Atmos. Chem. Phys. Discuss., 9, 25885–25914, 2009
www.atmos-chem-phys-discuss.net/9/25885/2009/

Atmospheric Chemistry and Physics Discussions

This discussion paper is/has been under review for the journal Atmospheric Chemistry and Physics (ACP). Please refer to the corresponding final paper in ACP if available.

Sediment records of highly variable mercury inputs to mountain lakes in Patagonia during the past millennium

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Received: 15 September 2009 – Accepted: 16 November 2009 – Published: 2 December 2009

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Published by Copernicus Publications on behalf of the European Geosciences Union.

Abstract

High Hg levels in the pristine lacustrine ecosystems of the Nahuel Huapi National Park, a protected zone situated in the Andes of Northern Patagonia, Argentina, have initiated further investigations on Hg cycling and source identification. Here we report Hg records in sedimentary sequences aiming at identifying atmospheric sources during the past millennium. In addition to global transport and deposition, a potential atmospheric Hg source to be considered is the local emissions associated with volcanic activity, considering that the Park is situated in the Southern Volcanic Zone. Two sediment cores were extracted from Lake Tonček, a small, high-altitude system reflecting mainly direct inputs associated with atmospheric contributions, and Lake Moreno Oeste, a much larger and deeper lake having an extended watershed covered mostly by native forest.

The sedimentary sequences were dated based on both ^{210}Pb and ^{137}Cs profiles. In addition, tephra layers were identified and geochemically characterized for chronological application and to investigate any association of volcanic eruptions with Hg records. Hg concentrations in sediments were measured along with 32 other elements, as well as organic matter, fossil chironomids, and biogenic silica. Observed background Hg concentrations, determined from the sequence domains with lower values, ranged from 50 to 100 $ng\,g^{-1}$ DW (dry weight), whereas the surficial layers reached 200 to 500 $ng\,g^{-1}$ DW. In addition to this traditional pattern, however, two deep domains in both sequences showed dramatically increased Hg levels reaching 400 to 650 $ng\,g^{-1}$ DW; the upper dated to the 18th to 19th centuries, and the lower around the 13th century. These concentrations are not only elevated in the present profiles but also many-fold above the background values determined in other fresh water sediments, as were also the Hg fluxes, reaching 120 to 150 $\mu g\,m^{-2}\,y^{-1}$ in Lake Tonček. No correlation was observed between Hg concentrations and the contents of organic matter, fossil chironomids, biogenic silica, or the other elements determined. However, a distinct increase of Hg concentrations was observed immediately above some tephra

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layers, suggesting a link to volcanic events. Extended fires is another potential atmospheric source to be considered because the earlier Hg peaks coincide with reported charcoal peaks, whereas the upper Hg peaks coincide with evidences of extended forest fires from tree-ring data and historical records.

1 Introduction

Even though aquatic ecosystems are globally exposed to mercury (Hg) by atmospheric inputs of increasing concern, few studies have been focusing on the sources, fate and history of freshwater systems of the Southern Hemisphere that are free from major contamination (Downs et al., 1998; Lamborg et al., 2002; Biester et al., 2007). Here, we used sediment profiles as historical archives to reveal changes in the Hg cycling in two lakes of the southern Andes over the past centuries. Although no relevant point sources of Hg from mining or industrial activities have been identified in the study region, high Hg levels in various ecosystem compartments have been reported, notably in both native and introduced fish species, where levels ranged from 0.06 to 4 $\mu g\,g^{-1}$ dry weight (DW) in liver, and from 0.07 to 2.5 $\mu g\,g^{-1}$ DW in muscle (Arribére et al., 2008), whereas Hg concentrations in lichens and mussels, used as air and water bioindicators, respectively, reached values compatible with locations exposed to moderate contamination (Ribeiro Guevara et al., 2004a, b), suggesting that the anomaly is not limited to aquatic systems.

The western part of the Park receives high precipitation, reaching 3000 $mm\,y^{-1}$. Therefore, global transport and wet deposition, a well-known Hg source to aquatic environments (Downs et al., 1998), should be considered to contribute to the Hg burden in the study region. But also other Hg sources have to be taken into account. Forest fires, volcanoes and geothermal vents, and Hg-enriched soils have been recognized as natural Hg sources to the atmosphere (Nriagu, 1989; Lindqvist et al., 1991; Schroeder and Munthe, 1998; Wiedinmyer and Friedly, 2007). Geological sources are associated to plate tectonic boundaries (Varenkamp and Brusek, 1984; Rasmussen, 1994), including areas of geothermal and volcanic activity, which are considered the foremost natural source of Hg (Nakagawa, 1999; Ferrara et al., 2000; Tomiyasu et al., 2000). Cataclysmic volcanoes have the potential to inject enough volatile Hg into the stratosphere to change the global and regional cycle of Hg for a few years, while quiescent degassing and moderate eruptions exhale directly into the troposphere and can have long-term effects also on the local environments (Langway et al., 1995). Geothermal activity has been associated with high Hg levels in soils and air at several places (Siegel and Siegel, 1975; Weissberg and Rohde, 1978; Varenkamp and Buseck, 1986). Volcanogenic Hg can readily enter the aquatic food chain after being released, enlarging bio-available stocks (Nriagu and Becker, 2003). Volcanic activity is a potential source to be considered in the present work since the lakes under study are enclosed in the Southern Volcanic Zone (SVZ), including several volcanoes active during the Holocene. Forest fires reduce drastically the pool of Hg in catchment soils, and releasing also biomass inventories, through elemental Hg volatilization to the atmosphere (Friedli et al., 2003; Sigler et al., 2003; Amirbahman et al., 2004; Harden et al., 2004), potentially enlarging sediment Hg burden after transport and wet or dry deposition. Up to 6 fold increase in Hg concentrations in sediments of Caballo Reservoir, New Mexico, USA, was observed after a forest fire and storm runoff, revealing that the combination of both phenomena enhanced the transport of Hg from the watershed to the water body (Caldwell et al., 2000), another pathway that may contributes increasing Hg contents in sediments after fires. Kelly et al. (2006) observed also in Lake Moab, Jasper National Park, Canada, that post-fire runoff mobilized a large short-term pulse of Hg.

