Source and trophic transfer of mercury in plankton from an ultraoligotrophic lacustrine system (Lake Nahuel Huapi, North Patagonia)

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Abstract The incorporation and trophic transfer of total and methyl mercury (THg, MeHg) were examined in three size classes of plankton (10–53, 53–200, and >200 μm size range) and a small planktivorous fish, *Galaxias maculatus*, from the large multi-branched Lake Nahuel Huapi (North Patagonia, Argentina). Three sites representing a large range of lake benthic–pelagic structures (based on depth and shoreline characteristics) and precipitation regimes were sampled. Nitrogen and carbon stable isotopes (δ^{15}N, δ^{13}C) were analyzed to assess Hg trophodynamics.

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Selenium concentrations were determined together with THg in order to consider its potential effect on Hg trophodynamics. High THg concentrations (0.1–255 μg g^{-1} dry weight (DW)) were measured in plankton, largely in inorganic form (MeHg: 3–29 ng g^{-1} DW, 0.02–7 % of THg, in the two larger size classes). A trend of increasing THg concentrations, varying in two to three orders of magnitude, with decreasing plankton size was associated with precipitation measured prior to each sampling event. Passive adsorption of dissolved Hg^{2+} from wet deposition and runoff is considered to be the principal Hg uptake mechanism at the base of the pelagic food web. Despite the initially high THg uptake in the smaller plankton classes, the transfer to *G. maculatus*, and consequently to the entire food web, is likely limited due to low proportion of MeHg to THg in plankton. Furthermore, evidence of *G. maculatus* with benthic feeding habits having higher impact on MeHg trophic transfer compared to the same species with more pelagic (e.g., zooplankton) feeding habits, was observed. Although there is a high THg uptake in plankton, limited amounts are incorporated in the entire food web from the pelagic compartment.

Keywords Mercury · Selenium · Plankton · Lacustrine food web · Lake Nahuel Huapi · North Patagonia

Introduction

Mercury (Hg) is a global pollutant that reaches even the most remote regions by atmospheric transport of emissions from both anthropogenic and natural sources. Deposited atmospheric inorganic Hg (Hg^{2+}) can be transformed into organic Hg in freshwater systems, mostly monomethyl-mercury (CH$_3$Hg$^+$ or MeHg) (Ullrich et al. 2001).
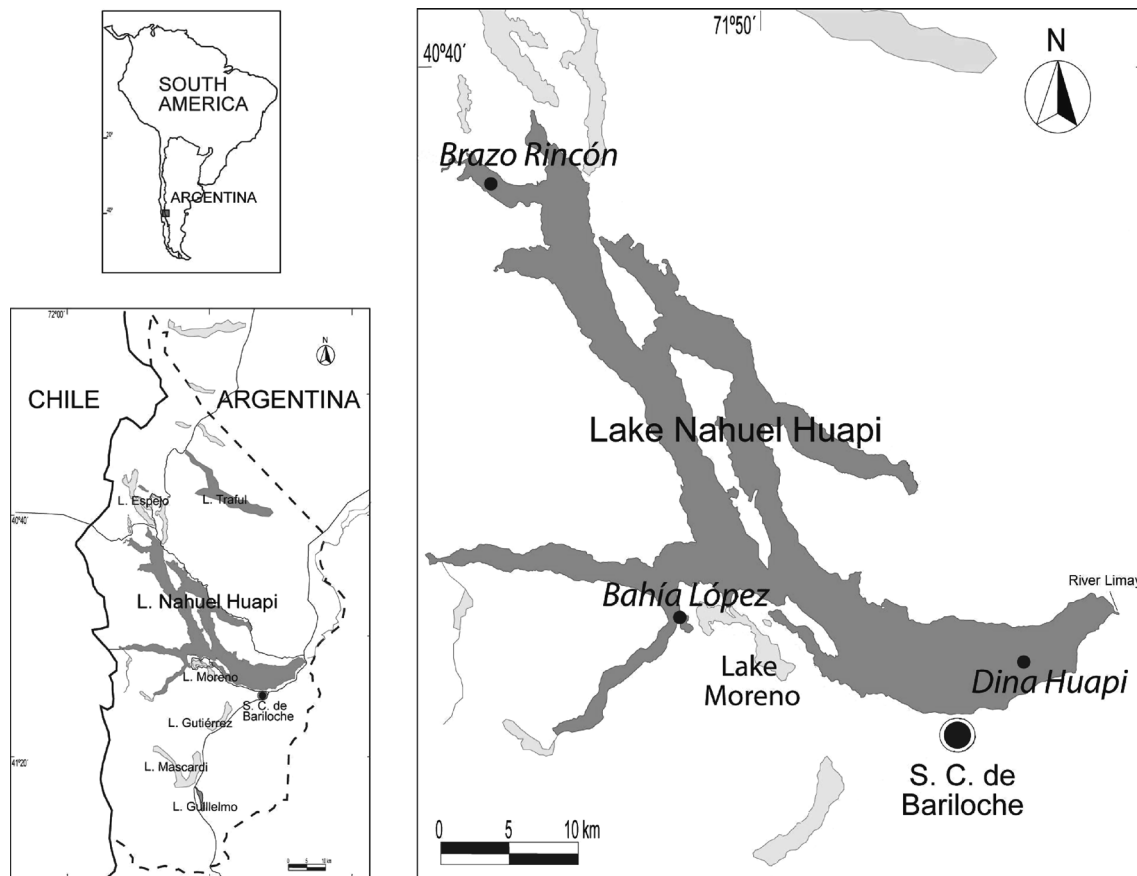
Fig. 1 Lake Nahuel Huapi, Nahuel Huapi National Park. Plankton and *Galaxias maculatus* sampling sites: Brazo Rincón (BR), Bahía López (BL), and Dina Huapi (DH)

