freeze-dried subsamples (Daga et al., 2016).

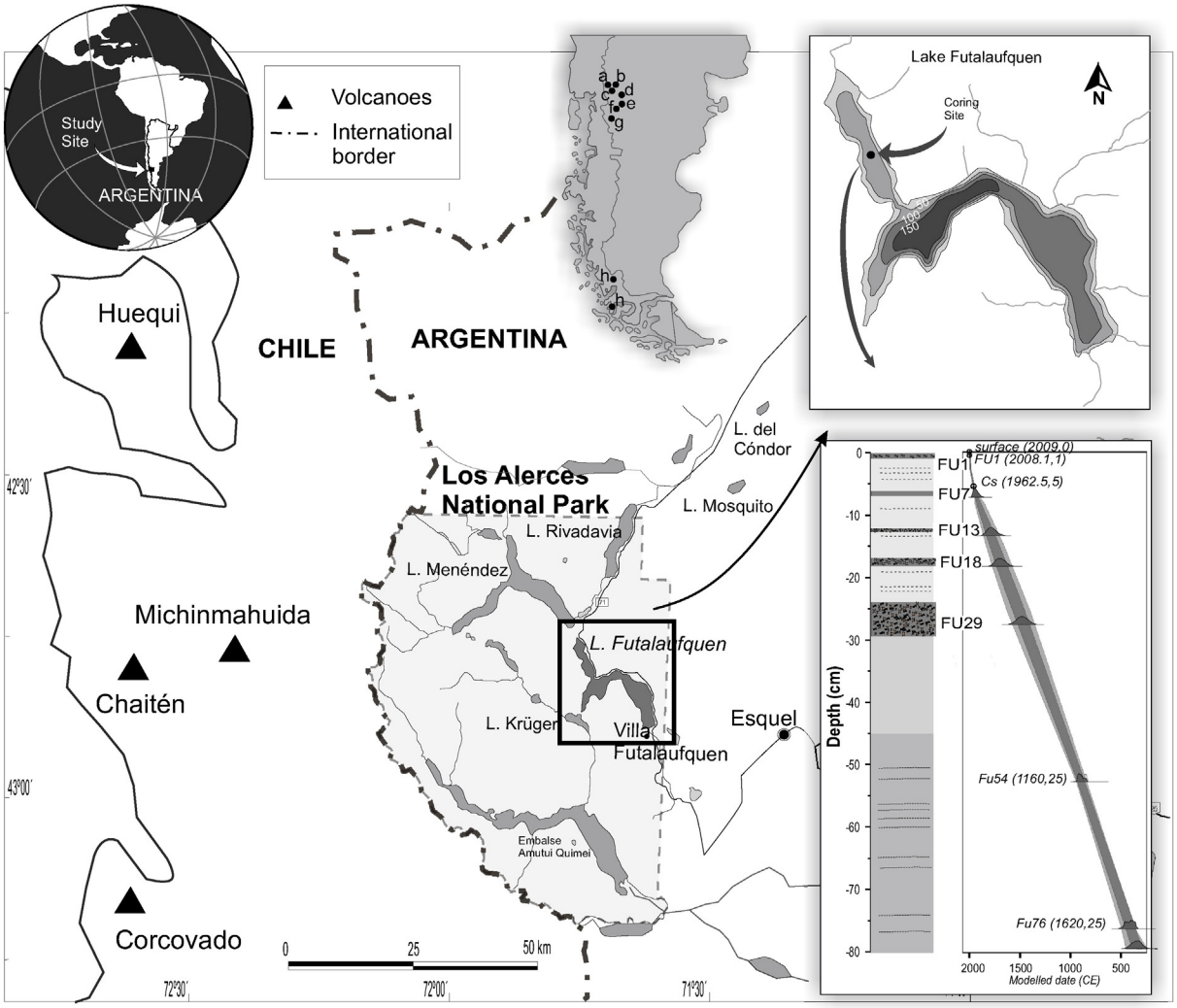

Fig. 1. Location of Lake Futalaufquen in Los Alerces National Park (LANP), Argentina, and closer volcanoes (filled triangles). Coring site and the sediment profile are shown. FU1, FU7, FU13, FU18, and FU29 represent tephra layers. A synthesis of the resultant age–depth model is presented right to the core profile: surface (2009,0) = top of the core (age of extraction, depth); FU1 (2008.1,1) = tephra FU1 used in the age model (age, uncertainty, depth); Cs (1962.5,5) = ^{137}Cs dating used in the age model (age, uncertainty, depth); FU7 to FU29 showed the age probability distribution calculated with age model; Fu54 and Fu76 represent the uncalibrated AMS ^{14}C ages (UGAMS 8488 and UGAMS 8489, respectively) with uncertainties (years BP, 1σ) (modified from Daga et al., 2016). For reference to letters (a to h) in southern South America (upper centre) refers to Fig. 4.

3.2. Chronology

The age–depth model was based on ^{137}Cs radionuclide measurement in upper layers, and two AMS radiocarbon dates (University of Georgia, USA) in deeper layers, calibrated and integrated using OxCal 4.2 software (Bronk Ramsey, 2009). The ^{137}Cs peak identified allowed to estimate a sedimentation rate of 30.2 ± 3.5 mg cm^{-2} y^{-1} in upper layers (7–0 cm depth), in agreement with AMS ^{14}C dating in deep layers (30.8 ± 4.2 mg cm^{-2} y^{-1} for 76–54 cm depth), suggesting a relatively constant sedimentation rate since ~400 CE. Fig. 1 includes the previously obtained age-depth model scheme of the sedimentary sequence (Daga et al., 2016).

3.3. Geochemistry

The determination of loss on ignition (LOI) was carried out in 0.5 g samples at 550 °C for 4 h after Heiri et al. (2001). LOI_{550} is considered as an indicator of organic matter (OM) content (Smol, 2008). The stable isotope composition of sedimentary organic carbon (δ^{13}C) and nitrogen (δ^{15}N) were analyzed on 10–20 mg of freeze-dried samples using a Europa 20–20 (Europa Scientific Ltd., Crewe, UK) continuous-flow stable isotope analyser with ANCA–SL preparation module for solid and liquid samples (Jožef Stefan Institute, Slovenia). All measurements were performed in triplicates and results were accepted if the standard deviation of the sample was <0.2‰ for both elements. If the standard deviation was larger, measurements were repeated until the obtained deviations were within the required limits. Accuracy of the results was controlled using certified reference materials (USGS 25, USGS 26 and USGS 40 for nitrogen and IAEA-CH6, IAEA-CH7 and USGS 24 for carbon) which were distributed randomly within each batch and was better than 0.2‰.

Total Hg (THg) concentrations in bulk sediments were measured with a Direct Mercury Analyser (Milestone DMA–80, Jožef Stefan Institute, Slovenia), in duplicate samples of 20–40 mg of freeze-dried, homogenized material, from each 1-cm layer of the sedimentary sequence. Analytical quality control was performed in this case by analyzing CRM BCR 280R (estuarine sediment; 0.128 ± 0.017 μg g^{-1} Hg certified concentration) and BCR 280R (lake sediment; 1.46 ± 0.20 μg g^{-1} Hg certified concentration). Also, standard solutions measurements were included every 5 sediment samples, to avoid calibration bias. The reproducibility of the detection system is checked periodically by analyzing different matrix sample sets. Duplicate variability with respect to mean value averaged 2.5%. When duplicate variation was higher than 5%, a third replicate was performed.

Major and trace elements Al, Fe, Mn, Rb, and Zr, used for comparison with Hg profile, were measured by Instrumental Neutron Activation Analysis (INAA). Sediment samples (approx. 100 mg) were irradiated in the RA–6 nuclear reactor (Bariloche, Argentina) in plastic vials by two irradiations; a short term one (1–2 min) to determine Al and Mn, and a long term (10*h*) to determine Fe, Rb, and Zr. Five gamma-ray spectra were collected in a coaxial HPGe detector. The absolute parametric method was used to determine the elemental concentrations. Analytical errors depend on the nuclear parameters of each element, irradiation conditions and composition of the sample varying between 4 and 10%. Certified Reference Materials NIST Buffalo River Sediment and IAEA SL1 Lake Sediment were analyzed together with the samples for analytical quality control.