In an earlier screening study on lake sedimentary sequences in the region (Ribeiro Guevara et al., 2005), upper layers, associated with 20th century accumulation periods, showed in most cases concentrations elevated above background levels, reaching values as high as 1 to 3 μg g^{-1} DW. However, Hg concentrations 3 to 5-fold above background were observed in deep layers, focusing hence our attention on natural inputs during the past millennium, and driving present work. Here, two dated sedimentary sequences were studied with a more sensitive technique for Hg determinations, and with additional methods to analyze also other elements and environmental tracers.

2 Experimental

2.1 Study site

The Nahuel Huapi National Park is situated in northern Patagonia, on the eastern slope of the southern Andes (40° 20′ to 41° 40′ S, 71° to 72° W; Fig. 1) and is the largest protected natural area of Argentina, covering approximately 7100 km^2 and comprising a drainage basin that includes three major river systems, thirteen lakes of more than 10 km^2, and several hundred small lakes and ponds. Within the Park's limits there are pristine as well as moderately impacted areas, such as the city and suburbs of San Carlos de Bariloche, with a population of circa 120 000 people. Its economy, as well as that of other small towns and villages in the Park, is largely based on tourism.

The Park is located in the Northern Patagonian Andes (39° to 45° S), a region that is part of the Southern Volcanic Zone (SVZ). The SVZ includes, at least 60 historically and potentially active volcanic edifices in Chile and Argentina, as well as three giant silicic caldera systems and numerous minor eruptive centers (Stern, 2004). The northern Patagonian segments of the volcanic arc include several active centers since the Miocene to present, among other Villarrica, Nilahue, Puyehue-Cordón Caulle, Cerro Puntiagudo, Osorno, and Calbuco, with several events registered in historical records since colonisation (Ramos, 1999; Stern, 2004). An analysis of volcanic ash records in short lacustrine sedimentary sequences from the region showed up to 9 tephra layers deposited in the past 1000 yr (Daga et al., 2008).

Two sedimentary sequences were extracted from Lake Tonček and Lake Moreno Oeste (Fig. 1). Lake Moreno Oeste is the western branch of Lake Moreno (41° 5′ S; 71° 33′ W, 758 m a.s.l.), draining into Lake Nahuel Huapi. Lake Moreno Oeste has a surface area of 6 km^2 and a maximum depth of 90 m, and is an ultraoligotrophic, warm monomictic system stratified from late spring to early autumn (Queimaliños et al., 1999;

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Díaz et al., 2007). The lake is surrounded mostly by closed native forest dominated by *Nothofagus dombeyi* and lesser amounts of *Austrocedrus chilensis*. This environment has persisted, with variations in the relative composition, during the last millennium (Whitlock et al., 2006). The sampling point selected is Llao Llao bay, a sub-basin with a rather flat bottom at 20 m depth, without tributaries.

Lake Tonček (41° 12′ S; 71° 29′ W, 1750 m a.s.l.) is a small lake with 0.03 km^2 surface and 12 m maximum depth, of glacial origin, situated in Catedral mountain approximately 16 km to the southeast of Lake Moreno Oeste, at the foot of high peaks with steep slopes. It is an ultraoligotrophic, dimictic system, with direct stratification in summer and 6 to 8 months of ice cover reaching a thickness of up to 2 m. Lake Tonček watershed is small, with an extension of approximately 2.5 km^2 including one smaller lake situated about 100 m higher, which is connected to Lake Tonček by a small inlet stream meandering across wetlands. Reddish coloration and sulphydric smell in these wetlands have been reported at the end of the summer, when eutrophication processes are developed, potentially impacting Hg cycling in the water body. The lake has two distinct sections: a deep central zone that is surrounded like a ring by a shallow outer zone which is 0.5 m deep and up to 30 m wide. The boundary between the two sections is a steep slope dropping to 12 m. Lake Tonček watershed is dominated by rocky ground deposits, and scattered timberline vegetation (*Nothofagus pumilio* "krummholz"). The water body encloses a simple trophic structure without fish, and also the community structure of zooplankton is relatively simple (Morris et al., 1995; Marinone et al., 2006).

2.2 Methods

Short sediment cores were extracted with a messenger-activated gravity corer from the deepest part of the lakes Moreno Oeste (Llao Llao bay), and Tonček (Fig. 1). Core lengths were 43 and 70 cm, respectively. The sediment cores were cut opened longitudinally using a portable circular saw to section the tube walls, sliding afterwards a copper plate through the sediment to divide it in two semi-cylindrical sections. Both sections were sub-sampled every 1 cm. Each sub-sampled sediment layer was freeze-dried until constant weight and homogenised. Tephra layers were identified visually in the sedimentary sequence before sub-sampling, whereas they were analyzed under binocular magnifying glass after freeze-drying.

The sediment accumulation rates of the sediment sequences were determined by ^{210}Pb and ^{137}Cs dating techniques (Joshi and Shukla, 1991; Robbins and Herche, 1993). ^{210}Pb, ^{226}Ra (in secular equilibrium with supported ^{210}Pb), and ^{137}Cs specific activity was measured in each layer by high-resolution gamma spectrometry. The Constant Rate of Supply model was used for ^{210}Pb dating. Correction of the old-date error of the model was implemented by logarithmic extrapolation to infinite depth (Ribeiro Guevara et al., 2003). For ^{137}Cs dating, the specific activity profiles were compared with the fallout sequence determined in this region, associated mainly with South Pacific nuclear tests from 1966 to 1974 (Ribeiro Guevara and Arribére). The dates for the events registered in both sedimentary sequences before 1900 were obtained by extrapolation of the sedimentation rate determined in upper layers, measuring the core depth in cumulative mass per surface unit, and discounting volcanic ashes from bulk sediments by estimating the fraction in each layer from the analysis under binocular microscope.

