



## Mercury in an ultraoligotrophic North Patagonian Andean lake (Argentina): Concentration patterns in different components of the water column

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### Abstract

The deep, ultraoligotrophic piedmont lakes of Northern Patagonia (Argentina) are located in pristine and barely impacted areas, along a wide latitudinal range. Several studies have reported moderate to high total mercury (Hg) concentrations and contrasting methylmercury ( $\text{CH}_3\text{Hg}^+$ ) production in different lake compartments. Sources of Hg for western Patagonian terrestrial and aquatic ecosystems are still not clear; while point sources can be ruled out and atmospheric deposition is a plausible source, along with contribution from active volcanic areas of the Andes. In this investigation, we reported a noticeably seasonal, spatial (between lake branches), and vertical (between water column strata) heterogeneity in the total Hg concentrations found in the pelagic zone of Lake Moreno. Sterile water samples taken in a depth profile of the lake showed moderate to high concentrations of  $\text{CH}_3\text{Hg}^+$  in autumn with a decreasing trend with depth. Our results indicated that Hg is largely allocated in the plankton fraction between 10–53  $\mu\text{m}$ ; which dominated within the euphotic (epilimnetic) zone of the lake due to the high densities attained by two species of the dinoflagellate *Gymnodinium*. The 53–200  $\mu\text{m}$  planktonic size fraction (comprising rotifers, ciliates and immature stages of crustaceans) and the > 200  $\mu\text{m}$  fraction (calanoid copepods and cladocerans) were found to bear strikingly lower total Hg concentrations, suggesting that the magnification of Hg at the planktonic consumer level is negligible.

**Key words:** Patagonia; deep lakes; total mercury; plankton

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### Introduction

Mercury (Hg) is a ubiquitous contaminant that can reach even remote aquatic ecosystems devoid of close natural or anthropogenic sources (Nriagu, 1989). This contaminant, mostly in its inorganic form ( $\text{Hg}^{2+}$ ), may enter the aquatic ecosystem by atmospheric deposition, watershed drainage, or wastewater discharges. Once in the system, methylmercury ( $\text{CH}_3\text{Hg}^+$ ) production from  $\text{Hg}^{2+}$  takes place by natural processes occurring in different biotic and abiotic compartments in the sediment and water column (Ullrich et al., 2001). The inorganic  $\text{Hg}^{2+}$  form predominates in the abiotic environment while the organic  $\text{CH}_3\text{Hg}^+$  form tends to bioaccumulate in the biological compartment (Ullrich et al., 2001), posing a potential threat to aquatic biota due its neurotoxicity.

The trophic levels at the base of pelagic food webs (e.g., picoplankton, phytoplankton, and zooplankton) are known to be a critical link in the transfer of Hg to higher trophic levels. In certain environments, plankton biomass has been found to be correlated negatively with Hg content in fish (Chen et al., 2005; Chen and Folt, 2005).

The deep, ultraoligotrophic piedmont lakes of Northern

Patagonia (Argentina) are located in pristine and barely impacted areas along a wide latitudinal range. Previous studies have reported moderate to high total Hg (THg) in different compartments of deep Andean lakes of the Nahuel Huapi National Park (Arribére et al., 2008; Ribeiro Guevara et al., 2004, 2005a); these levels are, however, within the range reported for other unpolluted systems. The impact of other heavy metals in the lakes of the study region have been also investigated (Arribére et al., 2008; Ribeiro Guevara et al., 2004, 2005a, 2005b). Sources of Hg in the aquatic ecosystems of western Patagonia are still not clear, however, atmospheric deposition and the volcanic activity of the Andes are plausible sources.

One of the most interesting patterns found in the Hg dynamics of Lake Moreno concerns the entry of  $\text{CH}_3\text{Hg}^+$  into the lake food web, which seems to occur mostly within the water column. The sediment appears to be minimal source of  $\text{CH}_3\text{Hg}^+$ , as it has a low potential for  $\text{Hg}^{2+}$  methylation (Ribeiro Guevara et al., 2009). Previous  $\text{Hg}^{2+}$  methylation studies with  $^{197}\text{Hg}$  radiotracer found that up to 50% conversion of inorganic  $\text{Hg}^{2+}$  to  $\text{CH}_3\text{Hg}^+$  in Lake Moreno water collected from 30 m depth corresponded to the deep chlorophyll maximum. Sterile water (< 0.2  $\mu\text{m}$  filtered) was found to contribute up to 30% to the process,

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whereas the presence of planktonic organisms  $< 50 \mu\text{m}$  and the presence of light accounted for the remainder of the measured Hg(II)-methylation (Ribeiro Guevara et al., 2008). This previous study suggests that the water column may play a key role in the conversion of  $\text{Hg}^{2+}$  to  $\text{CH}_3\text{Hg}^+$  in these deep lakes. The Patagonian lakes are also exposed to high levels of UV radiation and strong westerly winds, factors known to impact their light-depth regime, thermal structure and, ultimately, the development and adaptation of their biotic communities (Morris et al., 1995; Marinone et al., 2006; Modenutti et al., 2008).