4. Results

4.1. Elemental profiles

The Hg concentration profile is shown in Fig. 2, together with the OM indicator and the $\delta^{13}C$ values, dry bulk density, and abundances of Al, Fe, Mn, Rb, and Zr. These parameters were measured for comparison with Hg, in order to find some correlation explaining Hg distribution. In agreement with a stable sedimentation rate throughout the sequence, these elements do not show strong changes along the profile with the exception of the peaks correlated with tephra layers (Fig. 2). Slight variations in the measured parameters were observed also around 60 cm depth (Fig. 2), possibly responding to changes in environmental conditions (i.e., climate, bioproductivity, catchment processes) not reflected, however, in the Hg profile.

Mercury and OM profiles showed clear discrepancies and marked Hg peaks are not associated with OM (Fig. 2). For a better evaluation of this, the period of marked peaks (post-1300 CE) was separated from the relatively stable Hg levels (pre-1300 CE), showing no significant correlations ($r^2 = 0.06$; $p = 0.1$ and $r^2 = 0.04$; $p = 0.12$, respectively) between both variables in any case (Fig. 3a). On the other hand, $\delta^{13}C$ and $\delta^{15}N$ values of bulk organic matter scatter in a relatively narrow range of values (−27.6 to −25.8‰, and 0.89–2.7‰, respectively). Comparing these $\delta^{13}C$ (Fig. 2) and $\delta^{15}N$ values (not presented) whit Hg concentrations, no significant correlations were observed either ($r^2 = 0.0003$; $p = 0.31$ and $r^2 = 0.01$; $p = 0.16$, respectively).

Hg concentrations were normalized to lithophile elements Al, Rb, and Zr as tracers of allochthonous detrital mineral material (Boës et al., 2011). Discarding the values of these elements clearly associated with tephra layers, the strong increment of Hg relative to such elements remains clear (Fig. 3b). All the lithophile elements considered showed the absence of correlation with Hg. The Hg/OM and Hg/Al normalizations revealed conspicuous peaks of Hg content, not related to the inputs of terrestrial detritus or autochthonous organic matter (Fig. 3c). On the other hand, Hg concentrations showed no correlation with Fe ($r^2 = -0.01$, $p > 0.75$) and Mn ($r^2 = -0.01$, $p > 0.94$), as can be also observed in the differing elemental profiles (Fig. 2).

4.2. Hg concentrations and accumulation rates

Mercury accumulation rates (Hg_{AR}) were calculated for each layer (each 1-cm sediment segment) based on the Hg concentration and the deposition time estimated for each layer by the age-depth model

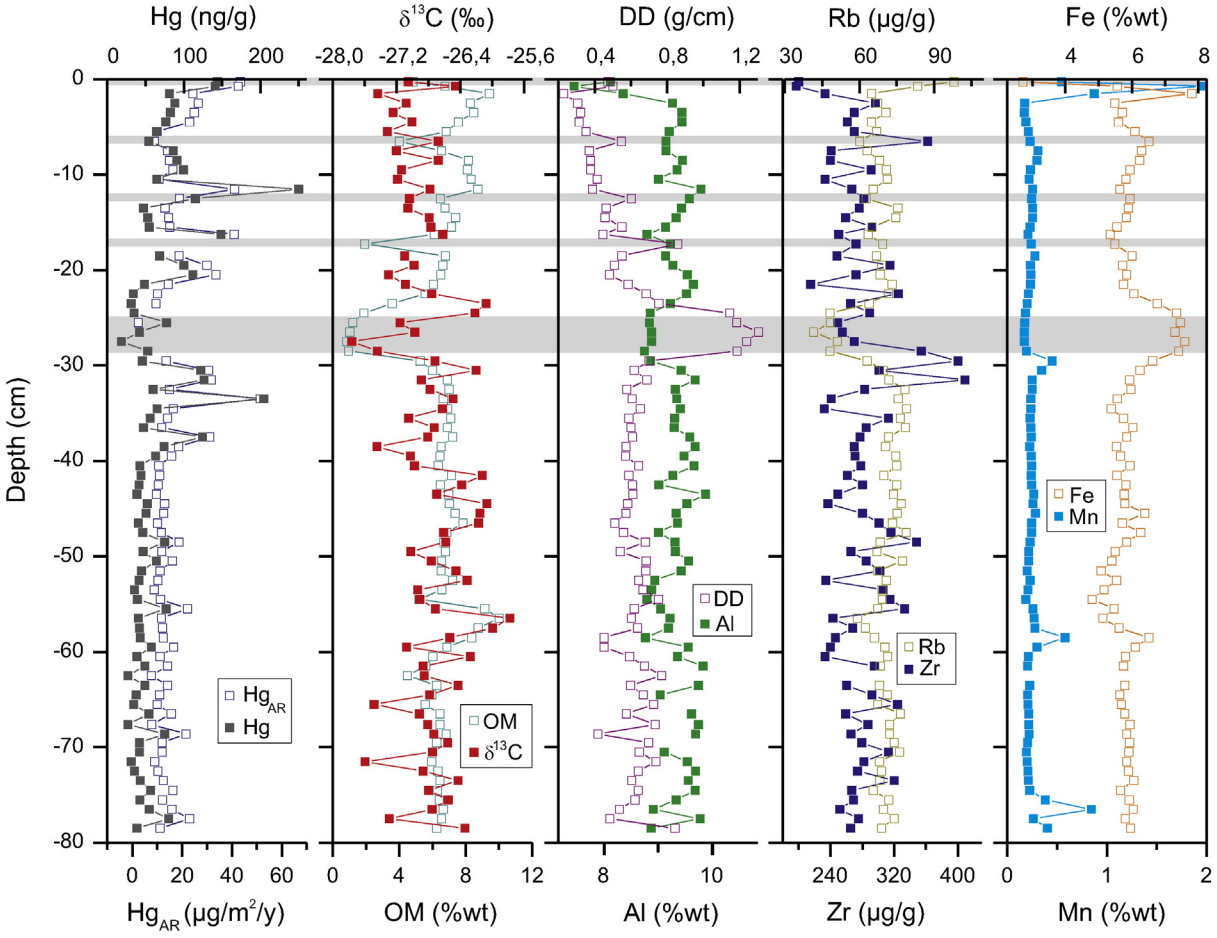

Fig. 2. Elemental profiles from Lake Futalaufquen. Hg: mercury concentration; Hg_{AR}: mercury accumulation rates; OM: organic matter and $\delta^{13}C$; DD: dry bulk density and Al, Rb and Zr, and Fe and Mn. Gray lines represent tephra layers.

