



## Mercury and selenium in the food web of Lake Nahuel Huapi, Patagonia, Argentina



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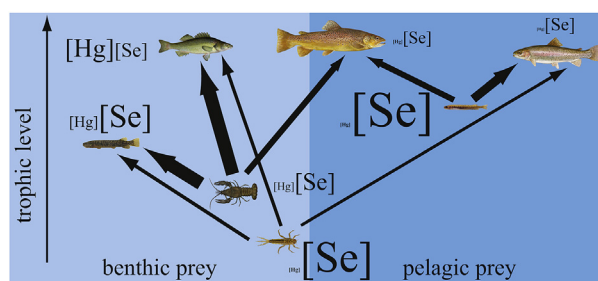
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### HIGHLIGHTS

- Total Hg and Se did not biomagnify in Lake Nahuel Huapi food web.
- Mercury bioaccumulation in top predator fish was habitat-dependent.
- Native and introduced fish had different Hg and Se bioaccumulation patterns.
- Se:Hg molar ratios were >1 in all organisms.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Despite located far from point sources of Hg pollution, high concentrations were recorded in plankton from the deep oligotrophic Lake Nahuel Huapi, located in North Patagonia. Native and introduced top predator fish with differing feeding habits are a valuable economic resource to the region. Hence, Hg and Se trophic interactions and pathways to these fish were assessed in the food web of this lake at three sites, using stable nitrogen and carbon isotopes.

As expected based on the high THg in plankton, mercury did not biomagnify in the food web of Lake Nahuel Huapi, as most of the THg in plankton is in the inorganic form. As was observed in other aquatic systems, Se did not biomagnify either.

When trophic pathways to top predator fish were analyzed, they showed that THg biomagnified in the food chains of native fish but biodiluted in the food chains of introduced salmonids. A more benthic diet, typical of native fish, resulted in higher [THg] bioaccumulation than a more pelagic or mixed diet, as in the case of introduced fish.

Se:THg molar ratios were higher than 1 in all the fish species, indicating that Se might be offering a natural protection against Hg toxicity.

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### 1. Introduction

Due to its high toxicity and because it accumulates in organisms, predominantly in fish, mercury (Hg) is probably the most studied

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trace element (Morel et al., 1998). It can be originated from natural sources such as volcanic activity, soil degassing, forest fires, and lacustrine and oceanic re-emissions (Morel et al., 1998; Nriagu and Becker, 2003; Rasmussen, 1994), as well as from anthropogenic sources such as mining and metal production, or fossil fuel burning (Pacyna et al., 2010, 2006), and it can be transported to remote regions primarily via long-range atmospheric transport (Fitzgerald et al., 1998; Hammerschmidt and Fitzgerald, 2006).

Among many several biological factors, trophic level seems to play a major role controlling Hg concentrations in biota, reaching the highest values (biomagnification) in top predator fish (Cabana et al., 1994; Morel et al., 1998), posing a serious health risk for humans who consume them. As fish acquire Hg mostly from their diet (Hall et al., 1997), food availability and trophic pathways can also affect Hg bioaccumulation due to its control on fish feeding and growth rate (Wang, 2012). As well, feeding habits seem to control Hg concentrations among fish, as in general, pelagic prey are important sources of Hg to fish than benthic prey (Karimi et al., 2016).

Selenium (Se) also originates from natural sources like volcanic eruptions, weathering of soils and rocks, wildfires, and volatilization from waterbodies and plants (Eisler, 1985; Floor and Román-Ross, 2012; Lantzy and Mackenzie, 1979) and from anthropogenic activities (e.g. mining, agricultural, petrochemical, and industrial manufacturing operations; Lemly, 2004).

Selenium, an essential element required for several functional Se-dependent proteins in most living organisms (Arteel and Sies, 2001), shows a narrow margin between nutritionally optimal and potentially toxic concentrations, and as well as Hg, diet is the dominant route of Se exposure in fish (Pelletier, 1985; Porcella et al., 1991; Presser and Luoma, 2010). Selenium has a protective effect against Hg toxicity due to the high affinity to form stable Hg-Se compounds, as Se can sequester Hg from the biological processes (Cuvin-Aralar and Furness, 1991; Yang et al., 2008). Accordingly, Se:Hg molar ratios above 1 in tissues were associated with a Se excess that could favor its protective action on Hg toxicity (Peterson et al., 2009; Ralston et al., 2007; Sørmo et al., 2011). Contrary to Hg, there is not a clear pattern concerning Se trophodynamics in food webs, as it was observed to biomagnify (Jasonsmith et al., 2008; Kehrig et al., 2009; Schneider et al., 2015), to decrease (Belzile et al., 2009), or showed no relationship with trophic level (Campbell et al., 2005; Ouédraogo et al., 2015).