In the current study, we analyzed THg concentrations in the pelagic base-of-food web compartment of the deep and ultraoligotrophic Lake Moreno (North Patagonia), taking into account differences in planktonic size fractions as a function of depth, as well as seasonal variations. We also studied the relative abundance of the species occurring in three size-fractions of planktonic assemblages ( $10\text{--}53 \mu\text{m}$ ,  $53\text{--}200 \mu\text{m}$ , and  $> 200 \mu\text{m}$ ) and analyzed the potential role of these biotic assemblages in the Hg dynamics of the pelagic zone.

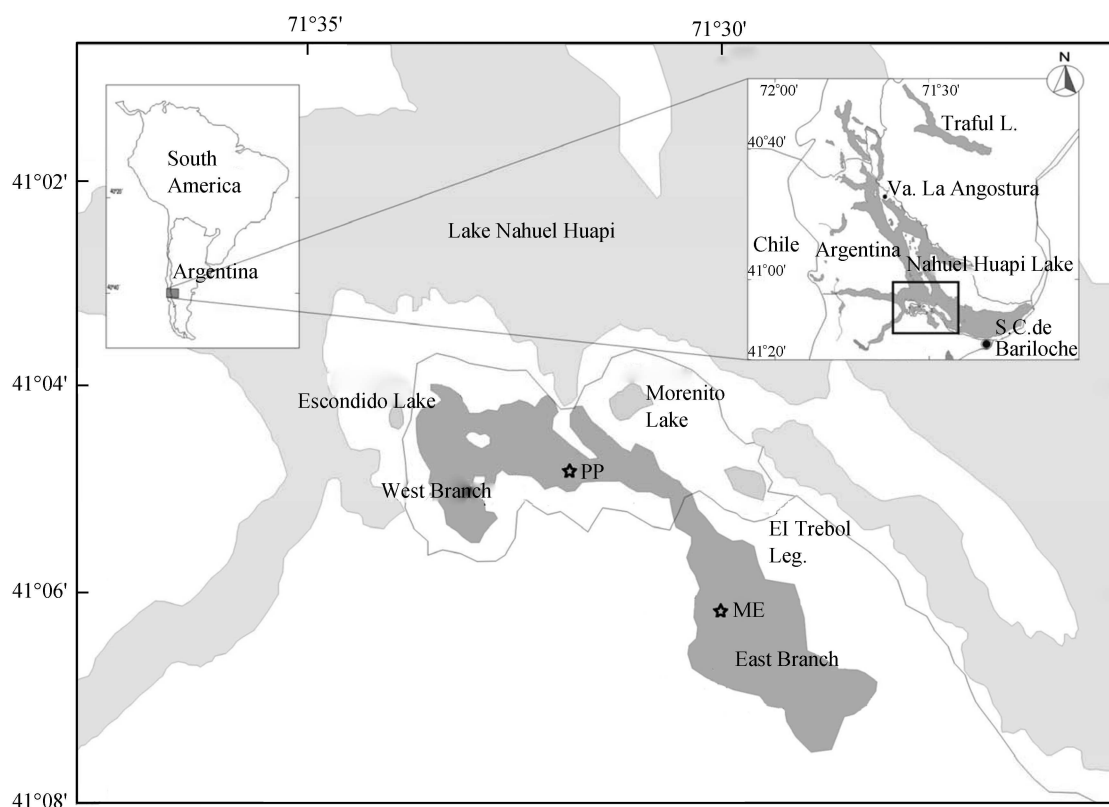
## 1 Experimental

### 1.1 Study site

The study was performed in Lake Moreno, a large piedmont lake located at  $41^\circ 5'S$ ;  $71^\circ 33'W$  and 758 m above sea

level in Northwestern Patagonia (Argentina) (Fig. 1). Lake Moreno has two well-defined branches (West and East) comprising a total surface of approximately  $9 \text{ km}^2$ , with waters flowing from the East Branch to the West Branch. The maximum depth of the West Branch is approximately 90 m whereas the East Branch reaches approximately 120 m. The lake is warm monomictic with temperature fluctuating between  $15$  and  $17^\circ\text{C}$  in the epilimnion, and averaging  $7^\circ\text{C}$  at the hypolimnion. Light penetrates deep in the water column (euphotic zone approximate 35 m depth) due to low water attenuation coefficients associated with the extremely low levels of dissolved organic carbon (Morris et al., 1995). Lake water is slightly acidic, with pH around 6.8. The lake is ultraoligotrophic, with low N and P concentrations (Queimaliños, 2002).

Lake Moreno is located in Nahuel Huapi National Park, and is strictly regulated with respect to water collection and wastewater spills. There is a growing urbanization in the watershed of lake Moreno, the potential impact of which have yet to be evaluated. Moreover, there is a golf course located on the Northern isthmus of the West Branch (Fig. 1). Hg contamination to soil and waters associated with fungicidal applications to golf courses has been reported by Matthews et al. (1995). While there is no record of this practice in the area it could be implied as a potential source of Hg to Lake Moreno, from either run off associated with past fungicidal applications or direct releases associated with current applications.



**Fig. 1** Map of Lake Moreno, Nahuel Huapi National Park, Patagonia (Argentina). PP and ME are the sampling sites located at the West Branch and East Branch of the lake, respectively.