The organic matter content (OM) of the freeze-dried sediments was estimated as loss on ignition (LOI) at 550°C for 4 h.

Total Hg was analyzed by atomic absorption spectrometry directly after high-temperature combustion and catalytic reduction using a Milestone Direct Mercury Analyser (DMA 80, Milestone Inc., Monroe, CT, USA, http://www.milestonesci.com/mercury-dma.php) according to the US-EPA Method 7473 (US-EPA, 2007), and following the quality assurance routines of the laboratory at ITM as specified under Swedish Accreditation (SWEDAC Nr. 1295, Swedish Board for Technical Assistance, http://www.swedac.se). Samples were frequently replicated (up to fourfold), and blanks and certified standard reference materials (here GBW07405/NCS DC 73323) were analyzed daily to assure adequate performance and accuracy. Detection limit (3 SD of blanks) for the applied procedure was $<3\,ng.g^{-1}$ DW. Precision (1 RSD at

>100 ng.g^{-1} DW) was 2% in homogenous reference samples and 4% in actual samples. Total Hg was determined in bulk sediment except for tephra layers, where the <63 μm fraction was analyzed.

The elemental composition of the sediment samples was determined by Instrumental Neutron Activation Analysis, as described by Daga et al. (2008). The elements measured were major elements including Al, Ca, Fe, Mg, Mn, Na, K, and Ti, rare earths elements La, Ce, Nd, Sm, Eu, Tb, Tm, Yb, Lu, and other relevant trace elements including Sb, As, Ba, Br, Cs, Zn, Co, Cr, Hf, Sc, Sr, Ta, Th, U, and V. The elements selected are biological and geological tracer that could provide information on environmental changes.

Records of subfossil chironomid assemblages were studied in Lake Tonček sediments by picking up head capsules from the sediment according to standard methods (Walker, 2001). The chironomid head capsules were mounted on microscope slides and identified using current taxonomic guides, determining the relative abundance profile of each taxon.

Biogenic silica (BSi) concentration was measured in Lake Tonček sediments using the method outlined by DeMaster (1981). Sediment samples that weighed about 20 mg were leached in 1% Na_2CO_3 over time, and aliquots were analyzed for BSi concentrations using the reduced molybdosilicate acid colorimetric method. Weight percent of total silica was plotted versus time and the extrapolated intercept was used to calculate the BSi concentration of the sediment.

3 Results

3.1 Sediment sequences dating

A sediment accumulation rate of 13.3 mg cm^{-2} y^{-1} (0.058 cm y^{-1}) and a ^{210}Pb flux of 23.7 Bq m^{-2} y^{-1} were determined in the upper 5 cm of the Lake Moreno Oeste sequence (Daga et al., 2008), whereas a sediment accumulation rate of 26.3 mg cm^{-2} y^{-1}

($0.105\,cm\,y^{-1}$) and a ^{210}Pb flux of $74.2\,Bq\,m^{-2}\,y^{-1}$ were obtained for the upper 7 cm of Lake Tonček. Tephra layers are evidenced in the ^{210}Pb profile as depressed or even negligible activities of unsupported ^{210}Pb (total ^{210}Pb minus supported ^{210}Pb, in secular equilibrium with ^{226}Ra). Such a decrease of unsupported ^{210}Pb is observed in the 0.4–0.7 $g\,cm^{-2}$ layer of the Lake Moreno Oeste sequence (Fig. 2), corresponding to the 1948–1970 deposition period, and in the 1.0–1.3 $g\,cm^{-2}$ layer of the Lake Tonček sequence (Fig. 3), corresponding to the 1953–1964 deposition period. This decrease is compatible with the Puyehue-Cordon Caulle and Calbuco volcanic events in 1960–1961 (Daga et al., 2008) causing bulk sediment dilution by volcanic ashes, which were also identified under binocular magnifying glass. Unsupported ^{210}Pb values in these layers were corrected before dating. It is necessary to emphasize that the dating before 1900, which is based on the assumption that there was no persistent change in sedimentation rate, is somewhat uncertain particularly for early events. An independent dating corroboration was obtained in the Lake Moreno Oeste sequence. The tephra layer MO5 (Fig. 4) could be associated with a volcanic event in 1759, in agreement with the ^{210}Pb and ^{137}Cs dating extrapolation.

Interestingly, the ^{210}Pb flux is three fold higher in Lake Tonček compared to Lake Moreno Oeste, and it is the highest measured in the region based on 10 sedimentary sequences studied in a previous work (Ribeiro Guevara et al., 2003). A positive correlation between ^{210}Pb flux and the OM concentration of the upper layer of these lakes was reported (Ribeiro Guevara et al., 2003), however Lake Tonček ^{210}Pb flux does not fit this correlation. The relative high ^{210}Pb flux to Lake Tonček sediments is consistent with the assumption that due to the characteristics of the catchment area, the sediments of this water body are a good recorder of atmospheric fallout, with relative low retention in the catchment area.

3.2 Mercury

The Hg concentration profiles of Lake Tonček and Lake Moreno Oeste, Llao Llao bay, sedimentary sequences are shown in Fig. 4, respectively. Hg fluxes to sediments (Fig. 5) were computed for each layer based on the core dating. The profiles of Hg concentration and Hg fluxes to the sediments of Lake Tonček sequence (Figs. 4 and 5) show five domains clearly demarcated. Low Hg levels were observed before 1200 and between 1350 and 1720, indicating background of 50 to 80 ng g^{-1} for concentration, and 15 to 25 μg m^{-2} y^{-1} for fluxes. In the upper core section, starting about 1900, Hg levels increase from low values (though above background) to reach a concentration of 200 ng g^{-1} and a Hg flux of 60 μg m^{-2} y^{-1} at present. Two intermediate sections show Hg values noticeably elevated above background. From 1720 to 1900, Hg peaks alternate with low to intermediate values, with higher values ranging in concentration from 380 to 480 ng g^{-1}, and in fluxes from 140 to 150 μg m^{-2} y^{-1}. From 1200 to 1350, Hg values show two marked peaks, which reach concentrations of 360 and 420 ng g^{-1} and fluxes of 110 and 130 μg m^{-2} y^{-1}, respectively. Lake Moreno Oeste Hg profiles (Figs. 4 and 5) exhibit a similar pattern as Lake Tonček, showing correlation in the occurrence of high Hg. Background Hg values range in concentration from 50 to 80 ng g^{-1}, and in Hg fluxes from 7 to 10 μg m^{-2} y^{-1}, while Hg peaks range in concentration from 300 to 650 ng g^{-1}, and in Hg fluxes from 35 to 55 μg m^{-2} y^{-1}.