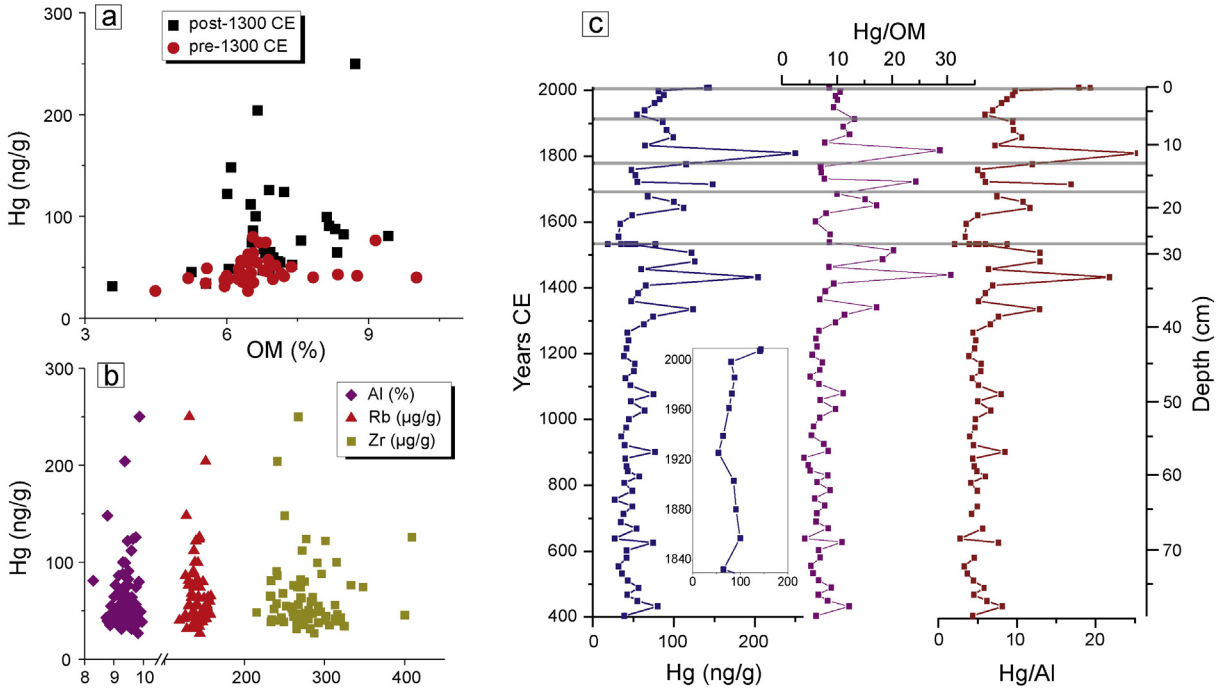

Fig. 3. (a) Hg versus OM, showing post- and pre-1300 CE separation, without significant correlation (see text); (b) Hg versus lithophile elements Al, Rb, and Zr, with no significant correlation observed ($r^2 = 0.001$, $p = 0.30$; $r^2 = -0.005$, $p = 0.42$; and $r^2 = -0.01$, $p = 0.78$, respectively); (b) Profiles of elemental Hg, Hg/OM, and Hg/Al with time.

(Daga et al., 2016), obtaining the Hg mass deposited per unit area per year for each layer (μg m^{-2} y^{-1}) (Fig. 2).

Mercury concentrations vary throughout the profile between 18 ng g^{-1} and 250 ng g^{-1}, with the Hg accumulation rates varying between 2 μg m^{-2} y^{-1} and 51 μg m^{-2} y^{-1} (Fig. 2). The lower Hg concentrations were measured from the sequence bottom to 40 cm depth (ca. 400–1300 CE), showing background or baseline concentrations for Lake Futalaufquen between 27 and 47 ng g^{-1}, and accumulation rates from 8 to 15 μg m^{-2} y^{-1}, with frequent peaks reaching 80 ng g^{-1}, corresponding the Hg_{AR} up to 23 μg m^{-2} y^{-1} (Fig. 2).

From 40 cm depth to the top of the sequence (ca. 1300 CE to present) several peaks are identified superimposed upon the background (Fig. 2). Three important peaks are located between 38 and 30 cm depth (ca. 1340–1510 CE), with concentrations of 124, 204, and 126 ng g^{-1}, and accumulation rates of 31, 51, and 32 μg m^{-2} y^{-1}, respectively, corresponding the 204 ng g^{-1} peak as the highest Hg_{AR} throughout the sequence. Other peaks are observed at 21 cm (ca. 1640 CE; 112 ng g^{-1} and 34 μg m^{-2} y^{-1}), and at 16 cm depth (ca. 1710 CE; 148 ng g^{-1} and 41 μg m^{-2} y^{-1}), with the highest Hg concentration of 250 ng g^{-1} at 11 cm depth (ca.1810 CE; 41 μg m^{-2} y^{-1} Hg_{AR}). At the core top another Hg peak is identified (143 ng g^{-1} and 43 μg m^{-2} y^{-1}). The lowest Hg concentration was measured at 28 cm depth (18 ng g^{-1}), the base of the thickest tephra layer. Although Hg concentrations showed a decreasing trend after each peak (from bottom to top), the background values did not reach the previous concentrations that is affected by a new peak. This looks like an increasing background since 1500 CE, but this was not supposed in the present work due to the decreasing tendency observed between peaks. On the contrary, background Hg concentrations in upper layers are higher than those in deep sediments and showed an increasing trend (from 64 to 81 ng g^{-1}), as well as the Hg accumulation rate seems to increase since mid-20th century from 10 to 26 μg m^{-2} y^{-1}, excluding the maximum in the top most centimetres possibly associated to the recent tephra from the Chaitén 2008 event (Fig. 2).

5. Discussion

Comparisons carried out between Hg and different parameters do not lead to certain associations regulating the distribution of Hg in the lake system. Organic matter is important controlling the dynamic of Hg in lake sediments (Kainz and Lucotte, 2006; Sanei and Goodarzi, 2006; Teisserenc et al., 2011). Measured $\delta^{13}C$ and $\delta^{15}N$ values are in the range typical of the autochtonous organic matter in oligotrophic lakes worldwide (Gu et al., 1996; Schelske and Hodell, 1991; Vreča and Muri, 2010), as well as the $\delta^{13}C$ values of C3 plant debris and soil organic matter (O'Leary, 1988; McCallister et al., 2004), which are the main source of organic matter for remote lakes under the forest line. The isotope variations with depth can be attributed to the variable productivity and temporal changes in the origin of detrital input into the lake (Lojen et al., 1997; Vreča and Muri, 2006, 2010). However, the lack of correlation between Hg, OM content, and the $\delta^{13}C$ and $\delta^{15}N$ values of organic matter indicates that Hg inputs are independent on both the bioproductivity of the lake and the soil erosion. Furthermore, the lack of correlation with stable lithophile elements (Fig. 3) confirm the erosion processes from catchment as an unworthy contribution to the sediment Hg content and distribution (Beal et al., 2013; Boës et al., 2011; Fitzgerald et al., 2005; Hermanns and Biester, 2013b; Perry et al., 2005), even in a volcanic region with more than 2000 mm of annual rain. Mercury peaks were not related to the mobility after deposition due to redox gradients either (Fig. 2) (Boyle, 2001; Percival and Outridge, 2013).

The rather stable behaviour of Hg in lake sediments, where peaks have not migrated vertically in response to the post-depositional conditions (Lockhart et al., 2000; Rothenberg et al., 2010; Rydberg et al., 2008) allows for evaluation of the Hg profile as the result of fluctuations of natural background sources and atmospheric deposition. Although the discussion will be focused on the important peaks identified in Lake Futalaufquen, natural background and global anthropogenic influence are considered.

5.1. Natural background and post-industrial Hg levels

The deepest part of the core (79–40 cm depth; ca. 400–1300 CE) shows Hg concentrations that can be defined as background values of Hg deposition previous to the first Hispanic settlements, between 27 and 47 ng g^{-1} (Hg_{AR} from 8 to 15 μg m^{-2} y^{-1}), whereas the upper part (40–0 cm depth; ca. 1300 CE to present), including pre- and post-industrial times, presents several peaks superimposed on an increasing background over the last century.

Background concentrations in Lake Futalaufquen (pre-1300 CE) are relatively stable and comparable to those measured in other lakes from Northern and Southern Patagonia (Table 1, Fig. 4), where backgrounds range between 30 and 200 ng g^{-1} (Hermanns and Biester, 2013a, 2013b; Ribeiro Guevara et al., 2010). In South America, Hg records covering the pre-1300 CE period are scarce, but several works relate ancient Hg periods to extensive gold and silver mining activities from pre-Inca cultures (Cooke and Bindler, 2015; Sun et al., 2006). However, a pre-1300 CE rather stable baseline is observed in this study. Increasing trends were found in the period between 1200 and 1600 CE in Peru (Beal et al., 2013; Cooke et al., 2009), whereas successive peaks are observed for the same time in Lake Futalaufquen, which are better explained by local/regional sources (see Section 5.2). The Hg values in the oldest sediments could be used as natural background levels in this region of the Southern Hemisphere.