## 1.2 Sampling

Plankton samples were collected seasonally in Lake Moreno in 2006 and 2007 at two different stations, one located in the West Branch (PP) and the other in the East Branch (ME) (Fig. 1). The samples were taken via vertical tow performed with three different plankton nets (10, 53 and 200  $\mu\text{m}$ ) from 20 and 50 m depth to surface at midday. Plankton samples were immediately size-fractionated as follows: (1) samples taken with the 10  $\mu\text{m}$  mesh net were sieved sequentially through 200  $\mu\text{m}$  and 53  $\mu\text{m}$  mesh nets obtaining a fraction corresponding to 10–53  $\mu\text{m}$ ; (2) samples taken with the 53  $\mu\text{m}$  mesh net were sieved through 200  $\mu\text{m}$  mesh nets, obtaining a fraction corresponding to 53–200  $\mu\text{m}$ ; (3) samples taken with the 200  $\mu\text{m}$  mesh were not sieved. All samples were concentrated at the laboratory by vacuum filtering through a 0.2  $\mu\text{m}$  nitric acid washed polycarbonate filter until reaching a volume < 250 mL. An 5 mL aliquot of the autumn samples were sub-sampled and preserved in 4% formaldehyde to determine the species composition and their relative abundance. All samples were freeze-dried to constant weight and sealed in quartz vials for Hg determination via Instrumental Neutron Activation Analysis (Arribère et al., 2008).

In order to determine the  $\text{CH}_3\text{Hg}^+$  content in Lake Moreno water, samples of unfiltered lake water were collected using a Schindler-Patalas trap (12 L) from 80, 30, and 5 m depth at station PP. The trap consists of a transparent acrylic box with no metal part in contact with the sample, and silicone seals for trace metal sampling. When the trap was deployed, the box top and bottom remained open, letting the water to flow through. Upon reaching the sampling depth, the trap pulled upwards closing the box top and bottom, keeping the water sample inside. The trap was cleaned in the laboratory previous to field work with an acid solution and then rinsed with distilled water, and rinsed again in the field with lake water prior to use. Water samples were transferred to the laboratory in acid washed plastic containers and stored in the dark. Subsequently, the previously unfiltered water samples were sequentially filtered through 53  $\mu\text{m}$  mesh net and 0.2  $\mu\text{m}$  pore filters (sterile filtration), and stored in Teflon bottles in the dark at room temperature for one week, until their arrival at the Department of Environmental Sciences, Jozef Stefan Institute (Ljubljana, Slovenia).

## 1.3 Laboratory analysis

The plankton species composition and relative abundance were examined under a direct microscope at 400 $\times$ . Aliquots of 1 mL were taken from concentrated (5 mL) autumn samples and transferred into a Sedgewick-Rafter counting chamber. All individuals in each 1 mL aliquot were counted and measured. A total of 5 aliquots were counted.

The specific dry weight of some planktonic species were obtained either from the literature (Bottrell et al., 1976; Stemberger and Gilbert, 1985) or by direct measurement of dried and pooled individuals collected from Lake Moreno. Such was the case of *Boeckella gracilipes*

and *Ceriodaphnia dubia*, of which 100 individuals were separated from bulk plankton samples using a Pasteur pipette, transferred to a pre-weighed GF/F filter and dried at 60°C until constant weight. The specific dry weight was used to evaluate the dry mass fraction corresponding to each species, taking into account the fraction of each species obtained from microscopic counts.

Total Hg concentration in the plankton samples was determined by Instrumental Neutron Activation Analysis. The samples were irradiated in the RA-6 nuclear reactor (Centro Atómico Bariloche, Argentina,  $\phi_{\text{th}} \approx 6 \times 10^{12}$  n/(cm<sup>2</sup>·sec);  $\phi_{\text{pi}} \approx 2 \times 10^{11}$  n/(cm<sup>2</sup>·sec)) for 24 hr. Gamma-ray spectra were collected using an intrinsic HPGe *n*-type detector, 12.3% relative efficiency and a 4096-channel analyser, whereas the spectra were analysed by using the GAMANAL routine included in the GANAAS package, distributed by IAEA (International Atomic Energy Agency). Elemental concentrations were determined using the absolute parametric method with nuclear constants from current tables (Firestone and Shirley, 1996; Mughabghab et al., 1981; Tuli, 2005). Analytical errors were computed as the propagation of the uncertainties associated with the nuclear parameters, the efficiency of the gamma-ray detection system, the neutron flux determinations, and the area of the specific emission considered. Standard reference materials (IAEA 336 lichen, IAEA 0390 algae environmental level, IAEA 0391 algae low level, IAEA 0392 algae high level, NRCC-DORM-2 dogfish muscle, and NRCC-TORT-2 lobster hepatopancreas), as well as sample replicates were analysed for analytical quality control. The results of the analysis showed good agreement with certified values, as well as among replicates.