Methylmercury is a powerful toxic chemical that biomagnifies in aquatic food webs more efficiently than Hg^{2+}, resulting in higher MeHg concentrations in upper trophic levels, affecting wild life and humans through fish consumption (Ullrich et al. 2001). Food web structure and coupling connections between pelagic and benthic habitats can play important roles in Hg trophodynamics (Chen et al. 2005; Stewart et al. 2008; Ullrich et al. 2001). In addition, selenium (Se) is an essential element in biological systems that has a high chemical affinity with Hg, being able to form insoluble Hg–Se complexes and sequestering Hg from the biological processes, neutralizing its toxic effects (Belzile et al. 2009; Sørmo et al. 2011); therefore, it should be considered in the study of Hg trophodynamics (Arcagni et al. 2013). Atmospheric Hg can reach different environments, particularly fresh water systems, via precipitation, both rain and snow, largely as inorganic species, in concentrations that can exceed 60 ng L^{-1} (Downs et al. 1998; Hall et al. 2005; Hammerschmidt and Fitzgerald, 2005). Precipitation also increases dissolved Hg budgets in aquatic systems through runoff, carrying Hg from soils and terrestrial systems (Downs et al. 1998).

Lake Nahuel Huapi is a federally-protected multi-branched large lake with no identified point or diffuse sources of anthropogenic Hg in the region. However, elevated Hg concentrations were measured in sediments and biota (Arribére et al. 2010; Ribeiro Guevara et al. 2005; Rizzo et al. 2011). Lake Nahuel Huapi is a large (surface area 557 km^2) and deep (max. depth 464 m) lake, particularly characterized by its seven branching arms, each with its own ecological and physical characteristics (Fig. 1). Lake Nahuel Huapi, with its widely varying characteristics across seven branches, can serve as an important study site for assessing different precipitation regimes and shoreline characteristics on Hg transfer through the planktonic food chain as well as the potential moderating effect of Se on Hg accumulation rates.

Previous research on oligotrophic lakes of North Patagonia Andes Mountains have revealed unusual characteristics regarding Hg behavior (Arcagni et al. 2013; Rizzo et al. 2010). Total Hg (THg) concentrations measured in plankton from the neighboring Lake Moreno (Fig. 1) were over 100 µg g^{-1} dry weight (DW), elevated in some fish species, but puzzlingly, biomagnification of THg was not

observed in the food web (Arcagni et al. 2013) even though biomagnification of other elements was detected (Revenga et al. 2011). This lack of biomagnification despite the elevated Hg in lake sediments points to either unusual food web trophodynamics or Hg bioavailability at the base of the food web.

Organisms at the base of pelagic food webs (pico-plankton, phytoplankton, and zooplankton) are known to be a critical link in the transfer of Hg to higher trophic levels (Chen and Folt 2005; Chen et al. 2005; Heimbürger et al. 2010; Stewart et al. 2008). In order to assess the relevance of the planktonic communities in the trophic transfer of Hg, it is essential to understand how organic Hg is transferred through the entire food web. *Galaxias maculatus* (common names: puyen chico or inanga) is an important widespread planktivorous fish in Patagonian lakes (Barriga et al. 2012; Cervellini et al. 1993). This small fish can have pelagic and benthic foraging habits (Barriga et al. 2012; Cussac et al. 1992), and, in turn, is considered key prey species for larger piscivorous fish (Juncos et al. 2011; Macchi et al. 1999, 2007; Vigliano et al. 2009).

Stable nitrogen (N) and carbon (C) isotopes analyses have been widely used to study food web structure, and also to study the transfer of contaminants in food webs (Lavoie et al. 2013). Stable nitrogen isotopes ratios (δ^{15}N) tend to increase 2–4 ‰ with each trophic level, making it possible to identify biomagnification and trophodynamic processes by correlating with THg and MeHg concentrations (Jardine et al. 2006). Stable carbon isotope ratios (δ^{13}C) show negligible fractionation (0.8–1 ‰) between trophic levels, but they can differ with carbon source (Campbell et al. 2000), and thus can be useful in evaluating dietary sources of Hg in food webs.

In this work, we studied the trophodynamics of MeHg and THg using δ^{15}N and δ^{13}C determinations in plankton and *G. maculatus* from three different sites in Lake Nahuel Huapi. Selenium concentrations were also determined in all samples in order to consider its potential effect on Hg trophodynamics. The selection of the sampling sites considered different benthic-pelagic structures, and different precipitation regimes.

We hypothesized that a study in Lake Nahuel Huapi, with its widely varying characteristics across seven branches, can serve as an important study site for assessing different precipitation regimes and shoreline characteristics on Hg transfer through the planktonic food chain as well as the potential moderating effect of Se on Hg accumulation rates.