In spite of numerous Hg peaks in Lake Futalaufquen after 1300 CE, base levels of both Hg concentrations and accumulation rates in pre-industrial period (approx. 1300–1850 CE) remain at comparable values to those of pre-1300 CE period (Fig. 3c). At the same time, the first signs of anthropogenic activities started to change the baselines in several lakes and peat bogs, both in Northern (Martínez-Cortizas et al., 1999) and Southern Hemisphere (Lacerda et al., 1999). Even though Hg baselines were stable before 1800 CE (excluding the peaks analyzed in Section 5.2), Biester et al. (2002) pointed out the relatively high pre-industrial values considering the smaller landmass in the Southern America, especially in the southernmost regions.

Anthropogenic emissions have clearly increased several folds relative to natural sources during industrial times. In Lake Futalaufquen deposition is observed during 20th century, marked by a ~1.6-fold increase in the Hg accumulation rate since ca. 1940 CE (Fig. 3). A slightly decrease around the 1990's is observed, while the peak recorded in the recent sediments was associated to a tephra layer (Fig. 3; see Section 5.2.2). Even without considering focusing corrections, the increase during the past century observed in our study (1.6, see Table 1) is the smallest compared to other analyzed environments in the austral part of South America, ranging from 1.4 to 10. The increase of Hg from pre-industrial to industrial times due to long-range atmospheric transport, including inter-hemispheric transport (Driscoll et al., 2013; Engstrom and Swain, 1997; Fitzgerald et al., 1998; Lamborg et al., 2002), is not so strong here; actually, it is lower than the model predicted values proposing a 2-to-3 fold increase for southern South America (Selin et al., 2008). At North Patagonia latitudes such increase seems to be smaller, or it is masked by the peaked profile (Fig. 4).

5.2. Mercury peaks

Considering the remote location of Lake Futalaufquen, the most relevant characteristics of Hg profile are the intense peaks recorded during the last 700 years, and other minor peaks pre-1300 CE. The identification of the source of Hg peaks is crucial, since they could be due to local or point Hg sources associated with natural events, the most important being geothermal activity and volcanic events (Bagnato et al., 2014; Nakagawa, 1999; Nriagu and Becker, 2003; Varekamp and Buseck, 1986), deforestation and soil erosion (Porvari, 2003), influence of organic matter (Teisserenc et al., 2011), forest fires (Brunke et al., 2001; Friedli et al., 2009; Nriagu, 1989), or any distal extensive anthropogenic source reaching the study area due to long-range transport (Fitzgerald et al., 1998). As was previously discussed, organic matter and catchment processes were discarded in the control of Hg distribution.

5.2.1. Pre-1300 CE

Peaks identified at approximately 430 CE (76 cm), 630 CE (69 cm), 900 CE (56 cm), and 1080 CE (45 cm depth) have similar concentrations, 2-to-3 fold higher than the background values. The source of such peaks remains unclear, but considering the study site position regarding the Southern Volcanic Zone, the volcanic origin of the gaseous Hg should be considered (Nriagu and Becker, 2003), even without clear tephra records (although a possible cryptotephra could be present at 55 cm depth from the elemental profiles variations). Very high Hg concentrations have been correlated with volcanic eruptions in historic and prehistoric times where anthropogenic sources cannot be identified, even for events that are ~10^6 years (Ribeiro Guevara et al., 2010; Roos-Barraclough et al., 2002; Schuster et al., 2002; Sial et al., 2013). Regional and local forest fires cannot be ruled out as source of these peaks

Table 1
Mercury concentrations and accumulation rates for pre- and post-industrial background values (without counting maximum increases) for both Southern and Northern Hemisphere lakes and peat bogs. The considered pre-industrial times vary and are specified for each work. Numbers in parentheses correspond to years CE. Pre-/post-industrial factors are also shown for comparison: the estimation was obtained considering the mean for the pre/post ranges showed for each work; * factor specifically mentioned in the referenced work; nd: no data.

	Pre-industrial or natural backgrounds		Post-industrial background (post-1850)		Mean factors pre/post-industrial Hg/Hg_{AR}
	Hg (ng g^{-1})	Hg_{AR} (μg m^{-2} y^{-1})	Hg (ng g^{-1})	Hg_{AR} (μg m^{-2} y^{-1})	
Southern hemisphere					
This study	27–47 (pre-1300)	8–15	64–81	10–26	2/1.6
Lakes Northern Patagonia Argentina (Ribeiro Guevara et al., 2010)	50–80 (pre-1200)	15–25	100–180	30–40	2.1/1.7
Lakes Northern Brazil (Lacerda et al., 1999)		1.7–2.6 (pre-1000)		15–30	nd/10
Peat bog Southern Chile (Biester et al., 2002)	25–75 (pre-1400)	2.5–3.9	80–100	5.7–6.8	1.8/2.5*
Lake Southern Chile (Hermanns and Biester, 2013a)	200 (pre-1300)	20–35			
Lakes Southern Chile (Hermanns and Biester, 2013b)	30–60 (pre-1850)	2.1–11.6	25–105	2.8–23.9	1.4/1.4–2.4*
Lake Central Argentina (Stupar et al., 2013)			17 (pre-1970) 28–81 (post-1970)		3.2/nd
Northern hemisphere					
Peat bog Spain (Martínez-Cortizas et al., 1999)	25–70 (pre-1300)	1.5–8	130–436	30–82	5.9/11.8
Peat bog Swiss (Roos-Barraclough et al., 2002)	25–70 (pre-1300)	1.1–2.5	50–100	~5–30	1.4/15*
Peat bogs Belgium (Allan et al., 2013)	20–50 (pre-1300)	0.8–2.8	~100–1130	~20–60	17/63*
Lakes Canada (Muir et al., 2009)		15.7 (pre-1850)			
Lakes USA (Perry et al., 2005)	<50 (pre-1850)	<5	10–150	10.4–66.3	2/3*
Lakes USA (Rothenberg et al., 2010)	110–260 (pre-1865)	~100	57–450	~200–450	1.1*/6.5
Lake USA (Gray et al., 2015)	50–97 (pre-1954)		88–100		4.8*/nd