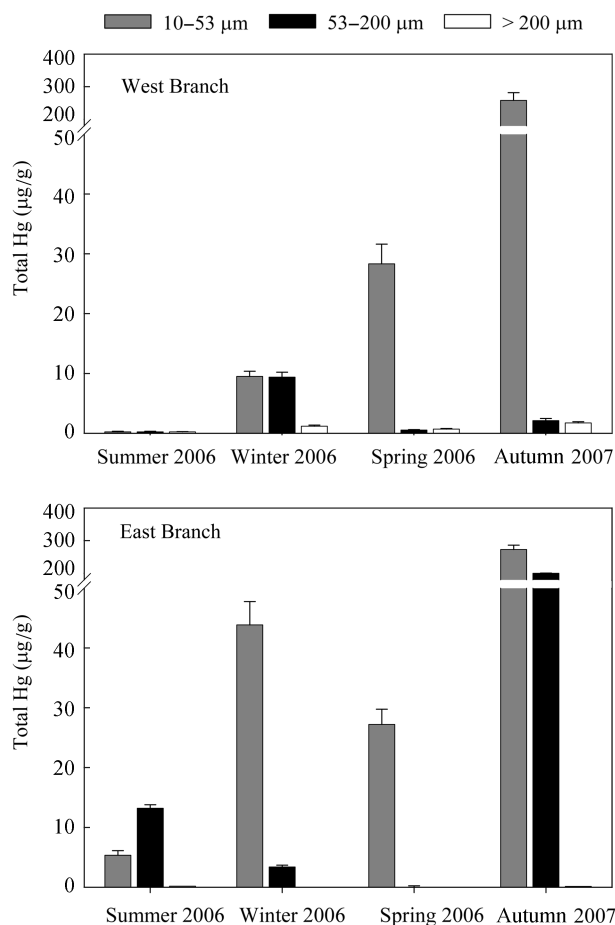
$\text{CH}_3\text{Hg}^+$  in filtered (0.2  $\mu\text{m}$ ) overlying water was determined by acidification and organic solvent extraction using  $\text{CH}_2\text{Cl}_2$ , back-extraction into water, aqueous-phase ethylation, gas chromatographic separation, pyrolysis and CVAFS detection (Liang et al., 1994).

## 2 Results

The freeze-dried biomasses of the size-fractionated plankton samples ranged from 3 to 19 mg dry weight (dw) for the 10–53  $\mu\text{m}$  fraction, 6 to 31 mg dw for the 53–200  $\mu\text{m}$  fraction, and 38 to 180 mg dw for the > 200  $\mu\text{m}$  fraction.

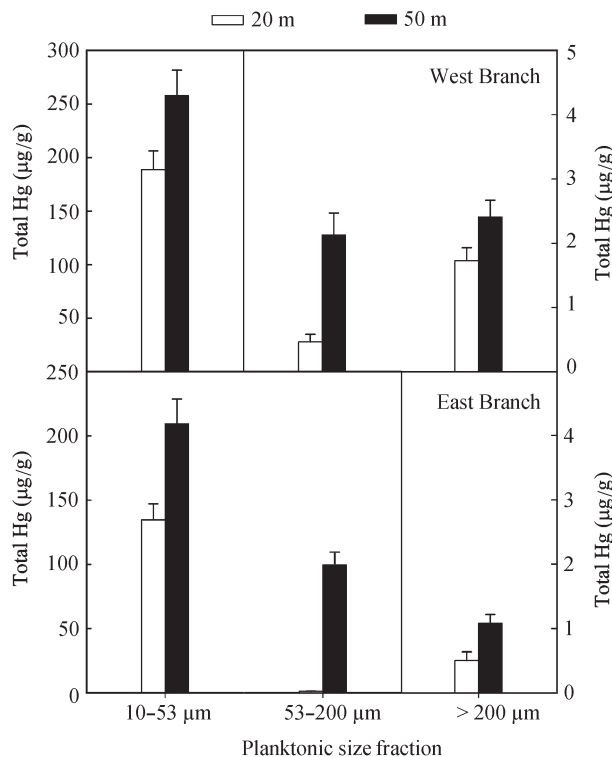
### 2.1 Seasonal patterns of THg in planktonic fractions

THg concentrations of size-fractionated plankton collected seasonally in Lake Moreno increased from spring to autumn (Fig. 2). Seasonal THg also varied between the East Branch and West Branch (Fig. 3). This variation may be related to the observed differences in plankton composition of the three size fractions (Fig. 4). It is worth noting that the pattern of THg concentration observed in the different size fractions was similar throughout seasons. In general, the highest THg concentration was associated with the 10–53  $\mu\text{m}$  plankton fraction, composed mostly by phytoplankton and mixotrophic ciliates, while much lower THg concentrations were observed in the two consumers fractions (53–200  $\mu\text{m}$  and > 200  $\mu\text{m}$ ) represented



**Fig. 2** Seasonal changes in total Hg concentration measured in the planktonic size fractions occurring in the upper 50 m of Lake Moreno. The error bars represent the propagated uncertainties computed as described in Section 1.3.