The specific aims of this work were: to determine THg uptake in the base of the pelagic food web, considering also the potential association with precipitation recorded at each sampling site; to evaluate the contribution of Hg from the pelagic compartment to the food web of Lake Nahuel Huapi; and to study MeHg trophic transfer via *G. maculatus* (a trophic connection between pelagic and benthic environments), the predominant MeHg pelagic pathway to top predators.

Materials and methods

Study site

Lake Nahuel Huapi is the largest lentic water body in Nahuel Huapi National Park (NHNP, 40°15′–41°34′S; 71°4′–72°54′W; Fig. 1). The lake, situated at 764 m above sea level, has seven branching arms creating separate bays, resulting in a 357-km shoreline. Due to the effect of the Andes mountain range, the prevailing westerly winds lose most of their humidity before crossing the mountains creating a steep west-east climatic gradient over the entire lake. As a consequence, in a stretch of less than 65 km, total annual precipitation decreases drastically from 3,000 mm in the westernmost side of NHNP to less than 700 mm on the eastern side. This steep precipitation gradient shapes plant coverage and distribution, and thus, while mountain slopes in the western side of the park are covered by dense Andean-Patagonian *Nothofagus* forest, its eastern borders are at the onset of the dry Patagonian steppe characterized by shrub lands. Lake Nahuel Huapi, with a 55 km long main axis extending from West to East (Fig. 1), covers the full spectrum of the described precipitation gradient. The lake is a warm monomictic oligotrophic system, with low total phosphorus (9 µg L^{-1}), total nitrogen (71 µg L^{-1}), and chlorophyll *a* (1.4 µg L$^{-1)}$. Typically, clarity, as measured by Secchi disk, was 18 m, pH was 7.5, and conductivity was 39 µS cm^{-1}. All lentic water bodies within the 4,260 km^2 watershed of Lake Nahuel Huapi drain precipitation and snow melt from Andean peaks, flowing into Lake Nahuel Huapi which in turn drains through a single outlet, River Limay (Fig. 1) (Díaz et al. 2007; Juncos et al. 2011; Quirós 1988).

Three sampling sites were selected: Brazo Rincón (BR), Bahía López (BL), and Dina Huapi (DH) (Fig. 1). The BR site has highest annual precipitation ~2,500 mm, a depth of 100 m, and is surrounded by highly productive *Nothofagus* forest close to the shorelines. The BL location was in a bay that receives moderate precipitation (~1,500 mm); is the shallowest site (50 m depth), surrounded by cobblestone beaches and a mixture of *Nothofagus* and *Austrocedrus chilensis* forest. Dina Huapi was the driest site (~800 mm), and is open and highly exposed site, with a steep littoral area characterized by unproductive cobblestone beaches.

Volcanic events are a well-known source of Hg on a regional or global scale (Nriagu and Becker 2003). Nahuel

Table 1 Plankton samples collected in Lake Nahuel Huapi

Sampling site (Fig. 1)	Lake depth hauled for sampling (m)	Plankton size class (μm)	Estimated biological fraction[a] (%)	C:N[b]
Brazo Rincón (BR) summer (February 2011)	85–45	10–53	79	10.0
		53–200	69	7.4
		>200	98–100[c]	–
Brazo Rincón (BR) summer (February 2011)	40–0	10–53	76	7.6
		53–200	94	6.6
		>200	98–100[c]	5.3
Brazo Rincón (BR) autumn (May 2011)	85–45	10–53	61	9.1
		53–200	51	8.9
		>200	99	4.5
Brazo Rincón (BR) autumn (May 2011)	40–0	10–53	82	9.8
		53–200	95	8.1
		>200	99–100[c]	4.5
Bahía López (BL) summer (February 2011)	40–0	10–53	85	–
		53–200	90	8.6
		>200	98	4.8
Bahía López (BL) autumn (May 2011)	40–0	10–53	69	8.4
		53–200	68	9.0
		>200	95	4.9
Dina Huapi (DH) summer (February 2011)	85–45	10–53	56	6.8
		53–200	59	10.0
		>200	98–100[c]	4.8
Dina Huapi (DH) summer (February 2011)	40–0	10–53	91	10.3
		53–200	86	8.5
		>200	98–100[c]	4.5

Estimated biological fraction and C:N ratios

[a] Biological fraction of the samples estimated by subtraction of the geological fraction determined with the concentration of the geochemical tracer Sm. See calculation and raw data in Supplementary Material files

[b] Carbon to nitrogen concentration ratios: raw data in Supplementary Material files

[c] Samarium was not detected in this sample; the range correspond to the detection limit of Sm determination

Huapi National Park is located in the Southern Volcanic Zone of the Andean Range, an active volcanic region with high historic eruptive frequency that impacts the Argentinean Patagonia due to the West–East predominant winds (Petit–Breuilh Sepúlveda 2004). Lake Nahuel Huapi is situated near by Puyehue-Cordón Caulle volcanic complex (PCCVC), just over the border in Chile. The PCCVC is an active center with latest explosive eruptions in 1960 and 2011 and permanent gaseous emissions from fumaroles. The most northwesterly point on Lake Nahuel Huapi is the BR branch which is situated just 35 km away from PCCVC, with the catchment area reaching the volcanic system and laying directly within predominant winds carrying PCCVC tephras and gaseous emissions (Bubach et al. 2012). Although PCCVC was not studied for Hg contributions to the environment, evidence of gaseous releases was observed previously (Higueras et al. 2013).