3.3 Environmental tracers

The analysis of fossil chironomids in the lake Lake Tonček sequence allowed the identification of twelve taxa corresponding to subfamilies Orthocladiinae, Tanypodinae, Podonominae and Chironominae (Tribu Chironomini). The dominant taxon of the chironomid community along the sequence was the cold-stenothermic *Pseudosmittia* Goetghebuer (Rizzo et al., 2007). The OM contents ranged from 6 to 18%, with the highest value in the upper most layer and decreasing in the tephra layers (Fig. 6). The BSi concentration exhibited a similar trend, with the exception of two peaks at the 7.5

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and 25 g cm^{-2} depth (Fig. 6). Selected major and trace element concentration profiles show different patterns (Figs. 6 and 7), rather constant for major Mn and Fe and trace elements As, Cr and Zn, and a noticeable increase of Sb at 1 g cm^{-2} depth with higher variability in the lower layers.

4 Discussion

4.1 Mercury levels

Sediment Hg concentrations reaching levels as high as 400 to 650 ng g^{-1} DW already during pre-industrial accumulation periods as observed in our pristine lakes are far above the background values of 10 to 200 ng g^{-1} observed in other lakes (Ribeiro Guevara et al., 2005). Also the rates of Hg accumulation are higher than background levels in the region, from 2 to 8 μg m^{-2} y^{-1} (Biester et al., 2002; Cooke et al., 2009) or in the North-American Arctic, where preindustrial fluxes range from 1 to 53 μg m^{-2} y^{-1} and present fluxes from 2 to 114 μg m^{-2} y^{-1} (Lockhart et al., 1998). In the upper Midwest of the USA Hg fluxes in pre-industrial sediment layers rarely exceed 20 μg m^{-2} y^{-1}, and the maximum fluxes observed here in a pristine area of the Southern Hemisphere were only exceeded by the highest values in urban areas with industrial pollution (200 to 300 μg m^{-2} y^{-1}, Engstrom and Swain, 1997). Even in a Hg deposition hotspot area in the USA, recent maximum values reached only 90 μg m^{-2} y^{-1}, after increasing constantly from 7 μg m^{-2} y^{-1} in 1880 (Hutcheson et al., 2008). Accordingly, the sediment domains with high Hg accumulation in our lakes during pre-industrial periods (up to 150 μg m^{-2} y^{-1}) must be associated to some abrupt phenomena generating Hg inputs to aquatic environments corresponding to industrial pollution.

4.2 Lakes and mercury

Several watershed features influence the Hg concentration in lake sediments. Parameters of catchment morphometry, such as large drainage area, high catchment and lakebed slopes, and large lake depths could be associated to elevated Hg concentrations in lake sediments (Grigal, 2002; Kainz and Lucotte, 2006). Moreover, dense forest zones in the catchment area are an important source of Hg to the aquatic systems (Kolka et al., 2001; Porvari et al., 2003; Driscoll et al., 2007). Therefore, according to the general characteristics of the water bodies and catchment areas, higher sediment Hg concentrations should be expected in Lake Moreno Oeste relative to Lake Tonček, with a smaller drainage area, shallower lake depths and almost absence of vegetation. Particular characteristics of the Lake Tonček watershed have to be considered regarding Hg concentrations in sediments. An important part of the watershed is covered by wetlands and this kind of lands and their internal processes (high rates of organic matter decomposition, sulphate-reducing conditions, potential for methylation) play an important role in the Hg cycle (Goulet et al., 2007; Driscoll et al., 2007; Selvendiran et al., 2008; Larssen et al., 2008). Further, the snow cover for 6 to 8 months per year facilitates the snow-to-air Hg reemission after photoreduction, which could alter the fate of Hg after atmospheric deposition as observed in high altitude/latitude environments (Schroeder et al., 1998; Lalonde et al., 2000; Steffen et al., 2008), although photoreduction also occurs in the water column for all lakes. Also, in warmer periods, the snowmelt and summer storms can represent a significant portion of the annual water and Hg flux from the watershed (Grigal, 2002; Schuster et al., 2008). These features may explain the differences in Hg sequestration between Lake Tonček and Lake Moreno Oeste, even though a detailed evaluation of the impact exceeds the frame of the present work.

Even though lakes may differ, our sediment data show substantial and apparently synchronous changes over time. It is remarkable that the Hg profiles in both sequences show a similar pattern regarding the domains of high pre-industrial Hg, supporting the hypothesis stated previously that external, abrupt phenomena generated substantial Hg inputs to these aquatic environments. The questions arising afterwards are on the records of environmental changes generated by these phenomena and on the Hg sources.