by ciliates, rotifers, copepods, and cladocerans. Overall, higher THg was found during autumn in both branches of Lake Moreno, with concentrations ( $\pm$  uncertainty) as high as  $(258 \pm 24)$   $\mu\text{g/g}$  dw in the West Branch and  $(209 \pm 19)$   $\mu\text{g/g}$  dw in the East Branch for 10–53  $\mu\text{m}$  fraction. THg concentrations approximately two orders of magnitude lower were measured within the larger planktonic fractions analyzed, 53–200  $\mu\text{m}$  and  $> 200$   $\mu\text{m}$  (Fig. 2), suggesting that planktonic consumers have a low potential for Hg biomagnification. However, there was a marked spatial difference in THg content during autumn in 53–200  $\mu\text{m}$  fraction, which reached  $(2.1 \pm 0.3)$   $\mu\text{g/g}$  dw in the West Branch and  $(100 \pm 10)$   $\mu\text{g/g}$  dw in the East Branch of Lake Moreno. The THg content was particularly low in 10–53  $\mu\text{m}$  plankton fraction during summer,  $(0.247 \pm 0.087)$   $\mu\text{g/g}$  dw in the West Branch and  $(5.34 \pm 0.77)$   $\mu\text{g/g}$  dw in the East Branch. Spring values were higher and similar in both branches  $(28.3 \pm 3.3)$   $\mu\text{g/g}$  in the West Branch and  $(27.2 \pm 2.6)$   $\mu\text{g/g}$  dw in the East Branch. In contrast, winter levels showed a clear spatial difference with values of  $(9.5 \pm 0.8)$   $\mu\text{g/g}$  dw in the West Branch and  $(48.8 \pm 3.9)$   $\mu\text{g/g}$  dw in the East Branch. This winter pattern contrasts with autumn and spring measurements, but the levels are comparable to those found in summer (Fig. 2).



**Fig. 3** Total Hg concentration in the planktonic size fractions in the upper 20 and 50 m during autumn at Lake Moreno. The error bars represent the propagated uncertainties computed as described in Section 1.3.

## 2.2 Vertical pattern of THg in planktonic fractions

THg contents during autumn were found to be always higher in samples from 0–50 m depth, compared to the 0–20 m depth, regardless of either the planktonic size fraction or the lake site (Fig. 3). These vertically integrated samples again showed the highest THg concentrations associated with 10–53  $\mu\text{m}$  fraction, and overall higher values in the West branch of Lake Moreno. In general, 53–200  $\mu\text{m}$  and  $> 200$   $\mu\text{m}$  size fractions had higher THg concentrations in 0–50 m integrated tow than in 0–20 m tow. In this case, the proportional contribution of these two fractions to total planktonic biomass was comparatively low in 0–20 m tow than that in 0–50 m tow, which is likely due to the typical distribution at deeper strata of the water column of most species comprised in these size fractions, as that pointed out by Balseiro et al. (2001).

## 2.3 Specific composition of planktonic size fractions

The size fractions analyzed were essentially dominated by only a few species of different groups. Within 10–53  $\mu\text{m}$  fraction, the dominant organisms were dinoflagellates such as *Gymnodinium paradoxum*, *G. uberrimum*, and the ciliates *Stentor araucanus* and *Ophrydium naumanii*. Other organisms such as rotifer species (the dominant *Polyarthra vulgaris* and more rare *Keratella cochlearis*, *Synchaeta* spp., and *Conochilus unicornis*), immature stages of crustaceans (nauplii, copepodids and cladoceran juveniles), and filamentous diatoms were found in 0–50 m plankton tow. Thus, samples from this deeper integrated sampling were more diverse than those from 0–20 m tow, indicating

the preference of several planktonic species for deeper strata and the prevalence of *Gymnodinium* spp. and ciliates in shallower waters within the euphotic zone of the lake.

The analyses of the proportion of biomass of different planktonic species in Lake Moreno revealed some differences between the West Branch and East Branch, considering the relative contribution of certain species to the biomass within the three size fractions studied (Fig. 4). In the West Branch, the most abundant species found within 10–53 µm fraction in 0–20 m tow were *Gymnodinium* spp., and the ciliates *S. araucanus* and *O. Naumanii*, while in 0–50 m tow there were also a few rotifers and small immature stages of copepods and cladocerans (nauplii and copepodides of *Boeckella gracilipes*, juveniles of *Bosmina longirostris*) (Fig. 4, upper panel).