Rainfall records at the watershed of each sampling site during the 15 days prior to plankton collection were compiled for all three sites (Table 2). The data were obtained from the Autoridad Interjurisdiccional de Cuencas de los Ríos Limay, Neuquén y Negro (AIC), a government institution responsible for managing the natural resources in both provinces, including meteorological monitoring (www.aic.gob.ar/aic/default.aspx#v)

Sample collection and preparation

In 2011, plankton samples were collected via vertical tows performed with three plankton nets with different mesh size in summer and autumn (February and May). Unfortunately, the DH site was not sampled in May 2011 due to high wind making it unsafe to operate a boat in high waves. Three plankton size classes were obtained: 10–53, 53–200 and >200 μm. To obtain each plankton sample 8 hauls were performed for the 10–53 μm size class, and 4 hauls for 53–200 and >200 μm classes. Typically, the 10–53 μm size class comprises phytoflagellates and diatoms; the 53–200 μm class includes rotifers, ciliates and immature stages of copepods and cladocerans, and the >200 μm class includes the larger copepods and cladocerans (Queimaliños 2002; Arribére et al. 2010). The composition of the planktonic communities can vary with lake depth due to strong changes in light intensity, as well as temperature profiles and other limnological parameters. For consistency, two deep vertical hauls were performed in the two

deepest sites, BR and DH, to sample the water column above and below the thermocline: from 85 to 45 m, and from 40 m to lake surface, while for the shallow site, BL, one vertical haul from near bottom (max. 50 m) was made (Table 1). All plankton samples were further concentrated in the laboratory by filtration until a volume of <250 mL was reached, and freeze-dried prior to analyses.

Galaxias maculatus were collected at the same time as the plankton sampling, using baited fish traps (30-cm diameter, 70-cm length, 2.5-mm double-funnel cylinder traps) left for 24 h at 2 m depth in shallower littoral areas, and by using seine nets in waist-depth depths. The specimens captured were grouped by length in 3–4, 4–5, and 5–6 cm class sizes, the whole head and internal organs removed, then freeze-dried. Pooled samples of 1–9 individuals from each size class were homogenized with titanium and Teflon tools, then freeze-dried.

All plastic vessels and bottles used in the field or in the laboratory were immersed in 50 % HNO3 for 15 days, and thoroughly rinsed with American Society for Testing and Materials (ASTM) grade 1 water. The NITEX® filters and filtering devices that could not stand acid cleansing were washed with EXTRAN® detergent and thoroughly rinsed with ASTM grade 1 water, as were plastic and titanium devices for sample processing.

Analytical procedures

Mercury and selenium determinations

Instrument Neutron Activation Analysis (INAA) was used to analyse THg in high concentration samples and Se in all samples, while lower THg concentration samples were analysed using a Direct Mercury Analyzer (DMA; Milestone DMA-80), which has a lower detection limit than INAA. Samples with intermediate THg concentrations were also analysed via DMA-80 to confirm the comparability of the two methods (see Supplementary Material files). The INAA determination of THg and Se were done by irradiating 1–200 mg of dried homogenized sample sealed in SUPRASIL-AN quartz ampoules at the RA-6 research nuclear reactor (Centro Atómico Bariloche, Argentina). Elemental concentrations were determined using the absolute parametric method (Rizzo et al. 2011). For DMA-80 determination of THg, 20–40 mg of dried homogenized sample were thermally decomposed in a continuous flow of oxygen. Elemental mercury released was trapped on a gold amalgamator and then desorbed to be measured by cold vapor atomic absorption spectrophotometry at 254 nm. In each set of analysis certified reference materials (CRMs) NRCC TORT-2 and DORM-2 for INAA determinations, and DORM-3 for DMA, were analyzed for analytical quality control; the results of the

analysis match with certified values, considering uncertainties (see Supplementary Material files).

A potentially confounding issue for Lake Nahuel Huapi plankton is that inorganic particulates of geological origin may also be collected by net sampling which could result in misleading Hg results. As a result, we also analysed a geochemical tracer, samarium (Sm), by INAA. Sm is a rare earth element which showed the highest sensitivity in the samples analyzed among the geochemical tracers that can be determined by INAA, and can be used to roughly evaluate the contribution of inorganic particles in plankton samples (Arcagni et al. 2013). Representative Sm concentrations in lake sediments for each sampling site were obtained from top layer of sedimentary sequences from Lake Nahuel Huapi (Ribeiro Guevara et al. 2005). The contribution of inorganic particulate to each plankton sample was estimated comparing Sm concentrations in plankton samples to that in bed sediments from this site (raw data and calculation equations are shown in Supplementary Material files).

Methylmercury concentrations were measured in dried homogenized samples via GC separation on an automated MeHg analyzer (Tekran Methyl Mercury Analyzer, model 2700) after MeHg isolation by distillation (Horvat et al. 1993). Distillation was performed in duplicate; MeHg determined for each distilled sample was done in duplicate. Samples with very low proportion of MeHg were below GC detection limit, due to high Hg^{2+} contamination from the higher inorganic fraction of THg after isolation by distillation. The CRM NRCC DORM-3 was analyzed for analytical quality control of MeHg determinations; the results of the analysis coincided with certified values, considering uncertainties (see Supplementary Material files). Also, duplicate samples were measured in independent distillation batches, with repeatable results. MeHg concentrations were also measured on the CRM IAEA 461 in four independent aliquots comparing the distillation, and acid dissolution and solvent extraction; both methods showed same results, considering uncertainties (see Supplementary Material files).