4.3 Environmental factors

The identification of tephra layers in the sediment sequences is the most concrete evidence of an environmentally disrupting phenomenon, as well as a potential Hg source: a volcanic eruption. Environmental changes can also be traced at the biological level. Here, the variations in chironomid communities was studied in the Lake Tonček sequence in order to identify population changes that could be associated to environmental events or Hg inputs although direct heavy metal pollution is recorded better in morphological deformities. Changes in the chironomid assemblages were observed in Lake Tonček sequence, some of them associated with tephra layers. The change of taxa in relative composition allowed the identification of two sections; the oldest accumulation period corresponding to the 11th to 17th centuries with taxa indicating a colder environment, followed by a period with temperate environment (Rizzo et al., 2007). But no correlation was observed between the variation in the chironomid assemblages and the two domains of high Hg. Moreover, the concentration profiles of the other elements as well as OM and BSi contents (Figs. 6 and 7), do not reproduce the Hg pattern nor do they show any correlation. The absence of correlation of the Hg concentration with the geochemical tracers studied suggests that no direct geological process in the water body or in the watershed can be associated with the high Hg values, whereas the lack of correlation with OM and BSi is not providing any evidence of biological processes explaining the high Hg values.

4.4 Mercury sources

The other question was on potential Hg sources that could explain in particular the two older domains of high Hg identified in the Lake Tonček and Lake Moreno Oeste sequences. One of them is the occurrence of local geothermal emissions (Varenkamp and Buseck, 1986; Nakagawa, 1999). Geothermal activity is usually manifested at the surface as emerging hot waters. Although there are some geothermal systems associated to recent magmatism near to this area, they are located along the Andean Range where the active volcanoes are located, about 50 km to the west (Fig. 1). Such indications have not been reported in or near Lake Tonček. There is no volcanic activity in this area that could provide the heat required to generate geothermal activity, and the geothermal energy generated from very deep heat sources is unlikely to reach 1750 m of altitude without emerging at any other site of the geological formation. On the other hand, the pattern of the Hg profile observed in Lake Moreno Oeste is similar, suggesting that concurrent phenomena generated the high Hg records in pre-industrial periods. Geothermal activity was not observed either in or near Lake Moreno. It seems unlikely that geothermal activity can be sufficiently extended to reach Lake Tonček and Lake Moreno Oeste without at the same time producing traces or reports of other geothermal manifestations. Therefore, geothermal activity is unlikely a Hg source to be considered here. Deforestation is another potential source of Hg to aquatic systems (Porvari et al., 2003). There are no records of massive deforestation previous to the Spanish colonization in this region, other than by extended forest fires. These were a common deforestation practice both before and after the Spanish colonization (Veblen et al., 2003), but may also have occurred naturally together with volcanic events (see below).

Volcanic events are a well-known source of Hg on a regional or global scale (Nriagu and Becker, 2003). For example, Schuster et al. (2002) observed in ice cores from the Upper Fremont Glacier, Wyoming, USA, Hg records associated with the eruptions of, among others, volcanoes Tambora (1815) and Krakatau (1883), situated in Indonesia,

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and determined a contribution of 6% from remote volcanic events to the Hg fallout over the last 270 yr. Tephra layers are fall ash deposits recording volcanic events that if associated to an increase in Hg concentration in the deposit or in the upper adjacent layer, give evidence of Hg releases produced by the volcanic eruption. Tephras TK1 and MO2, which correlate in time and correspond to a possible mixing of products from events at the volcanoes Calbuco and Cordón Caulle (Fig. 1) according to the geochemical characterization (Daga et al., 2008), show a significant increase of Hg in the overlying layer (Fig. 4), suggesting the occurrence of Hg gaseous emissions concurrent with the eruption impacting the aquatic systems. Moreover, the micro-tephra in Lake Tonček and tephra MO1 (Fig. 4), corresponding to a volcanic event in 1960–1961, precede also an increase in the Hg level. Tephra TK6 could be correlated in time with MO5, which shows a noticeable Hg increase in the overlying layers (Fig. 4). Tephra TK6 corresponds to a mixing layer with products from both Calbuco and Cordón Caulle events, while MO5 corresponds clearly to a Cordón Caulle eruption (Fig. 1). The upper sequence domain with high Hg concentrations shows tephras, or an overlying layer, with high Hg concentrations alternating layers with lower values. These Hg concentrations are the highest determined in the profile. Due to the sharp variations it is not possible to determine an increase over previous levels (Fig. 4), but also these high Hg concentrations could be evidence of a volcanic source. In the lower sequence domain with high Hg, tephra layers are concurrent in Lake Moreno Oeste but these volcanic events are not registered in Lake Tonček (Fig. 4). Nevertheless, these high Hg concentrations may be associated to gaseous emissions linked to volcanic events since volcanic ashes can show a highly variable spatial distribution (Daga et al., 2008), while the dynamics of Hg transport could be different.

Fires are a potential source of atmospheric Hg. Whitlock et al. (2006) studied the incidence of fires in this region during the last 10 000 yr by measuring charcoal concentrations in a sedimentary sequence extracted from Lake El Trébol, situated near Lake Moreno Oeste (Fig. 1). They computed also the ratio of (grass charcoal)/(total charcoal) which provides information about what component of the vegetation was burning and thus a distinction of surface fires that largely burn grass and herbs, fires that burn both surface cover and woody plants in a patchy manner, and stand-destroying crown fires. At Lake El Trébol, charcoal records declined between 3300 to 2000 yr before present (BP) and returned to high values between 1500 and 500 yr BP. The last 2000 y section of this sequence features variable fire-episode magnitudes, high fire frequency, and short fire-free intervals. Two fire episodes of high magnitude were registered in the Lake El Trébol sequence around 800 and 900 yr BP, the more recent being the highest in charcoal contents during the 10000 yr BP period studied. They are associated to a high peak of the ratio of (grass charcoal)/(total charcoal), thus representing the burning of grass and herbs. These high charcoal records are coincident with the lower domain of high Hg domain observed in Lake Moreno Oeste and Lake Tonček with a date estimated to 1200 to 1350.

Forest fires release other trace elements to the atmosphere together with Hg (e.g. As, Br, Ca, Cr, Fe, Mg, Mn, Se, Ti, V, or Zn) in aerosols or gaseous form, but their imprint in lake sediment sequences depends strongly on the transport dynamics in the atmospheric media, in the watershed and in the water column (Yamasoe et al., 2000; Radojevic, 2003), and no correlation between fires and trace element contents in lake sediment sequences was observed in some cases (MacDonald et al., 1991; Virkanen, 2000). Moreover, high Hg enrichment in air above background concurrent with no significant variation in any other trace elements, was observed associated with forest fires (Anttila et al., 2008). Therefore, the lack of correlation between Hg and the other trace elements analyzed in the present work does not preclude forest fires as a potential Hg source.