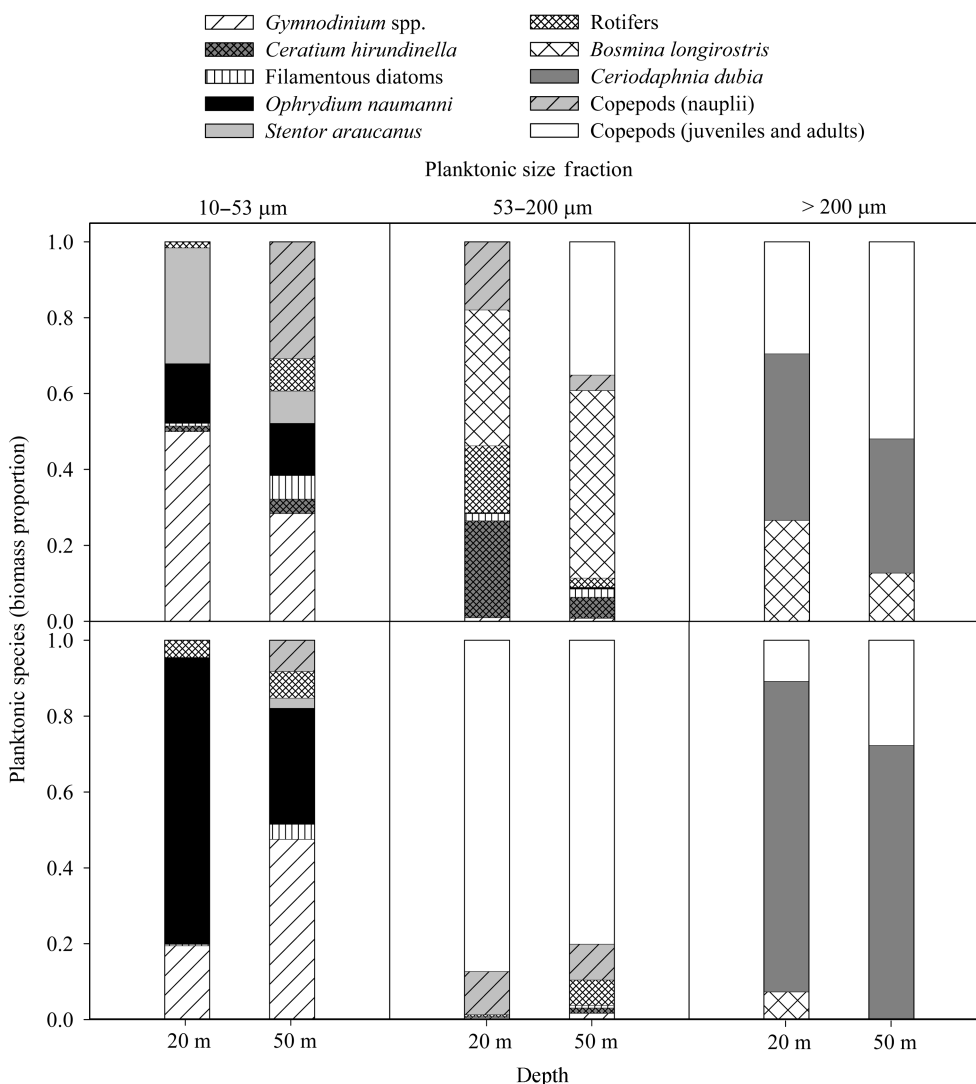
In 0–20 m tow, 53–200 µm fraction was mostly composed of the dinoflagellate *Ceratium hirundinella*, rotifers and juveniles of *B. longirostris*. In 0–50 m tow, the species composition was similar, however immature stages of the copepod *B. gracilipes* contributed largely to biomass. The > 200 µm fraction was mostly composed of the cladocerans *B. longirostris* and *Ceriodaphnia dubia*, and

by the copepod *B. gracilipes*. The copepod total biomass was higher in 0–50 m tow.

Some interesting differences between the two lake branches were noted for the different size fractions (Fig. 4). Briefly, in the East Branch, *S. araucanus* and *B. longirostris* were absent, with a consequent diminution in the diversity in their corresponding size fractions. Thus, in the East Branch of Lake Moreno, the 10–53 µm fraction was almost exclusively composed of high proportions of *O. naumanii* and *Gymnodinium* spp., while 53–200 µm fraction was dominated by immature stages of *B. gracilipes*, and > 200 µm fraction was dominated by the cladoceran *C. dubia* (Fig. 4, lower panel)

### 2.4 Methylmercury in water

Dissolved CH<sub>3</sub>Hg<sup>+</sup> in Lake Moreno waters collected at 5, 30, and 80 m in the pelagic zone of site PP decreased with depth. For the samples filtered through 53 µm mesh, CH<sub>3</sub>Hg<sup>+</sup> concentrations were 0.68, 0.36, and 0.26 ng/L at 5, 30, and 80 m depth, respectively, whereas CH<sub>3</sub>Hg<sup>+</sup> concentrations in sterile water (0.2 µm filtered) were 0.47 and 0.19 ng/L at 5 and 30 m depth, respectively. These values



**Fig. 4** Biomass proportion of the different planktonic species present in the size fractions collected in the upper 20 and 50 m depth of Lake Moreno in autumn. Upper panel: PP (West Branch); lower panel: ME (East Branch).

should be taken cautiously since samples were stored for one week prior to laboratory determination which may have influenced  $\text{CH}_3\text{Hg}^+$  contents. Hg transformation is very dynamic and, particularly, Lake Moreno water is highly reactive even in sterile condition (Ribeiro Guevara et al., 2008).

### 3 Discussion

It is recognized that dietary pathways in food webs are fundamental to quantitatively describe metal bioaccumulation (Wang, 2002). Mercury, in particular, is a potentially toxic pollutant that can occur naturally in aquatic ecosystems, and poses a serious risk to wildlife and human health through fish consumption (Karimi et al., 2007). The toxicological effects of Hg depend on the chemical species present, and the occurrence of different mercurial compounds are known to be driven by various physical, chemical, and biological factors (Ullrich et al., 2001). Biomagnification of Hg in aquatic ecosystems occurs as the organic  $\text{CH}_3\text{Hg}^+$  species. In contrast,  $\text{Hg}^{2+}$  may biodiminish up the food chain because of its comparatively reduced assimilation and higher loss through excretion (Mason et al., 1996; Tsui and Wang, 2004). Many studies have attempted to examine the trophic transfer of Hg by analyzing abiotic (sediments and water) and biotic compartments (phytoplankton, zooplankton and fish). Chen and Folt (2005) pointed out that the accumulation of Hg by the plankton is potentially the source of the high variation observed in Hg levels in higher trophic level biota among lakes.