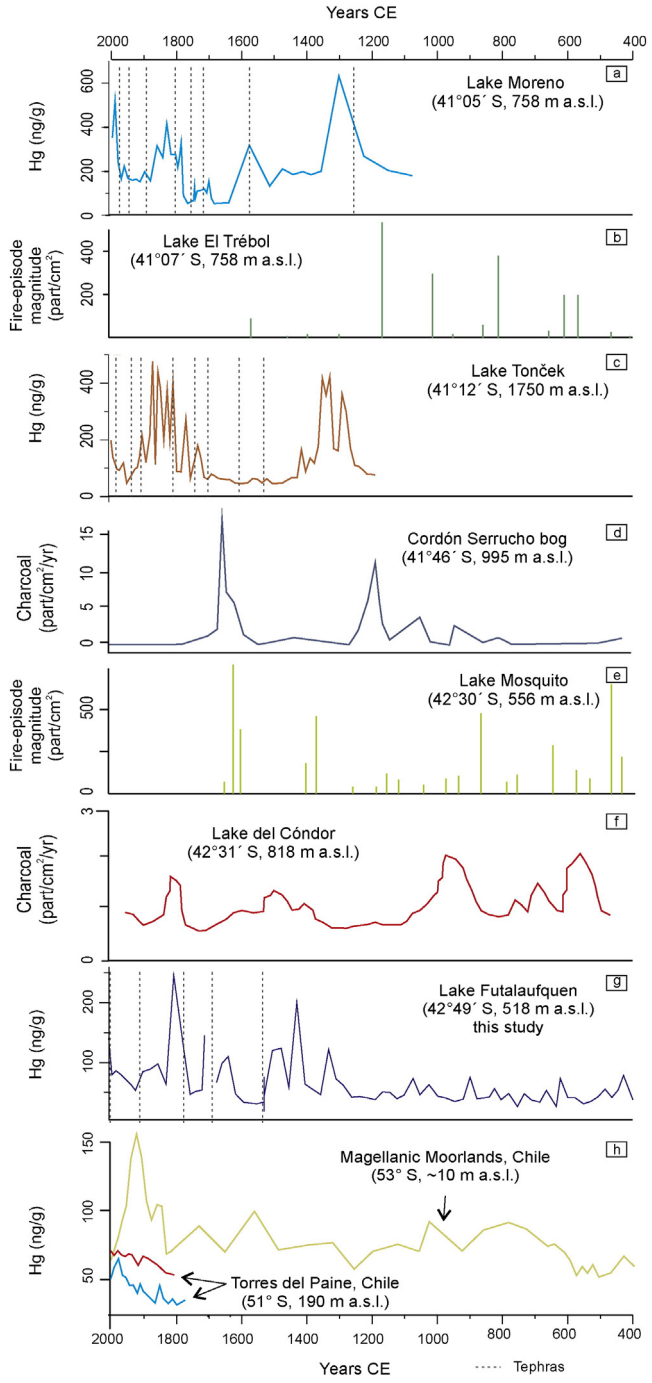

Fig. 4. Mercury, tephras, and fire reconstruction records from Patagonia ordered by increasing latitude (from top to bottom; m a.s.l. = meters above sea level) (see Fig. 1 for locations). Tephra deposition and wild fires are considered as sources of Hg. (a, c) Hg concentration profiles from Lakes Moreno and Tónček, respectively, and position of the tephras identified (modified from Ribeiro Guevara et al., 2010); (b, e) fire-episode magnitude reconstructions from Lakes Trébol and Mosquito, respectively (modified from Whitlock et al., 2006); (d) charcoal record from Cordón Serrucho bog (modified from Markgraf et al., 2013); (f) charcoal record from Lake El Cóndor (modified from Iglesias et al., 2011); (g) Hg profile and position of tephra layers from Lake Futalaufquen, this study; (h) Hg record from Magellanic moorlands (modified from Biester et al., 2002) and Torres del Paine records (modified from Hermanns and Biester, 2013b).

due to Hg liberation during biomass burning (Brunke et al., 2001; Driscoll et al., 2013; Lacerda et al., 1999). Several fire reconstructions both in Chilean and Argentinean Patagonia reported increase and variable fire activity over the last 3000 years (Abarzúa and Moreno, 2008; Henríquez et al., 2015; Whitlock et al., 2006, 2007). In fact, numerous fire episodes were identified during this period in lakes Mosquito and del Cóndor (Whitlock et al., 2006; Iglesias et al., 2011), close to the Lake Futalaufquen (Figs. 1 and 4).

5.2.2. Fires and volcanoes as Hg sources post-1300 CE

High Hg peaks in Lake Futalaufquen sequence are frequent during the last 700 years: the highest values are grouped at approximately 1340–1510 CE (38–30 cm depth), 1640–1810 CE (22–11 cm depth), and at the most recent layer, 2008 CE (0–0.5 cm depth) (Fig. 3c; Table 1). Hg measurements in other lake sediments to which our study site could be compared are very scarce. However, the peaked periods observed in the present work showed a broad similarity with previous Hg records from two lakes situated 200 km North of Lake Futalaufquen (Fig. 4), with different size, catchment characteristics, and altitude (Ribeiro Guevara et al., 2010). These authors reported two periods of drastic increase of Hg concentrations, reaching 400–650 ng g^{-1}, during 14th, and 18th to 19th centuries (Table 1, Fig. 4) (Ribeiro Guevara et al., 2010). The relative agreement with present data demonstrates the regional character of the processes that generated the Hg distribution. Ribeiro Guevara et al. (2010) correlated these periods of high Hg with volcanic events and fires. Recent paleolimnological studies in the region have focused on the Holocene fire history providing additional information to constrain Hg correlations (Fig. 4).

5.2.2.1. Interval 1340–1510 CE. These peaks are comparatively high considering the deposition period, reaching Hg_{AR} 2 to 6 times higher than the background (Fig. 3c). Point anthropogenic contamination source or ancient local mining are ruled out due to the pristine conditions in the area, even at present. However, the Inca mining period has been identified during 1200–1600 CE in Peruvian lakes (Beal et al., 2013; Cooke and Bindler, 2015; Cooke et al., 2009), and also as far as in the Antarctic islands (Sun et al., 2006), evidencing that Hg^0 originated from smelting could be transported over long distance, in contrast to more local previous emissions of cinnabar dust (Cooke et al., 2009). Nevertheless, the successive short-lived peaks observed during this period in Lake Futalaufquen are more probably related to a frequent regional phenomenon rather than to the Inca mining. In this sense, explosive volcanic eruptions can first be ruled out because of the absence of tephra deposits in this period, and the volcanic gas emission without ejecta cannot be confirmed.

Wild fires are another potential source of atmospheric Hg with short term effects (Brunke et al., 2001; Driscoll et al., 2013; Friedli et al., 2009). In Northern Patagonia, Ribeiro Guevara et al. (2010) correlated the 14th century Hg peaks to forest fires. Recently, several works focused on fire reconstructions in Patagonia. Three Hg peaks are identified in this period in Lake Futalaufquen sequence: approx. 1340 CE, the highest at 1430 CE, and another at 1480–1510 CE. Reconstructions of local fires in lakes located 45–60 km to the NW of Lake Futalaufquen, reported fire episodes around 1360 CE in lake Mosquito (Whitlock et al., 2006) and around 1400–1500 CE in lake Cóndor (Iglesias et al., 2011). These local fire episodes could generate accumulation of sedimentary Hg from atmospheric deposition corresponding to our peaks between 1340 CE and 1510 CE (Fig. 4). Around 100–190 km North of Lake Futalaufquen, a coetaneous fire was identified at around 1200 CE at several locations, such as Cordón Serrucho (Markgraf et al., 2013), Padre Laguna and Huala Hué lakes (Iglesias et al., 2012), and Trébol lake (Whitlock et al., 2006). Although this episode did not affect the Lake Futalaufquen based on data presented, it could be related to the pre-1350 CE Hg peaks identified by Ribeiro Guevara et al. (2010) (Fig. 4).

The increase of fire events has been reported during the last 3000 years also in Chilean territory, at similar latitudes as Lake Futalaufquen: marked charcoal peaks occur between 1150 and 1450 CE in Chiloe Island (Abarzúa and Moreno, 2008), and during the last 500–1000 years in Chilean continent (Henríquez et al., 2015).

Considering the westerlies at these latitudes, the fires recorded at Chilean side could be a source of Hg^0 to the Argentinean side. However, charcoal records from Patagonia (Chile and Argentina) showed spatial variability during the last 3000 years, explained by regional climate (inter-annual and inter-decadal climate variability, ENSO effects), vegetation changes, as well as the use of fire by native population together with foreigner settlements (Fletcher and Moreno, 2012; Holz et al., 2012; Moreno et al., 2010; Whitlock et al., 2007). Therefore, the Hg record in Lake Futalaufquen at approx. 1340–1510, and the Hg records in northernmost lakes before 1350 CE (Ribeiro Guevara et al., 2010) record local to regional fire episodes, and heterogeneity of regional climatic patterns (Whitlock et al., 2007).

5.2.2.2. Interval 1640–1810 CE. Hg peaks in this interval probably originate from different Hg sources. Two peaks are located immediately above tephra layers (Fig. 3c). The peak at 16.5 cm depth is on top of a tephra correlated with a historical poorly known eruption from Huequi volcano, around 1700 CE (Daga et al., 2016). The highest Hg peak of the sequence, at 12 cm depth, corresponds to the overlying layer of a mixed tephra dated to about 1780 CE (from Michinmahuida accessory cones and Chaitén volcano; Daga et al., 2016). In Northern Patagonia, Ribeiro Guevara et al. (2010) attributed 18th–19th century peaks to both fires and volcanic events (Fig. 4). Even though the source of these Hg peaks can be attributed to volcanic eruptions, they do not correspond to the same local/regional sources that impacted the lakes studied by Ribeiro Guevara et al. (2010), corroborating the importance of Southern Volcanic Zone activity for the global Hg budget.