Carbon and nitrogen stable isotopes determinations

Stable N and C isotopes were measured at the Queen's Facility for Isotope Research in Kingston, ON, Canada, via DELTAplusXP continuous flow stable isotope ratio mass spectrometer. Each sample was finely ground, weighed into tin capsules, and combusted in an elemental analyzer to 1,800 °C. Combustion gases CO_2 and N_2 were analyzed with via DELTAplusXP. Stable isotope variations ($\delta^{15}N$, $\delta^{13}C$) were expressed in parts per thousand (‰) relative to reference materials (Pee Dee belemnite limestone for carbon and atmospheric nitrogen standard for N), according to the

equation $\delta X = (R_{sample}/R_{standard} - 1) \times 1000$, where X is ^{13}C or ^{15}N and R is $^{13}C/^{12}C$ or $^{15}N/^{14}N$ (Revenga et al. 2011). Total C and N concentrations were measured as well. Lake Duplicates and CRM IAEA–8548, and in-house standards (lipid-extracted Atlantic salmon muscle, red tilapia muscle, and chicken blood) were analyzed for analytical quality control, as described elsewhere (Revenga et al. 2011).

Analytical results are reported in Supplementary Material files.

Statistics

Data group differences were tested with ANOVA followed by Tukey post hoc test. Correlations between two variables were assessed by least square linear fit and ANOVA test, with significance determined at $p < 0.05$ for Type-II error. Total Hg and MeHg concentrations are reported in graphs with total uncertainties, including random and systematic contributions.

Fig. 2 Total Hg in plankton collected from Lake Nahuel Huapi, Nahuel Huapi National Park

Results and discussion

Allochthonous contributions to plankton samples

The organic fraction of each plankton size class (Table 1) was estimated by subtracting the inorganic component estimated via Sm concentrations. The organic fraction in >200 μm plankton size class ranged from 95 to 100 % for all sites and sampling periods. The organic fraction was also high (76–95 %) in the smaller size classes in the 40–0 m hauls in BR and in DH, and in BL in summer (Table 1). Lower values (51–79 %) were observed in the smaller size classes in the deeper hauls in BR and DH (80–45 m, both), and BL (40–0 m) in autumn (Table 1), probably due to fine bed sediment re-suspension.

The carbon to nitrogen concentration ratio in plankton (C:N, Table 1) can be used to infer allochthonous contributions of carbon to the lake, such as inorganic particles and organic detritus. C:N values over 6.6, the Redfield proportion, can indicate increased allochthonous contributions (Stewart et al. 2008; Wetzel 2001). The inorganic fraction estimated from Sm concentrations was very low to negligible in the 200 μm plankton size class, corresponding to C:N ratios from 4.5 to 5.3 (Table 1), showing both methods consistently indicated negligible allochthonous contributions in the plankton hauls. Although the inorganic fraction estimated from Sm concentrations increased in the smaller size classes (5–49 %), C:N ratios remained near-Redfield proportion (6.6–10.3 %; Table 1) associated with limited allochthonous contributions of carbon (Stewart et al. 2008).
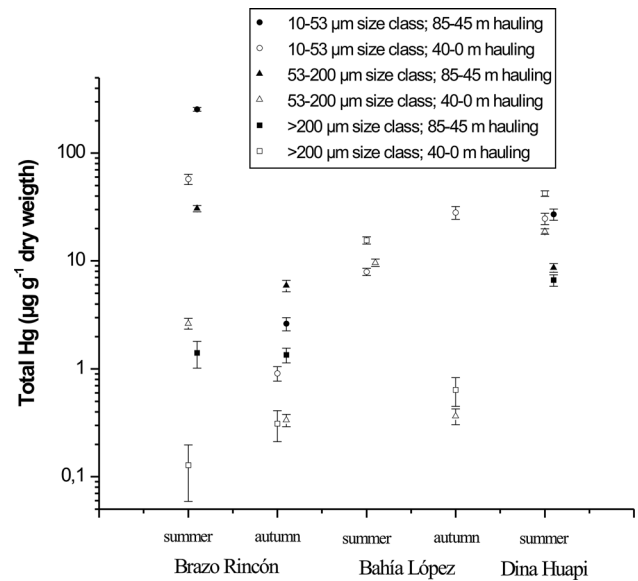