The Hg dynamics in Lake Moreno certainly involves processes occurring in sediments and in water column. Previous studies performed in this lake have reported THg concentrations in sediments up to  $3 \mu\text{g/g dw}$  (Ribeiro Guevara et al., 2005a), although the sediments tested exhibited little potential for  $\text{CH}_3\text{Hg}^+$  production (Ribeiro Guevara et al., 2009). Also, THg concentrations up to 4 and  $7 \mu\text{g/g dw}$  have been reported in fish muscle and liver, respectively. Levels of THg in fish from the low-impacted Lake Moreno are higher than values reported from other pristine areas of the world, and may exceed the maximum  $\text{CH}_3\text{Hg}^+$  criteria level for fish as recommended by Argentine and US regulations (Arribére et al., 2008). Lake Moreno is not an isolated case in this regard; fish from oligotrophic lakes of other pristine areas may carry higher Hg burdens than those from more productive and eutrophic systems (Chen et al., 2005; Chen and Folt, 2005).

In most deep ultraoligotrophic lakes of the Patagonian Andes, the pelagic food web is a critical component of overall lake dynamics (Balseiro and Modenutti, 1998; Balseiro et al., 2007). The typical pelagic community of deep Andean lakes has low diversity and encompasses highly endemic biota (Modenutti et al., 1998). In Lake Moreno, the base of the food chain is characterized by a microbial community composed by picoplankton (autotrophic and heterotrophic bacteria), a few species of nanoplanktonic flagellates and *dinoflagellates* *Gymnodinium paradoxum* and *G. uberrimum* (Queimaliños, 2002). One of the most

interesting features of this lake is that the ciliates *Stentor araucanus* and *Ophrydium naumanii* dominate the zooplankton, and that a large proportion of the lake's total chlorophyll is packaged in their endosymbiotic algae (Queimaliños et al., 1999; Modenutti et al., 2008). Chlorophyll values in Lake Moreno are very low, with upper-end values of  $2 \mu\text{g/L}$ . This stems from the low abundances of phytoflagellates (up to  $1 \times 10^3$  cells/mL; Queimaliños et al., 1999) and ciliates (up to 6 ind./L; Modenutti et al., 2008).

Recently, Ribeiro Guevara et al. (2008) showed that water column compartment may play a key-role in Hg dynamics of Lake Moreno. Filter sterilized lake water ( $< 0.2 \mu\text{m}$ ) and to a lesser extent pelagic biota  $< 20 \mu\text{m}$  (mostly nanoplanktonic algae) were found to facilitate  $\text{CH}_3\text{Hg}^+$  production in laboratory experiments.

The present study examined THg concentration in pelagic organisms of Lake Moreno, associated with three size classes ( $10\text{--}53 \mu\text{m}$ ,  $53\text{--}200 \mu\text{m}$  and  $> 200 \mu\text{m}$ ), which make up most of the planktonic biomass and include phytoplankton and zooplankton species. The fraction  $< 10 \mu\text{m}$ , which in Lake Moreno is composed by picoplankton (autotrophic and heterotrophic bacteria) and mixotrophic nanoflagellates such as *Rhodomonas lacustris* and *Chrysochromulina parva* (Queimaliños et al., 1999), was not included in this study due to its low relative biomass as well as to methodological constraints regarding the sample size biomass necessary for THg determination.

In Lake Moreno, the THg concentration was highest in  $10\text{--}53 \mu\text{m}$  fraction of the pelagic food web, regardless of the site or integrated water depth analyzed (Figs. 2 and 3). The high THg concentration found for  $10\text{--}53 \mu\text{m}$  fraction (up to  $300 \mu\text{g/g dw}$ ) is likely associated with *dinoflagellates* and ciliates that constitute the major proportion of the biomass. THg concentrations associated with two larger pelagic size fractions ( $53\text{--}200 \mu\text{m}$  and  $> 200 \mu\text{m}$ ) were about two orders of magnitude lower than the phytoplankton and ciliates, which suggests a sharp decrease of THg from producers to consumers (Figs. 2 and 3). The food web structure of Lake Moreno resembles a typical food web found in marine systems, with trophic transfers between phytoplankton, calanoid copepods, and fish. Wang (2002) found that the biodiminution of metals in this classical marine food web results from the effective efflux of metals by the copepods and a low assimilation by fish. In freshwaters, beyond several key chemical variables (pH, alkalinity, dissolved organic matter and  $\text{SO}_4^{2-}$ ), disturbances in watershed and plankton abundance have been found to be negatively correlated with Hg accumulation in lake biota. Hg content in plankton and fish has been reported to decline with increasing chlorophyll and plankton abundance (Pickhardt et al., 2002; Chen and Folt, 2005; Chen et al., 2005). Pickhardt et al. (2002) demonstrated experimentally that algal blooms can reduce Hg burdens in algae and indirectly on zooplankton, whereas large bodied zooplankton such as crustaceans accumulates preferentially  $\text{CH}_3\text{Hg}^+$  over  $\text{Hg}^{2+}$  and are thought to be a major source of Hg for fish (Kainz and Mazunder, 2005; Mason and Tremblay, 2003; Kainz

et al., 2002). The mechanisms involved in the dilution effect by algal blooms are related to the finite budget of Hg available for algal uptake and to the low ratio of particulate:dissolved metal that is found at higher particle densities (i.e., algae). Overall, the result is a decrease in Hg bound to particles and a potential differential binding of Hg to dissolved substances (Pickhardt et al., 2002; Chen and Folt, 2005). Dilution of Hg due to algal bloom logically propagates to zooplankton resulting in a lower THg uptake by this fraction as well as has been reported for *Daphnia*, cyclopid, and calanoid copepods (Pickhardt et al., 2002; Tsui and Wang, 2004). Hg accumulation has been observed to decline with increasing growth rates and food quality in crustacean *Daphnia* (Karimi et al., 2007) and also through Hg efflux due to excretion, molting, and maternal transference to offspring (Tsui and Wang, 2004).