Stable carbon and nitrogen isotope analyses (SIA) have been widely used to study energy flow, food web structure, and to estimate trophic position in aquatic ecosystems (Post, 2002). Also, over the past few years, SIA has been contributing to ecotoxicological studies by linking animal populations to their diet and ultimate contaminant source (Jardine et al., 2006). Stable nitrogen isotope ratios ( $\delta^{15}\text{N}$ ) increases with trophic level as consumers are enriched in  $^{15}\text{N}$  relative to its diet (DeNiro and Epstein, 1981). Since biomagnifying element concentrations, such as Hg, also tend to increase with increasing trophic level, a linear relationship between these elements and  $\delta^{15}\text{N}$  in organisms within a food web can be used to evaluate biomagnification (Lavoie et al., 2013). In addition, as stable carbon isotope ratios ( $\delta^{13}\text{C}$ ) show negligible fractionation with food assimilation (DeNiro and Epstein, 1978), they can be used to estimate if the C source of an organism was originated in the pelagic or the littoral environment (France, 1995), and therefore can be useful in evaluating the dietary sources of Hg and Se in food webs (e.g. Lescord et al., 2015; McIntyre and Beauchamp, 2007; Wang et al., 2014).

Lake Nahuel Huapi, although located within a protected area in Nahuel Huapi National Park (NHNP) with no identified points or diffuse sources of anthropogenic Hg and Se in the region, presented elevated concentrations in biota and sediments (Arribère et al.,

2010, 2008; Ribeiro Guevara et al., 2005; Rizzo et al., 2014, 2011). Nahuel Huapi National Park is located east of the Southern Volcanic Zone of the Andean Range, an active volcanic region with several historical and recent eruptive events (Naranjo and Stern, 2004). These events have impacted NHNP with tephra containing Hg and Se due to the predominant winds that blow from west to east (Ribeiro Guevara et al., 2005).

Previous studies in NHNP showed that in the smaller ultra-oligotrophic Lake Moreno, which discharges into Lake Nahuel Huapi, THg did not biomagnify in its food web due to the high THg concentrations recorded in plankton that exceeded  $200 \mu\text{g g}^{-1}$  dry weight (dw) (Arcagni et al., 2013). Similar THg concentrations were observed in plankton from Lake Nahuel Huapi, however, methylmercury concentrations were much lower ( $0.0043 \pm 0.0015 \mu\text{g g}^{-1}$ ), indicating that most Hg in plankton was in the inorganic form (Rizzo et al., 2014). No trend regarding the trophic transfer of Se was observed in Lake Moreno, as the concentrations were fairly consistent across trophic levels (Arcagni et al., 2013).

In this study we analyzed the THg and Se distribution and trophodynamics in the food web of Lake Nahuel Huapi, an oligotrophic lake located in Northwest Patagonia. Data from three sites within the lake were compared and THg and Se pathways to native and introduced top predator fish with different feeding habits, benthic and pelagic, were assessed using nitrogen and carbon stable isotopes. Our hypotheses are: 1) based on previous results from Lake Nahuel Huapi (Rizzo et al., 2014) and from Lake Moreno (Arcagni et al., 2013), THg and Se concentrations are not expected to biomagnify in the food web; 2) THg and Se concentrations in top predator fish may be influenced by different feeding habits; 3) THg and Se concentrations at the base of the food web may be related with different carbon sources (benthic/pelagic); and 4) based on several studies (Peterson et al., 2009; Ralston et al., 2007; Sørmo et al., 2011) Se:Hg molar ratios may indicate if Se is in excess against Hg playing a protective role against its toxicity.