However, volcanic activity cannot explain all Hg peaks observed in the 17th and 18th century: this is the case of the peak at about 1640–1660 CE (Fig. 3c). Although active volcanoes may generate isolated gaseous emissions, the lack of evidence of such processes in the Southern Volcanic Zone does not allow the unambiguous correlation of this Hg peak with volcanic provenance. Actually, a charcoal peak around 1600 CE identified in a lake 45 km to the NE of Lake Futalaufquen (Whitlock et al., 2006), represents a more reasonable source for the Hg peak in 1640–1660 CE (Fig. 4), considering possible shifts in both age-depth models. Fires for grazing related to the first European settlements in the area seem to be a widespread regional phenomenon (Haberzettl et al., 2006). More evidence provides studies on 18th and 19th century, when Native Americans and Europeans used intentional burning for several purposes, often triggering extended wildfires (Kitzberger et al., 1997; Veblen et al., 2003). Younger Hg peaks associated with tephra layers could also have received contributions from extended fires (Fig. 4), although there are reports of a general decline of fire episodes during the last 500 years (Whitlock et al., 2006).

5.2.2.3. Most recent peak, 2008 CE. The Hg peak on the top of the sediment core exhibits a 2-fold increase of Hg_{AR} compared to the underlying layer, and coincides with 2008 Chaitén event. This volcano is located close to the Lake Futalafuquen, 70 km west of the sampling site (Fig. 1). Although gaseous emissions from this volcano have not been characterized, the pyroclastic dispersion is documented (Alfano et al., 2011) reaching also the Lake Futalaufquen (Daga et al., 2016). As was observed, not all tephras are enriched in Hg, which can be explained by differences between volcanoes, the eruptive stage, and their contribution of gaseous emissions.

6. Conclusions

Here we combine limited studies of Hg cycling for the Southern Hemisphere that is a remote and relatively pristine area. After discarding the organic matter and catchment erosion as controls of the Hg distribution, the most relevant feature of the Hg depth profile of the Lake Futalaufquen sediment are the intense peaks of atmospheric origin observed during the last 700 years. In the period between approximately 1340 and 1510 CE there is a clear association of Hg concentration in the sediments to the regional fire episodes (not limited to the watershed), which can be slightly variable in time with changing latitudes due to regional climatic patterns. On the other hand, during the last 300 years, the Hg record was associated mainly with volcanic eruptions in northernmost Patagonia, together with fairly irregular fire episodes due to anthropogenic burning for settlement population along the Andes. The general increasing Hg trend observed both in the Southern and Northern Hemispheres since pre-industrial times, even in remote areas, was not clearly observed at Northern Patagonian latitudes. However, a slight increase (1.6-fold) was observed in the Hg accumulation rate during the last century at Lake Futalaufquen. This increase rate was the lowest among the investigated sites in southern South America. Regarding the background levels, the pre-1300 CE Hg concentrations can be considered the baseline for this region; however, to confirm these values as the true natural background, it would be necessary to go further back in time.

Although it has been proposed that remote headwater lake sediment cores are the best material to analyse past depositional rates of Hg because of minimal local inputs due to erosion, southern pristine environments with different catchment features and basin/lake surface relationship have shown a very good reproducibility of the atmospheric depositional patterns. Nevertheless, more studies are necessary to fully understand the Hg distribution in the Southern Hemisphere, both on the Hg depositional history in lake and bog sediments, as well as on the suggested sources. Volcanism exerts influence on Hg deposition all along Patagonia and gaseous emissions should be characterized in Andean active volcanic zones in order to better characterize the Hg contribution as well as that of the other gaseous species to the global natural budgets. Moreover, forest fires are a very common phenomenon observed every year in the region due to natural and anthropogenic forcing, with a total lack of studies on their emissions and effects.

Acknowledgements

The authors wish to express their gratitude to Mr. Ricardo Sánchez for his collaboration in sampling and sample conditioning and to the reactor RA6 operation staff for their assistance in sample analysis. We thank to Dr. Leonardo Buria (National Parks Administration) and the personnel from the Los Alerces National Park for the support in fieldwork. We also thank to three anonymous reviewers and to the associate editor Mae Sexauer Gustin for their comments at the revision stage. This work was partially funded by SeCTyP 06/C339, Fundación Balseiro (2010/2011), and PICT 2012-280 projects, and the research programme P1-0143 of the Slovenian Research Agency (ARRS).

References

Abarzúa, A.M., Moreno, P.I., 2008. Changing fire regimes in the temperate rainforest region of Southern Chile over the last 16,000 years. Quat. Res. 69, 62–71.
Alfano, F., Bonadonna, C., Volentik, A.C., Connor, C.B., Watt, S.F.L., Pyle, D.M., Connor, L.J., 2011. Tephra stratigraphy and eruptive volume of the May, 2008, Chaitén eruption, Chile. Bull. Volcanol. 73, 613–630.
Allan, M., Le Roux, G., Sonke, J.E., Piotrowska, N., Streel, M., Fagel, N., 2013. Reconstructing historical atmospheric mercury deposition in Western Europe using: Misten peat bog cores, Belgium. Sci. Total Environ. 442, 290–301.
Bagnato, E., Tamburello, G., Avard, G., Martinez-Cruz, M., Enrico, M., Fu, X., et al., 2014. Mercury fluxes from volcanic and geothermal sources: an update. In: GF, Zellmer, Edmonds, M., SM, Straub (Eds.), The Role of Volatiles in the Genesis, Evolution and Eruption of Arc Magmas. Geol Soc Lond Spec Publication, p. 410 http://dx.doi.org/10.1144/SP410.2.
Beal, S.A., Jackson, B.P., Kelly, M.A., Stroup, J.S., Landis, J.D., 2013. Effects of historical and modern mining on mercury deposition in Southeastern Peru. Environ. Sci. Technol. 47, 12715–12720.
Biester, H., Kilian, R., Franzen, C., Woda, C., Mangini, A., Schöler, H.F., 2002. Elevated mercury accumulation in a peat bog of the Magellanic moorlands, Chile (53°S) – an anthropogenic signal from the Southern Hemisphere. Earth Planet. Sci. Lett. 201, 609–620.
Boës, X., Rydberg, J., Martinez-Cortizas, A., Bindler, R., I, Renberg, 2011. Evaluation of conservative lithogenic elements (Ti, Zr, Al, and Rb) to study anthropogenic element enrichments in lake sediments. J. Paleolimnol. 46, 75–87.
Boyle, J., 2001. Redox remobilization and the heavy metal record in lake sediments: a modelling approach. J. Paleolimnol. 26, 423–431.