Several features of Lake Moreno may explain the observed THg diminution with increasing trophic level. Algal uptake of Hg would likely include waterborne  $\text{CH}_3\text{Hg}^+$  and, in the case of mixotrophic algae, also the direct and indirect transference from bacteria. In Lake Moreno, the phytoplankton is dominated by mixotrophic flagellates and ciliates, *Ophrydium* and *Stentor*, which at different extents include bacteria in their diet (Queimaliños, 2002; Modenutti et al., 2008; Kamjunke et al., 2009). Besides, the direct contribution of  $\text{CH}_3\text{Hg}^+$  from bacterial diet in macrozooplankton can be high as pointed out by Kainz and Mazunder (2005). The direct uptake of waterborne  $\text{CH}_3\text{Hg}^+$  is one plausible source of this compound for all biota inhabiting Lake Moreno since dissolved  $\text{CH}_3\text{Hg}^+$  concentrations as high as 0.68 ng/L have been measured in the lake. It thus can be hypothesized that the particulate  $\text{CH}_3\text{Hg}^+$  may come from both dietary or waterborne uptake, since most algae present in the fraction < 50  $\mu\text{m}$  could incorporate this compound from bacteria or directly from water. Tsui and Wang (2004) have provided strong evidence that both food and water exposure are important sources of  $\text{CH}_3\text{Hg}^+$  for freshwater biota.

The decline in THg observed from 10–53  $\mu\text{m}$  to > 200  $\mu\text{m}$  fraction may be explained by considering some characteristics of Lake Moreno food web. The size fraction 10–53  $\mu\text{m}$  may be partially consumed by larger fractions considered in this study. In particular, the dominant crustacean, *B. gracilipes* consumes particles < 33  $\mu\text{m}$  which include nanoplanktonic flagellates such *Rhodomonas* and *Chrysochromulina* (both < 10  $\mu\text{m}$ ), *dinoflagellates* (ca. 33  $\mu\text{m}$ ), and oligotrich ciliates (20–50  $\mu\text{m}$ ) (Balseiro et al., 2001). From the perspective of dietary Hg transfer, the THg present in *B. gracilipes* would be a function of Hg associated with its food, namely *Gymnodinium* spp., oligotrich ciliates, and nanoplanktonic flagellates. Subsequently, we hypothesize that only a small proportion of THg measured in the smallest plankton fraction considered in this study could be easily transferred to macrozooplankton. In addition, calanoid copepods have an outstanding depuration capacity (Wang, 2002), which may be enhanced due to the high selenium levels in Lake Moreno (Arribére et al., 2008). The fact that *B. gracilipes* ingests small oligotrich ciliates is also an inter-

esting feature of this food web that needs to be taken into account. Nevertheless, the potential for Hg transfer among these planktonic components deserve much more attention. Mesozooplankton can accumulate more Hg when fed on protozoans compared to phytoplankton, which may derive from the fact that metals ingested from protozoan prey may be already converted in a bioavailable liquid fraction within digestive vacuoles (Twining and Fisher, 2004). Excretion, molting, and transference to the progeny are known to modulate THg content in zooplankton (Tsui and Wang, 2004). Debris and faecal pellets of organisms may be considered as sinks in terms of Hg transfer, since they ultimately settle to the bottom, fuelling with their Hg content the benthic biotic compartment.

Another area requiring further investigation is the role of ciliates and their position in the transfer of elements to higher trophic levels. Large ciliates such as *Ophrydium* and *Stentor* may be suitable prey for fish. In fact, *Stentor* has been reported to be preyed upon by juveniles of the native fish *Galaxias maculatus* (púyen) and also by the exotic trout *Oncorhynchus mykiss* (Kamjunke et al., 2009).

Overall, the concentration pattern of THg in the pelagic compartment of Lake Moreno can be described as a pronounced diminution from lower to higher trophic levels. However, the surprisingly high content of THg in the planktonic 10–53  $\mu\text{m}$  fraction may explain the elevated Hg burdens measured in fish.

Although pelagic food webs of Andean lakes appear simple, the trophic interactions within them are complex and the role of certain components requires further analyses to elucidate their relevance with regard to Hg dynamics. For example, the microbial food web seems to play a key role not only for phytoplankton dynamics but also for zooplankton as well. Thus, the significance of these relationships in Hg transfer within the food web may be crucial in this ultraoligotrophic lake. Understanding the role of pelagic compartment in the Hg dynamics of Lake Moreno deserves further studies and would likely provide relevant ecological insights with respect to other deep lakes of the region, which share similar features in terms of communities, food web dynamics and Hg sources.

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