## 2. Materials and methods

### 2.1. Study site

Lake Nahuel Huapi, the largest ( $557 \text{ km}^2$ ) and deepest (464 m) lentic water body in Argentine North Patagonia (Quirós and Drago, 1985), is an ultraoligotrophic to oligotrophic lake (total dissolved phosphorus  $3.96\text{--}4.57 \mu\text{g L}^{-1}$ , Chlorophyll *a*  $0.85\text{--}1.93 \mu\text{g L}^{-1}$ ; Modenutti et al., 2013), of glacial origin that has been classified as warm monomictic with summer stratification (Diaz et al., 2007, Fig. 1). Three sites were selected in Lake Nahuel Huapi for this study. Brazo Rincón (BR) is situated on the northwestern part of the lake in the rainiest region of NHNP; Bahía López (BL), with precipitation rates between the dense rainforest and the dry Patagonic steppe, and Dina Huapi (DH), which is located in the driest region of the lake (Fig. 1, Rizzo et al., 2014). The sampling sites and the lake's food web composition and structure were described in Arcagni et al. (2015).

### 2.2. Sampling and sample conditioning

Biofilm and benthic macroinvertebrates such as insect larvae, crayfish *Samastacus spinifrons*, crabs *Aegla* spp., snails *Chilina* sp., mussels *Diplodon chilensis*, and amphipods *Hyalella* sp. were sampled in February 2011. Native fish creole perch (*Percichthys trucha*), big puyen (*Galaxias platei*), velvet catfish (*Olivaichthys viedmensis*), and small puyen (*Galaxias maculatus*), and the introduced salmonids rainbow trout (*Oncorhynchus mykiss*) and brown trout (*Salmo trutta*) were obtained in May 2011. Three plankton size fractions, P1 class ( $10\text{--}53 \mu\text{m}$ ), P2 class ( $53\text{--}200 \mu\text{m}$ ), and P3 class