Bronk Ramsey, C., 2009. Bayesian analysis of radiocarbon dates. Radiocarbon 51, 337–360.
Brunke, E., Labuschange, C., Slemr, F., 2001. Gaseous mercury emission from a fire in the Cape Peninsula, South Africa, during January 2000. Geophys. Res. Lett. 28, 1483–1486.
Cooke, C.A., Bindler, R., 2015. Lake sediment records of preindustrial metal pollution. In: Blais, J.M., et al. (Eds.), Environmental Contaminants. Developments in Paleoenvironmental Research 18. http://dx.doi.org/10.1007/978–94-017-9541-8_6.
Cooke, C.A., Balcom, P.H., Biester, H., Wolfe, A.P., 2009. Over three millennia of mercury pollution in the Peruvian Andes. PNAS 106, 8830–8834. http://dx.doi.org/10.1073/pnas.0900517106.
Daga, R., Ribeiro Guevara, S., Arribére, M., 2016. New records of late Holocene tephras from Lake Futalaufquen, Northern Patagonia. J. S. Am. Earth Sci. 66, 232–247. http://dx.doi.org/10.1016/j.jsames.2015.12.003.
Driscoll, C.T., Mason, R.P., Chan, H.M., Jacob, D.J., Pirrone, N., 2013. Mercury as a global pollutant: sources, pathways, and effects. Environ. Sci. Technol. 47, 4967–4983.
Durnford, D., Dastoor, A., Figueras-Nieto, D., Ryjkov, A., 2010. Long range transport of mercury to the Arctic and across Canada. Atmos. Chem. Phys. Discuss. 10, 6063–6086.
Engstrom, D.R., Swain, E.B., 1997. Recent declines in atmospheric mercury deposition in the Upper Midwest. Environ. Sci. Technol. 31, 960–967.
Fitzgerald, W.F., Engstrom, D.R., Mason, R.P., Nater, E.A., 1998. The case for atmospheric mercury contamination in remote areas. Environ. Sci. Technol. 32, 1–7.
Fitzgerald, W.F., Engstrom, D.R., Lamborg, C.H., Tseng, C., Balcom, P.H., Hammerschmidt, C.R., 2005. Modern and historic atmospheric mercury fluxes in Northern Alaska: global sources and Arctic depletion. Environ. Sci. Technol. 39 (2), 557–568.
Fletcher, M., Moreno, P., 2012. Vegetation, climate and fire regime changes in the Andean region of southern Chile (38°S) covaried with centennial–scale climate anomalies in the tropical Pacific over the last 1500 years. Quat. Sci. Rev. 46, 46–56.
Friedli, H.R., Arellano, A.F., Cinnirella, S., Pirrone, N., 2009. Mercury emissions from global biomass burning: spatial and temporal distribution. In: Pirrone, N., Mason, R. (Eds.), Mercury Fate and Transport in the Global Atmosphere: Emissions, Measurements and Models. Springer, pp. 193–220.
González-Ferrán, O., 1995. Volcanes de Chile. Instituto Geográfico Militar de Chile, Santiago de Chile.
Gray, J.E., Van Metre, P.C., Pribil, M.J., Horowitz, A.J., 2015. Tracing historical trends of Hg in the Mississippi River using Hg concentrations and Hg isotopic compositions in a lake sediment core, Lake Whittington, Mississippi, USA. Chem. Geol. 395, 80–87.
Grigal, D.F., 2002. Inputs and outputs of mercury from terrestrial watersheds: a review. Environ. Rev. 10, 1–39. http://dx.doi.org/10.1139/A01-013.
Gu, B., Schelske, C.L., Brenner, M., 1996. Relationship between sediment and plankton isotope ratios (δ13C and δ15N) and primary productivity in Florida lakes. Can. J. Fish. Aquat. Sci. 53, 875–883.
Haberzettl, T., Wille, M., Fey, M., Janssen, S., Lücke, A., Mayr, C., 2006. Environmental change and fire history of southern Patagonia (Argentina) during the last five centuries. Quat. Int. 158, 72–82.
Heiri, O., Lotter, A.F., Lemcke, G., 2001. Loss on ignition as a method for estimating organic and carbonate content in sediments: reproducibility and comparability of results. J. Paleolimnol. 25, 101–110.
Henríquez, W.I., Moreno, P.I., Alloway, B.V., Villarosa, G., 2015. Vegetation and climate change, fire-regime shifts and volcanic disturbance in Chiloé Continental (43°S) during the last 10,000 years. Quat. Sci. Rev. 123, 158–167.
Hermanns, Y.M., Biester, H., 2013a. A 17,300-year record of mercury accumulation in a pristine lake in southern Chile. J. Paleolimnol. 49, 547–561.
Hermanns, Y.M., Biester, H., 2013b. Anthropogenic mercury signals in lake sediments from southernmost Patagonia, Chile. Sci. Total Environ. 445–446, 126–135.
Holz, A., Haberle, S., Veblen, T.T., De Pol-Holz, R., Southon, J., 2012. Fire history in western Patagonia from paired tree–ring fire–scar and charcoal records. Clim. Past 8, 451–466.
Iglesias, V., Whitlock, C., Bianchi, M.M., Villarosa, G., Outes, V., 2011. Holocene climate variability and environmental history at the Patagonian forest/steppe ecotone: Lago Mosquito (42°29′37.89″S, 71°24′14.57″W) and Laguna del Cóndor (42°20′47.22″S, 71°17′07.62″W). The Holocene 22, 1297–1307.
Iglesias, V., Whitlock, C., Bianchi, M.M., Villarosa, G., Outes, V., 2012. Climate and local controls of long-term vegetation dynamics in northern Patagonia (Lat 41°S). Quat. Res. 78, 502–512.
Kainz, M., Lucotte, M., 2006. Mercury concentrations in lake sediments – revisiting the predictive power of catchment morphometry and organic matter composition. Water Air Soil Pollut. 170, 173–189. http://dx.doi.org/10.1007/s11270-006-3009-z.
Kitzberger, T., Veblen, O., Villalba, R., 1997. Climatic influences on fire regimes along a rain forest-to-xeric woodland gradient in northern Patagonia, Argentina. J. Biogeogr. 24, 35–47.
Lacerda, L.D., Ribeiro, M.G., Cordeiro, R.C., Sifeddine, A., Turcq, B., 1999. Atmospheric mecury deposition over Brazil during the past 30,000 years. Cienc. Cult. J. Braz. Assoc. Adv. Sci. 51, 363–371.
Lamborg, C.H., Fitzerald, W.F., Damman, A.W., Benoit, J.M., Balcom, P.H., Engstrom, D.R., 2002. Modern and historic atmospheric mercury fluxes in both hemispheres: global and regional mercury cycling implications. Glob. Biogeochem. Cycles 16, 1104. http://dx.doi.org/10.1029/2001GB001847.
Lindqvist, O., Johansson, K., Aastrup, A., Anderson, A., Bringmark, L., Hovsenius, G., et al., 1991. Mercury in the Swedish environment - recent research on causes, consequences and corrective methods. Water Air Soil Pollut. 55, 1–261.
Lockhart, W.L., Macdonald, R.W., Outridge, P.M., Wilkinson, P., DeLaronde, J.B., Rudd, J.W.M., 2000. Tests of the fidelity of lake sediment core records of mercury deposition to known histories of mercury contamination. Sci. Total Environ. 260, 171–180.
Lojen, S., Ogrinc, N., Dolenec, T., 1997. Carbon and nitrogen stable isotope fractionation in the sediment of Lake Bled, Slovenia. Water Air Soil Pollut. 99, 315–323.
Markgraf, V., Iglesias, V., Whitlock, C., 2013. Late and postglacial vegetation and fire history from Cordón Serrucho Norte, northern Patagonia. Palaeogeogr. Palaeoclimatol. Palaeoecol. 371, 109–118.
Martínez-Cortizas, A., Pontevedra-Pombal, X., García-Rodeja, E., Nóvoa Muñoz, J.C., Shotyk, W., 1999. Mercury in a Spanish peat bog: archive of climate change and atmospheric metal deposition. Science 284, 939–942.
McCallister, S.L., Bauer, J.E., Cherrier, J.E., Ducklow, H.W., 2004. Assessing sources and ages of organic matter supporting river and estuarine bacterial production: a multiple-isotope (Δ14C, δ13C and δ15N) approach. Limnol. Oceanogr. 49, 1687–1702.
Moreno, P.I., Kitzberger, T., Iglesias, V., Holz, A., 2010. Paleofires in southern South America since the last glacial maximum. PAGES News 18, 75–77.
Muir, D.C., Wang, X., Yang, F., Nguyen, N., Jackson, T.A., Evans, M.S., et al., 2009. Spatial trend and historical deposition of mercury in eastern and northern Canada inferred from lake sediment cores. Environ. Sci. Technol. 43, 4802–4809.
Nakagawa, R., 1999. Estimation of mercury emissions from geothermal activity in Japan. Chemosphere 38, 1867–1871.
Nriagu, J., 1989. A global assessment of natural sources of atmospheric trace metals. Nature 338, 47–49.
Nriagu, J., Becker, C., 2003. Volcanic emissions of mercury to the atmosphere: global and regional inventories. Sci. Total Environ. 304, 3–12.
O'Leary, M.H., 1988. Carbon isotopes in photosynthesis. Bioscience 38, 328–336.
Paruelo, J.M., Beltrán, A., Jobbágy, E., Sala, O.E., Golluscio, R.A., 1998. The climate of Patagonia: general patterns and controls on biotic processes. Ecol. Austral. 8, 85–101.
Percival, J.B., Outridge, P.M., 2013. A test of the stability of Cd, Cu, Hg, Pb and Zn profiles over two decades in lake sediments near the Flin Flon Smelter, Manitoba, Canada. Sci. Total Environ. 454–455, 307–318.
Perry, E., Norton, S.A., Kamman, N.C., Lorey, P.M., Driscoll, C.T., 2005. Deconstruction of historic mercury accumulation in lake sediments, Northeastern United States. Ecotoxicology 14, 85–99.
Petit-Breuilh Sepúlveda, M.E., 2004. La historia eruptiva de los volcanes hispanoamericanos (siglos XVI al XX). In: Servicio de Publicaciones Exmo (Ed.)Serie Casa de los Volcanes No. 8. Cabildo Insular de Lanzarote, Huelva, Spain.
Pirrone, N., Mahaffey, K.R., 2005. Where we stand on mercury pollution and its health effects on regional and global scales. In: Pirrone, N., KR, Mahaffey (Eds.), Dynamics of Mercury Pollution on Regional and Global Scales. Springer, pp. 1–21.
Pizzolón, L., 1995. Lago Futalaufquen. In: Calcagno, A., Fioriti, M., Pedrozo, F., et al. (Eds.), Catálogo de lagos y embalses de la Argentina.
Porvari, P., 2003. Sources and fate of mercury in aquatic ecosystems. Monographs of the Boreal Environment Research, p. 23.
Ribeiro Guevara, S., Bubach, D., Arribére, M., 2004a. Mercury in lichens of Nahuel Huapi National Park, Patagonia, Argentina. J. Radioanal. Nucl. Chem. 261, 679–687.
Ribeiro Guevara, S., Bubach, D., Vigliano, P.H., Lippolt, G., Arribére, M., 2004b. Heavy metals and other trace elements in native mussel diplodon chilensis from Northern Patagonia lakes, Argentina. Biol. Trace Elem. Res. 102, 245–264.
Ribeiro Guevara, S., Meili, M., Rizzo, A., Daga, R., Arribére, M., 2010. Sediment records of highly variable mercury inputs to mountain lakes in Patagonia during the past millennium. Atmos. Chem. Phys. 10, 3443–3453.
Rizzo, A., Arcagni, M., Arribére, M.A., Bubach, D., Ribeiro, Guevara S., 2011. Mercury in the biotic compartments of Northwest Patagonia lakes, Argentina. Chemosphere 84, 70–79.
Rizzo, A., Arcagni, M., Campbell, L., Koron, N., Pavlin, M., Arribére, M.A., et al., 2014. Source and trophic transfer of mercury in plankton from an ultraoligotrophic lacustrine system (Lake Nahuel Huapi, North Patagonia). Ecotoxicology 23 (7), 1184–1194.
Roig, F.A., Villalba, R., 2008. Understanding climate from Patagonian tree rings. Dev. Quat. Sci. 11, 411–435.
Roos-Barraclough, F., Martínez–Cortizas, A., García–Rodeja, E., Shotyk, W., 2002. A 14500 year record of the accumulation of atmospheric mercury in peat: volcanic signals, anthropogenic in£uences and a correlation to bromine accumulation. Earth Planet. Sci. Lett. 202, 435–451.
Rothenberg, S.E., Kirby, M.E., Bird, B.W., DeRose, M.B., Lin, C., Fen, X., et al., 2010. The impact of over 100 years of wildfires on mercury levels and accumulation rates in two lakes in southern California, USA. Environ. Earth Sci. 60, 993–1005. http://dx.doi.org/10.1007/s12665-009-0238-7.
Rydberg, J., Gälman, V., Renberg, I., Bindler, R., 2008. Assessing the stability of mercury and methylmercury in a varved lake sediment deposit. Environ. Sci. Technol. 42 (12), 4391–4396. http://dx.doi.org/10.1021/es7031955.
Sanei, H., Goodarzi, F., 2006. Relationship between organic matter and mercury in recent lake sediment: the physical–geochemical aspects. Appl. Geochem. 21, 1900–1912.
Schelske, C.L., Hodell, D.A., 1991. Recent changes in productivity and climate of Lake Ontario detected by isotopic analysis of sediments. Limnol. Oceanogr. 36, 961–975.
Schroeder, W.H., Munthe, J., 1998. Atmospheric mercury, an overview. Atmos. Environ. 32, 809–822.
Schuster, P., Krabbenhoft, D., Naftz, D., Cecil, L.D., Olson, M.L., Dewild, J.F., et al., 2002. Atmospheric mercury deposition during the last 270 years: a glacial ice record of natural and anthropogenic sources. Environ. Sci. Technol. 36, 2303–2310.
Selin, N.E., Jacob, D.J., Yantosca, R.M., Strode, S., Jaeglé, L., Sunderland, E.M., 2008. Global 3-D land-ocean-atmosphere model for mercury: present-day versus preindustrial cycles and anthropogenic enrichment factors for deposition. Glob. Biogeochem. Cycles 22, GB2011. http://dx.doi.org/10.1029/2007GB003040.
Sial, A.N., Lacerda, L.D., Ferreira, V.P., Frei, R., Marquillas, R.A., Barbosa, J.A., et al., 2013. Mercury as a proxy for volcanic activity during extreme environmental turnover: the Cretaceous–Paleogene transition. Palaeogeogr. Palaeoclimatol. Palaeoecol. 387, 153–164.
Smol, J.P., 2008. Pollution of Lakes and Rivers, A Paleoenvironmental Perspective. Blackwell Publishing, USA, p. 383.
Sprovieri, F., Pirrone, N., Ebinghaus, R., Kock, H., Dommergue, A., 2010. A review of worldwide atmospheric mercury measurements. Atmos. Chem. Phys. 10, 8245–8265. http://dx.doi.org/10.5194/acp-10-8245-2010.