Extended forest fires associated with human activities occurred indeed during the 18th and 19th centuries. Native Americans affected fire regimes and the landscapes of Northern Patagonia through intentional burning for various purposes, which occasionally might have lead to wildfires (Veblen et al., 2003). European settlement, starting in the region about 1850 but earlier in Chile (since the end of the 17th century), was associated with large fires for forest clearance, intensive livestock grazing, and opening of paths across the Andes through the forest (Veblen et al., 1992). From 1890 to 1920 extensive areas of wet forests were burned in the study region by European settlers, in a failed effort to convert forests to cattle pasture (Kitzberger et al., 1997). Particularly, direct observation of large burns was reported in 1787 in the Lake Nahuel Huapi region, towards the lake South-West (Veblen et al., 2003). By analyzing tree-ring data, Kitzberger et al. (1997) determined the occurrence of an extended fire in Lake Roca (Fig. 1) in 1827. These fires may well have had an impact directly on the Lake Tonček watershed due to the predominantly westerly winds, reaching possibly also Lake Moreno Oeste watershed (Fig. 1). These events coincide with the upper domain of high Hg at Lake Tonček and Lake Moreno Oeste sedimentary sequences. In both periods, the fire records are concurrent with ENSO (El Niño-Southern Oscillation) events which may enhance environmental conditions favouring extended fires.

In conclusion, the correlation of both high Hg domains in the Lake Moreno Oeste and Lake Tonček sequences with records of extended fires in the region suggests that this source, as well as the volcanic activity, could have generated the high levels and variations of Hg concentrations and accumulation rates observed in these pristine lakes already in pre-industrial times.

Acknowledgements. P. Kärrhage is gratefully acknowledged for technical assistance with the Hg analyses, and also R. Sánchez for the collaboration in sediment sampling. This work was funded by project PICT 13-13276, Agencia Nacional de Promoción Científica y Tecnológica, Argentina.

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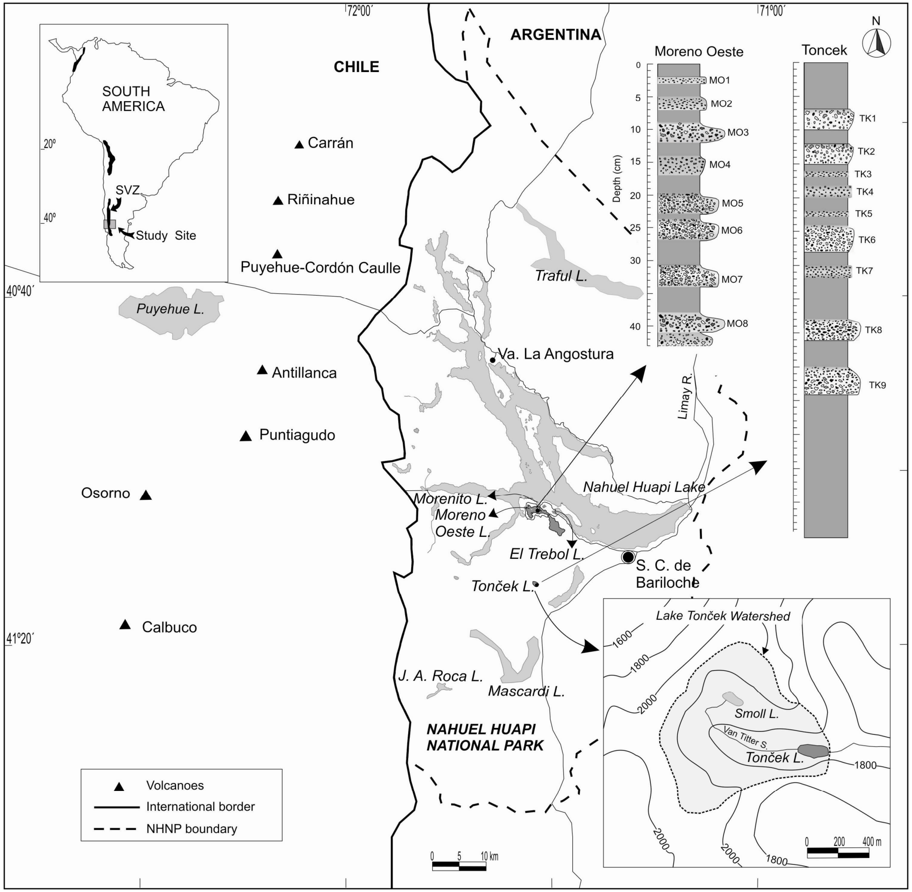

Fig. 1. Study area. Section of Nahuel Huapi National Park, northern Patagonia, Argentina.