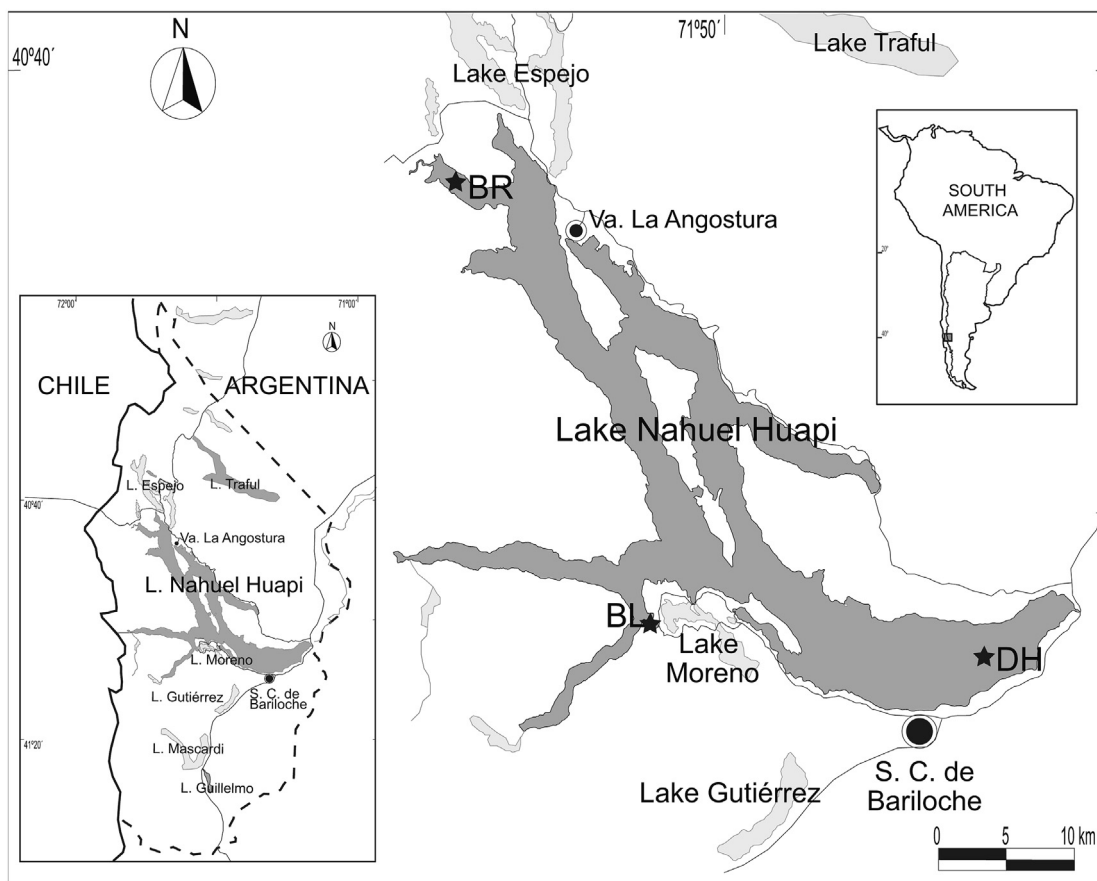


Fig. 1. Lake Nahuel Huapi, Nahuel Huapi National Park. Biota sampling sites Brazo Rincón (BR), Bahía López (BL) and Dina Huapi (DH).

(>200  $\mu\text{m}$ ) were sampled in both sampling campaigns. Composition and techniques used to collect and to process this community are detailed in Arcagni et al. (2015). Muscle tissue was removed from mollusks, large crustaceans, and fish larger than 80 mm; hepatopancreas or liver was also removed and analyzed separately. Head and guts were removed from fish smaller than 80 mm, whereas the rest of these organisms were analyzed whole. All samples were homogenized with titanium and Teflon<sup>®</sup> devices and freeze-dried until constant weight, then grounded to fine powder using a Teflon<sup>®</sup> pestle and mortar for analysis.

### 2.3. Mercury and selenium analysis

Instrument Neutron Activation Analysis (INAA) was used to determine Se and THg concentrations, whereas THg in low concentrations was determined by a Direct Mercury Analyzer (DMA; Milestone DMA-80). Samples with intermediate THg concentrations were analyzed via DMA and INAA to confirm the equivalence of both techniques. INAA determination were performed 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. For DMA determinations, 20–40 mg of dried homogenized sample were thermally decomposed in a continuous oxygen flow. The elemental Hg 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 matched with certified values (Table A1).

All total mercury [THg] and selenium [Se] concentrations are expressed in dry weight basis.

### 2.4. Stable isotope analysis

Stable carbon and nitrogen isotopes were measured via DELTA<sup>plus</sup>XP continuous flow stable isotope ratio mass spectrometer at the Queen's Facility for Isotope Research at Queen's University, Kingston, ON, Canada. To check the quality of analysis for every 10 carbon/nitrogen samples we ran standard reference materials and in-house standards (Table A2). Duplicates were also run every 10 samples which produced a difference between samples of ( $\pm$ SD) ( $\delta^{13}\text{C} = 0.13\%$ ,  $\delta^{15}\text{N} = 0.27\%$ ,  $n = 25$ ). Stable isotope values ( $\delta$ ) were expressed in parts per thousand (‰) relative to the C and N reference materials (Pee Dee Belemnite limestone and atmospheric nitrogen standard respectively), as follows:

$$\delta(\text{‰}) = \left[ \left( \frac{R_{\text{sample}}}{R_{\text{standard}}} \right) - 1 \right] \times 1000 \quad (1)$$

### 2.5. Data analysis

Se:Hg molar ratios were calculated by dividing the element's concentration by the molecular weight, 78.96 and 200.59 for Se and Hg, respectively. Linear regressions between Log transformed [THg]

and [Se] against trophic level ( $\delta^{15}\text{N}$ ) and carbon source ( $\delta^{13}\text{C}$ ) were assessed to analyze its trophic transfer in the food web at each site and the specific food chain of salmonids, creole perch and big puyen. Prey selection for each fish species was based on stomach content analysis for these species in Lake Nahuel Huapi following Juncos et al. (2015). Prey with an Index of Relative importance (IRI) higher than 15% were chosen considering the fish size range and prey items obtained at each site. Crayfish and insect larvae were chosen for creole perch from BL and BR, crayfish and small puyen for creole perch from DH and brown trout from BR, insect larvae and small puyen for rainbow trout from BL, insect larvae and amphipods for rainbow trout from BR, small puyen for rainbow trout from DH, and crayfish and amphipods for big puyen from BR.

Trophic transference of an element can be calculated using the following equation:

$$\text{Log}_{10}[X] = b * \delta^{15}\text{N} + a \quad (2)$$

where [X] is the concentration of the element, and b, the slope of the regression, is an indicator of the biomagnification rate when its value is positive (Kidd et al., 1995).