Stern, C., 2004. Active Andean volcanism: its geologic and tectonic setting. Rev. Geol. Chile 31, 161–206.
Stupar, Y.V., Schäfer, J., García, M.G., Schmidt, S., Piovano, E., Blanc, G., et al., 2013. Historical mercury trends recorded in sediments from the Laguna del Plata, Córdoba, Argentina. Chem. Erde 74, 353–363.
Sun, L., Yin, X., Liu, X., Zhu, R., Xie, Z., Wang, Y., 2006. A 2000-year record of mercury and ancient civilizations in seal hairs from King George Island, West Antarctica. Sci. Total Environ. 368, 236–247. http://dx.doi.org/10.1016/j.scitotenv.2005.09.092.
Teisserenc, R., Lucotte, M., Houel, S., 2011. Terrestrial organic matter biomarkers as tracers of Hg sources in lake sediments. Biogeochemistry 103, 235–244.
Varekamp, J., Buseck, P., 1986. Global Hg flux from volcanic and geothermal sources. Appl. Geochem. 1, 65–73.
Veblen, T.T., Kitzberger, T., Raffaele, E., Lorenz, D., 2003. Fire history and vegetation changes in northern Patagonia, Argentina. In: Veblen, T.T., Baker, W.L., Montenegro, G., Swetnam, W.T. (Eds.), Fire and climatic change in temperate ecosystems of the Western Americas. Springer, New York, USA, pp. 259–289.
Vila, A., Borrelli, L., 2011. Cattle in the Patagonian forests: feeding ecology in Los Alerces National Reserve. For. Ecol. Manag. 261, 1306–1314.
Vreča, P., Muri, G., 2006. Changes in accumulation of organic matter and stable carbon and nitrogen isotopes in sediments of two Slovenian mountain lakes (Lake Ledvica and Lake Planina), induced by eutrophication changes. Limnol. Oceanogr. 1, 781–790.
Vreča, P., Muri, G., 2010. Sediment organic matter in mountain lakes of north-western Slovenia and its stable isotopic signatures: records of natural and anthropogenic impacts. Hydrobiologia 648, 35–49.
Whitlock, C., Bianchi, M.M., Bartlein, P.J., Markgraf, V., Marlon, J., Walsh, M., et al., 2006. Postglacial vegetation, climate, and fire history along the east side of the Andes (lat 41–42.5°S), Argentina. Quat. Res. 66, 187–201.
Whitlock, C., Moreno, P.I., Bartlein, P., 2007. Climatic controls of Holocene fire patterns in southern South America. Quat. Res. 68, 28–36.