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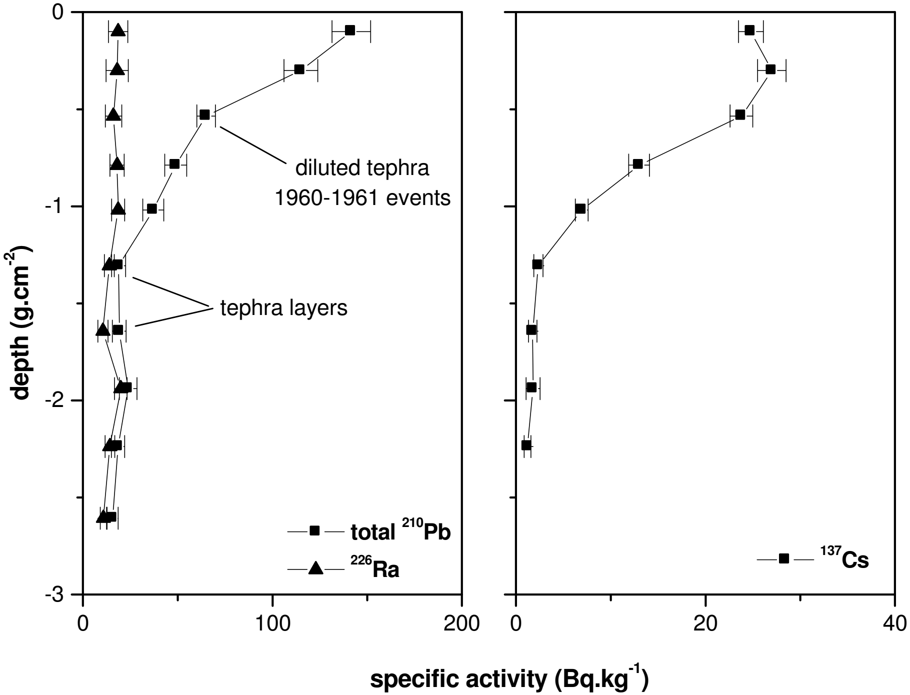

Fig. 2. Moreno Oeste sedimentary sequence. Specific activity profiles ^{137}Cs, ^{210}Pb, and ^{226}Ra (in secular equilibrium with supported ^{210}Pb).

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Sediment records of highly variable mercury inputs to mountain lakes

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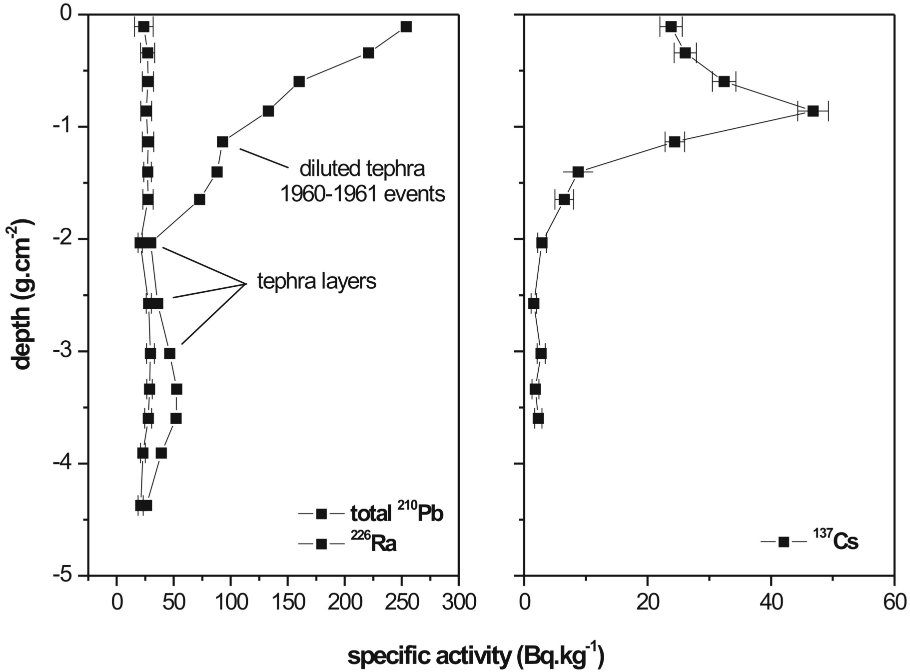

Fig. 3. Lake Tonček sedimentary sequence. Specific activity profiles ^{137}Cs, ^{210}Pb, and ^{226}Ra (in secular equilibrium with supported ^{210}Pb).

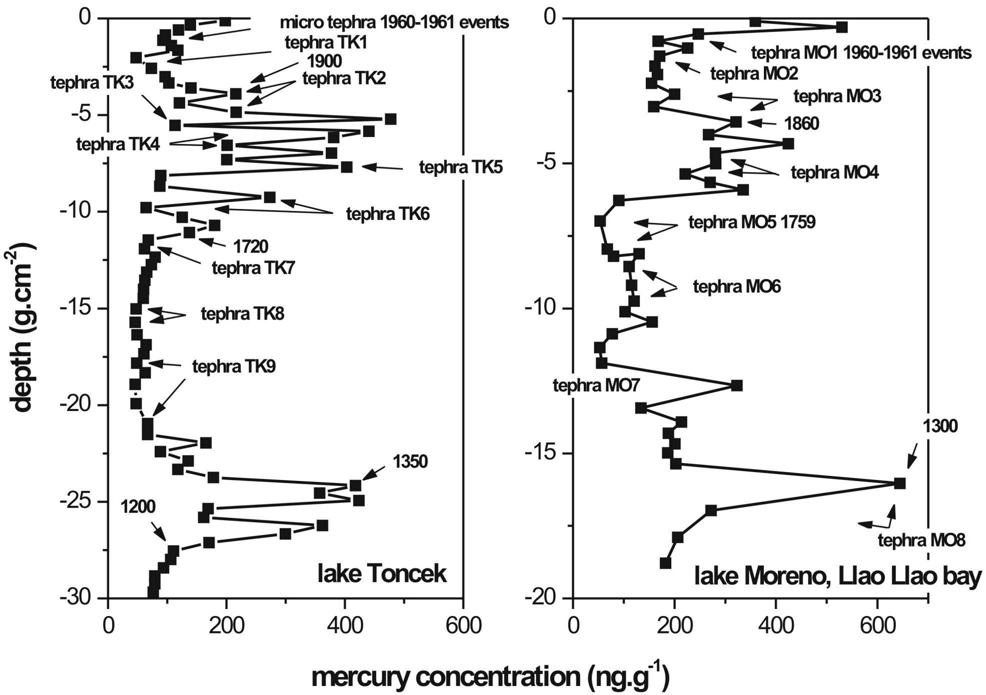

Fig. 4. Mercury concentration profiles. Lake Tonček and Lake Moreno Oeste (Llao Llao bay) sedimentary sequences.