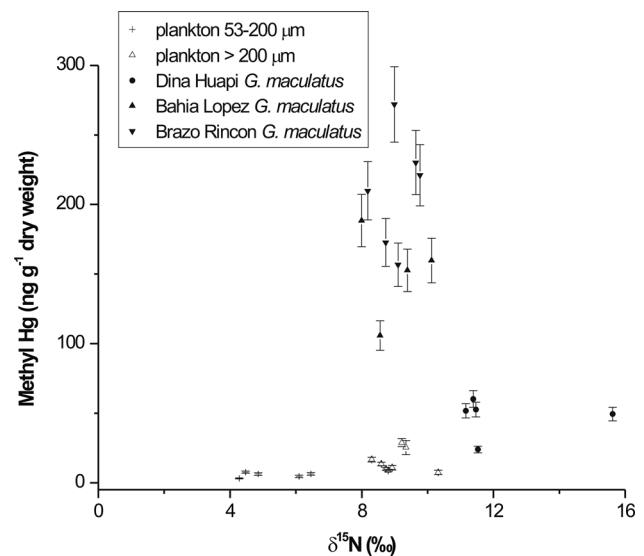**Fig. 3** Methyl Hg versus $\delta^{15}N$ ratios determined in plankton and *Galaxias maculatus* collected from Lake Nahuel Huapi, Nahuel Huapi National Park

As it will be discussed later, hypothesized THg uptake processes in plankton are passive, and this may also occur in allochthonous particulates. Therefore, no correction of THg plankton haul concentrations due to allochthonous contributions to plankton samples were done (Fig. 2). No significant MeHg concentration is expected in the geological fraction of plankton samples, compared with MeHg concentrations in the organic fraction. Methylmercury concentrations in plankton samples were corrected by the

dilution effect of the geological contribution, using the fraction estimated with the geochemical tracer. Corrected MeHg concentrations (Fig. 3) improved those correlations presented following, and they were considered for further discussion.

Mercury in plankton

THg concentrations in plankton from Lake Nahuel Huapi varied over three orders of magnitude from 0.1 to 255 µg g^{-1} DW (Fig. 2). Summer plankton samples from BR exhibited a similar trend at both hauling depths; THg concentrations increased one order of magnitude with each smaller size class. In autumn, however, THg concentrations showed a narrower span of values among the three size classes at both hauling depths (Fig. 2). As well, THg concentrations in summer BL and DH plankton samples showed slight variations among the three size classes, with DH plankton tending to be higher than BL samples. Similar to plankton from BR in summer, a trend of higher THg within the smaller size class was observed in autumn in BL, with two orders of magnitude higher THg concentration in the 10–53 µm size class with respect to the 53–200 and >200 µm classes (Fig. 2).

Methylmercury concentrations in the 53–200 and >200 µm plankton size classes, those consumed by G. maculatus, are shown in Fig. 3. MeHg concentrations in the 53–200 µm size class ranged from 3 to 7 ng g^{-1} DW, and in the >200 µm class ranged from 8 to 29 ng g^{-1} DW; the fraction of MeHg to THg ranged in 0.02–0.9 % and in 0.06–6.7 % in each class respectively, indicating that largely most planktonic Hg is in the inorganic form.

Similar patterns were observed for plankton from neighboring Lake Moreno, a tributary lake of Lake Nahuel Huapi (Fig. 1) (Arcagni et al. 2013). Total Hg concentrations in plankton ranged from 0.1 to 260 µg g^{-1} DW, with the highest values corresponding to the 10–53 µm size class. Methylmercury in plankton ranged from 6 to 90 ng g^{-1} DW, and was only 0.2–3 % of THg in plankton (Arcagni et al. 2013), which are among the lowest found in the literature for both pristine and contaminated aquatic systems (Gorski et al. 2003; Kehrig et al. 2009; Watras et al. 1998). The low percent MeHg relative to THg are due to high THg concentrations in Lake Nahuel Huapi and Lake Moreno plankton, given that the absolute MeHg values are similar to those reported in the literature. In fact, those low MeHg concentrations are in line with those from a recent ocean study which reported MeHg concentrations in marine macro zooplankton from different sites ranging from 4 to 160 ng g^{-1} DW (Hammerschmidt et al. 2013, and references therein), whereas typical MeHg to THg fraction ranges between 11 and 83 % in both pristine and contaminated aquatic systems (Belzile et al. 2006; Gorski

et al. 2003; Hammerschmidt et al. 2013; Kehrig et al. 2009; Watras et al. 1998).

In a previous work, laboratory radiolabelled Hg^{2+} amendment experiments with NHNP lake waters showed a strong and fast passive Hg^{2+} uptake in native algae Crytomonas erosa cultures (Diéguez et al. 2013). According to these results, and considering that most planktonic Hg is in the inorganic form, we hypothesized that the THg trend observed in BR in summer and in BL in autumn is predominantly due to this uptake process. Passive adsorption of dissolved Hg^{2+} is mainly a surface mechanism. Smaller plankton species have higher surface–volume ratio, and hence higher specific surface per mass unit, leading to higher Hg accumulation by passive adsorption in the smaller size classes. Dissolved Hg^{2+} may also be adsorbed onto inorganic particulate and organic detritus, having no influence the contribution of these two kind of non-planktonic material in the qualitative interpretation. Therefore, plankton passive adsorption is an uptake mechanism that is consistent with the trend observed of increasing THg concentrations with each smaller size class. Due to fast plankton turnover, Hg not incorporated to the food web is deposited to sediments shortly after uptake, although Hg^{2+} reduction and re-emission may also occur.

Precipitation increases dissolved Hg budgets in aquatic systems through runoff, also carrying Hg input by wet and dry deposition directly to the watershed (Downs et al. 1998; Hall et al. 2005). The trend of strong increases in THg concentrations with smaller plankton size classes observed in summer BR and autumn BL collections coincided with precipitation patterns within 3–5 days prior to sampling. If there were no prior rainfall within the past 3–5 days then the Hg concentration trend is not as clearly delineated (Table 2; Fig. 2). Moreover, for the neighboring Lake Moreno, the highest THg concentrations in plankton, upto 260 µg g^{-1} DW, were obtained in autumn, which is the rain season in the region (Arribére et al. 2010). This is noteworthy because the steep mountain slopes and bathymetry in BR and BL watersheds will result in significant water discharges into both sites after a precipitation event within very short time periods.

The direct drainage area of BL is small but receives water from Lake Moreno watershed, with a drainage area of 140 km^2 (Queimaliños et al. 2012) (Fig. 1). BR has a drainage area of 235 km^2, 73 % covered by dense Andean–Patagonian Nothofagus forest. Atmospheric Hg deposition in forested systems with dense canopy foliage and heavy precipitation will lead to increased forest Hg through-fall and litter fall and subsequently, significant terrestrial Hg contributions to runoff entering lakes after heavy precipitation events (Driscoll et al. 2007; Grigal 2002).

The correlation between rainfall and the THg concentration trend in plankton is consistent with the hypothesis

Table 2 Cumulative precipitation in the catchment area of each sampling site over 3, 5, 10 and 15 prior to plankton sampling

Sampling site	Cumulative precipitation prior to plankton sampling[a] (mm)			
	3 days	5 days	10 days	15 days
Brazo Rincón, summer (February 2011)	22	29	29	84
Brazo Rincón, autumn (May 2011)	0	0	19	23
Bahía López, summer (February 2011)	0	9	9	9
Bahía López, autumn (May 2011)	3.6	15.5	32	71
Dina Huapi, summer (February 2011)	0	0	0	0

Station El Rincón: 40° 43′ 30″S, 71° 48′ 13.2″W; 791 m above sea level. Station Bahía López: 41° 4′ 27.6″ S, 71° 34′ 5.4″W; 774 m above sea level. Station Nahuel Huapi: 41° 3′ 21.73″S, 71° 8′ 49.28″W; 779 m above sea level. Including precipitation during the first sampling day when the sampling lasted 2 days

[a] Data provided by Autoridad Interjurisdiccional de Cuencas de los Ríos Limay, Neuquén y Negro (AIC). Station El Rincón corresponding to Brazo Rincón site (BR); station Bahía López, corresponding to Bahía López site (BL); station Nahuel Huapi, corresponding to Dina Huapi site (DH)

of passive adsorption of dissolved Hg^{2+} to plankton surface, indicating wet deposition in the drainage area and Hg removed from soils by runoff, to be the main sources of dissolved Hg^{2+}. This uptake process of Hg in the pelagic compartment is dynamic, involving extraordinary changes in THg concentrations in short time periods, given the high turnover of planktonic organisms and the variations of dissolved Hg^{2+} concentrations, and depending also on other parameters such as the dissolved organic matter concentrations and its quality, as it was previously demonstrated in laboratory experiments (Diéguez et al. 2013).

Selenium

In contrast to THg, Se concentrations varied in a very narrow range, with no significant differences between sites or other sampling conditions. In plankton, Se concentrations varied from 1.3 to 2.9 µg g^{-1} DW (average: 2.2 µg g^{-1} DW; SD: 0.50 µg g^{-1} DW), and from 0.9 to 2.1 µg g^{-1} DW in *G. maculatus* samples (average: 1.8 µg g^{-1} DW; SD: 0.3 µg g^{-1} DW) (see Supplementary Material files). These concentrations are similar to those observed in Lake Moreno (Fig. 1), that ranged from 0.5 to 3 µg g^{-1} DW in littoral and pelagic organisms (Arcagni et al. 2013), showing a consistent Se source to the food web in the region.

Selenium can sequester Hg as part of stable compounds in biological tissues, and was reported associated with increased MeHg elimination due to high dietary Se in large fish species in fresh water systems (Bjerregaard et al. 2011; Sørmo et al. 2011). This is due to the high affinity of Hg and Se in biological systems to form, with an equimolar relation, mercury selenide (HgSe). Selenium, unlike Hg, is an essential element for metabolic activity, and its concentration is physiologically regulated. Higher Se availability may increase Se protective action against the toxicity of MeHg. This potential effect can be evaluated by analyzing Se to Hg molar ratio (Se:Hg); Se:Hg molar ratios over 1 imply Se molar excess in the tissue respect to HgSe, increasing the chance of Hg detoxification processes. Due to high THg concentrations, Se:Hg in plankton is below 1 in most cases. But Se:Hg in *G. maculatus* are consistently far over 1 (average: 23.9; SD: 6.8) (see Supplementary Material files), values compatible with potential MeHg detoxification and Hg sequestration by Se. These high Se:Hg values in *G. maculatus* are evidence of relevant incidence of Se in Hg trophodynamic, given the key position of these small fish in the lacustrine food webs of the region.

The link of Hg in the pelagic compartment within the lake food web

Galaxias maculatus is a native small fish that represents an important link between plankton and piscivorous fish (Juncos et al. 2011; Macchi et al. 2007; Vigliano et al. 2009). It has a plastic and generalist life cycle that involves ontogenetic-associated changes in diet and habitat (Cervellini et al. 1993). Pelagic *G. maculatus* larvae and juveniles are known to feed on plankton such as the copepod *Boeckella gracilipes* as well as ciliates (*Ophrydium* sp. and *Stentor* sp., which are included in the 53–200 µm size class) (Barriga et al. 2012; Kamjunke et al. 2009). Furthermore, littoral adults of *G. maculatus* feed on plankton in addition to Chironomidae larvae, amphipods and other small benthic prey (Cervellini et al. 1993).