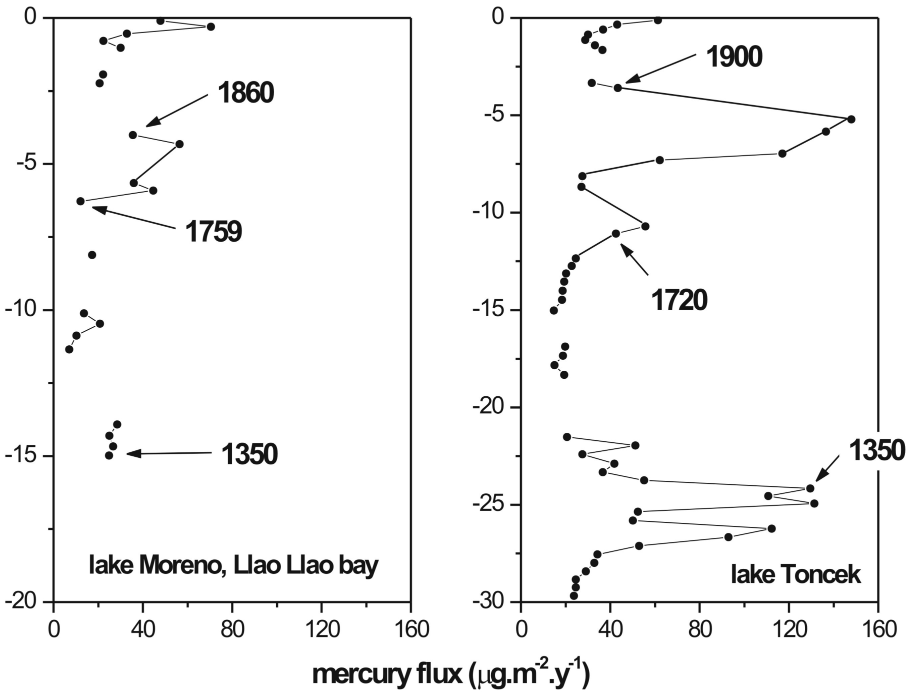

Fig. 5. Mercury fluxes to sediments. Lake Moreno Oeste (Llao Llao bay) and Lake Tonček sedimentary sequences.

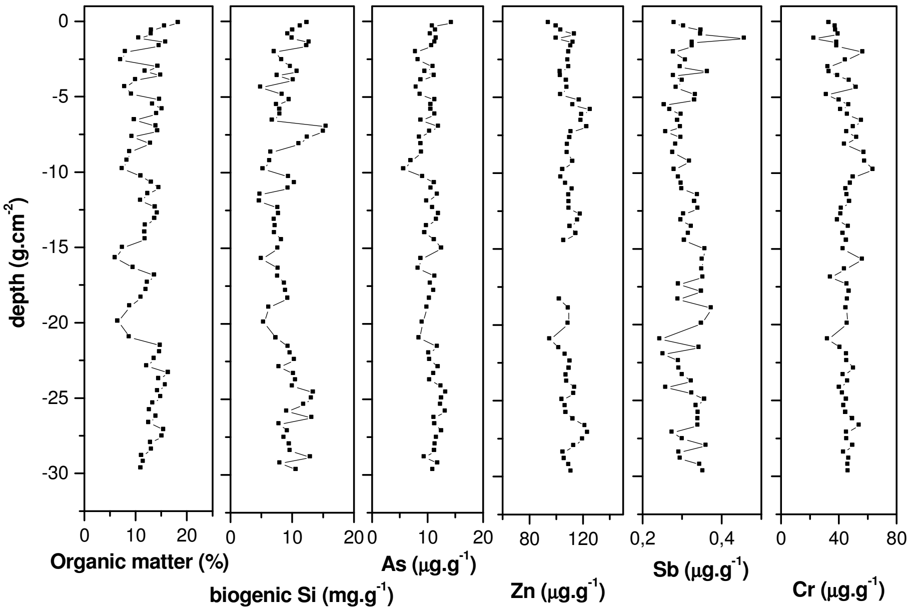

Fig. 6. Lake Tonček sedimentary sequence. Organic matter, biogenic Si and heavy metals concentration profiles.

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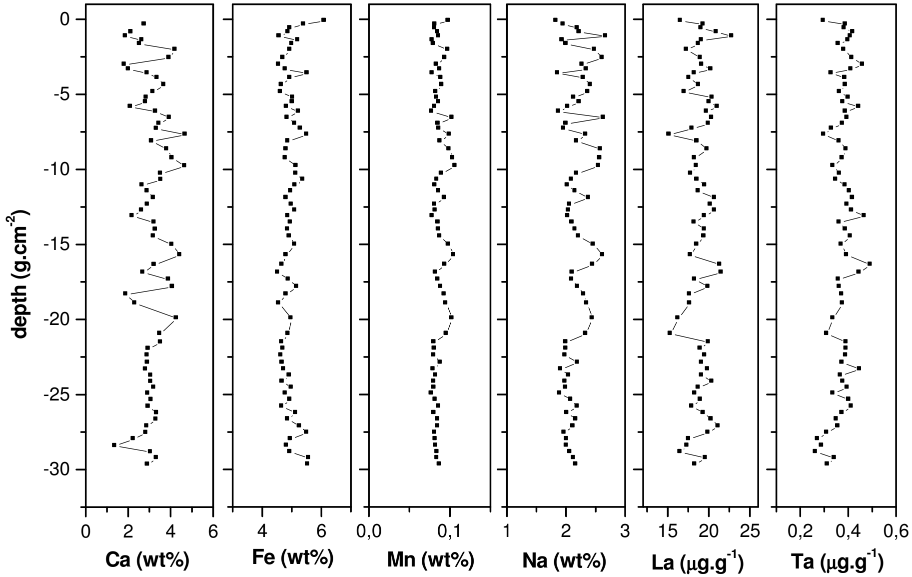

Fig. 7. Lake Tonček sedimentary sequence. Selected major elements and geochemical tracer concentration profiles.

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