Littoral *G. maculatus* samples showed significantly higher δ^{15}N in DH (11–16 ‰) than in BR and BL (8–11 ‰) (ANOVA followed by Tukey test). In DH, *G. maculatus* δ^{15}N ratios are higher than plankton, but in BR and BL are similar to > 200 µm plankton size class and higher than benthic prey (0.3–2.2 ‰ in insect larvae and *Hyallela* sp.; unpublished data). In contrast, *G. maculatus'* δ^{13}C values (−26 to −20 ‰) were higher than those obtained in zooplankton in the three sites (−33 to −24 ‰), and slightly higher or similar than those from benthic prey from BR and BL (no benthic macroinvertebrates were obtained from DH).

The δ^{15}N and δ^{13}C trends between *G. maculatus* respect to plankton and benthic prey items are consistent with a more planktonic diet of *G. maculatus* in DH, and a more
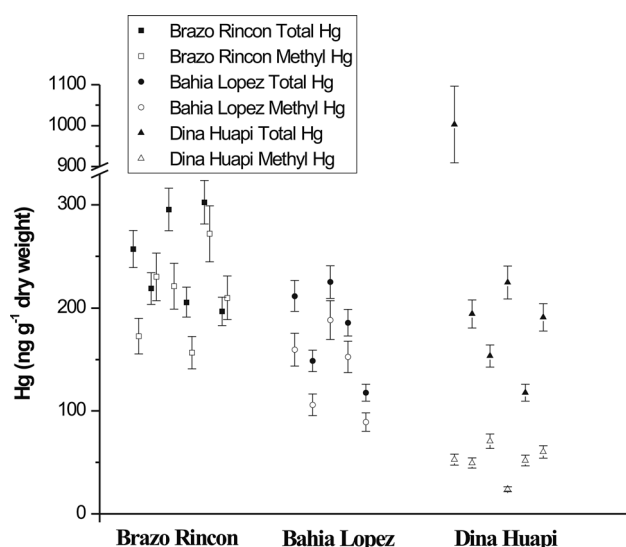
Fig. 4 Methyl Hg and Total Hg determined in *Galaxias maculatus* collected from Lake Nahuel Huapi, Nahuel Huapi National Park

benthic diet in BR and BLake This is also consistent with the characteristics of the sampling sites, with more developed benthic habitat in BR and BL in respect to DH.

Although there are no significant differences in THg concentrations in *G. maculatus* among the three sites studied (0.12–1.0 µg g^{-1} DW) (ANOVA followed by Tukey test), MeHg concentrations were significantly lower in DH (24–60 ng g^{-1} DW) compared to BR and BL (89–270 ng g^{-1} DW) (ANOVA followed by Tukey test). The ratio of MeHg to THg ranged between 70 and 100 % in BR and BL, and decreased to 5–50 % in DH (Fig. 4). The low MeHg to THg ratio in *G. maculatus* from DH is consistent with a more pelagic diet, considering that Hg in both size classes of plankton eaten by this fish (53–200 and > 200 µm) is largely in the inorganic form. MeHg concentrations in 53–200 and >200 µm plankton size classes, and in *G. maculatus* from DH exhibited a positive linear correlation with $\delta^{15}N$ ratios ($R^2 = 0.56$, ANOVA $p = 0.0002$), consistent with MeHg biomagnification in this pelagic food web section. On the contrary, *G. maculatus* from BR and BL, with apparently a more benthic diet based on $\delta^{15}N$ values, had higher MeHg concentrations, implying higher MeHg transfer to the upper food web levels. These results contrast with those in other fresh water systems showing higher contributions of Hg from pelagic carbon sources to fish compared with the benthic base of food web (Kidd et al. 2003; Stewart et al. 2008), differences observed also in other studies on fish diet and Hg (Chumchal and Hambright 2009; Eagles-Smith et al. 2008a, b). These results highlight the relevance of the benthic-pelagic coupling in Hg food web transfer.

Conclusions

Very high THg concentrations (0.1–255 µg g^{-1} DW) were measured in plankton from Lake Nahuel Huapi, comprised largely of inorganic Hg (MeHg in 3–7 ng g^{-1} DW in the 53–200 µm size class, and in 8–29 ng g^{-1} DW in the >200 µm class). Association of increasing THg concentrations in smaller plankton with precipitation was observed, and passive adsorption of dissolved Hg^{2+} from wet deposition and runoff is hypothesized to be the principal uptake mechanism in the base of the pelagic food web based on work developed in laboratory studies (Diéguez et al. 2013). Despite the very high THg uptake in plankton, the Hg transfer to *G. maculatus*, and to the entire food web through this trophic pathway, is limited due to the low MeHg concentrations. Furthermore, *G. maculatus* with apparently more benthic feeding habits showed to have higher impact in MeHg trophic transfer, limiting the incidence of Hg from the pelagic compartment, with implications for biomagnification of Hg through the littoral food web.

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