Spatial differences were assessed by one-way ANOVA, as well as [THg] and [Se] differences between prey items at each site. Differences in [THg] and [Se] between liver and muscle in fish were evaluated using (Student's *t*-test), and relationships between fish length and [THg] and [Se] were analyzed by linear regressions. Differences or regressions were considered significant at  $p < 0.05$  for Type-II error. All statistical tests were performed using XLSTAT v7.5 add-in for Microsoft Office Excel and Statistica® v8.0.

### 3. Results and discussion

#### 3.1. Selenium and mercury concentrations

Total mercury concentrations [THg] in individual samples spanned up to four orders of magnitude in the three sites, from  $0.050 \mu\text{g g}^{-1}$  in crayfish to  $260 \mu\text{g g}^{-1}$  in P1 in BR, from  $0.031 \mu\text{g g}^{-1}$  in small puyen, to  $28.7 \mu\text{g g}^{-1}$  in P1 in BL, and from  $0.027 \mu\text{g g}^{-1}$  in rainbow trout to  $43.1 \mu\text{g g}^{-1}$  in P3 in DH (Fig. 2, Tables A3 and A4). Selenium concentrations [Se] were less variable, spanning one order of magnitude, from  $0.580 \mu\text{g g}^{-1}$  in stoneflies to  $4.37 \mu\text{g g}^{-1}$  in snails in BR, from  $0.530 \mu\text{g g}^{-1}$  in biofilm to  $3.61 \mu\text{g g}^{-1}$  in crabs in BL, and from  $0.465 \mu\text{g g}^{-1}$  in rainbow trout muscle to  $4.57 \mu\text{g g}^{-1}$  in small puyen in DH (Fig. 2, Tables A3 and A4).

An analysis of variance showed there were no differences in the [THg] and [Se] in fish muscle of the same size range between the three sites. Spatial differences, however, were observed in some of the macroinvertebrate taxa, but no trend was observed regarding one site having higher [THg] or [Se] than the others (e.g. [THg] was higher in snails and mayfly larvae from BL but it was higher in crayfish from BR; [Se] was higher in crabs and crayfish from BR; Fig. 2).

Total Hg concentrations in muscle were higher than in liver in native creole perch and big puyen, but the opposite trend was observed in salmonids. Similarly, both trends were found in other studies (Cizdziel et al., 2003; Havelková et al., 2008; Jewett and Duffy, 2007; Polak-Juszczak, 2015; Robinson et al., 1995; Yang et al., 2010). Most of Hg in fish liver is in the inorganic form, as it is an organ where demethylation can occur and inorganic Hg is accumulated as it may be sequestered by binding proteins, or accumulated in Se-Hg stable compounds (Khan and Wang, 2009; Scheuhammer et al., 2007). Several authors have reported that when [THg] in muscle is below  $2.5 \mu\text{g g}^{-1}$ , concentrations in liver are lower or similar to those in muscle tissue (Cizdziel et al., 2003; Drevnick et al., 2008; Goldstein et al., 1996). Conversely, when

[THg] in muscle is above  $5.0 \mu\text{g g}^{-1}$ , concentrations in liver are higher than those in muscle (Goldstein et al., 1996). These observations imply that fish can tolerate low [Hg], but when tissue concentrations exceed approximately  $1.0 \mu\text{g g}^{-1}$ , Hg is redistributed from the muscle increasing the Hg burden in the liver (Goldstein et al., 1996). In Lake Nahuel Huapi fish with the lowest [THg] (less than  $0.250 \mu\text{g g}^{-1}$ ) were rainbow and brown trout, which had higher [THg] in livers than in muscle, in contradiction with this assumption.

Selenium concentrations were higher in liver than in muscle in all the fish species analyzed. Other studies have also reported higher Se concentrations in fish liver than in muscle (Ciardullo et al., 2008; Mason et al., 2000; Swift, 2002; Yang et al., 2010), fact that can be explained since the liver, along with other organs such as kidney and ovaries, are known to be the primary organs of Se storage in fish (Lemly, 1999; Swift, 2002). The high concentration of Se in these organs reflects the dietary uptake (Jasonsmith et al., 2008). Selenium concentrations in fish liver from Lake Nahuel Huapi were in general lower or within the expected range of values from non-contaminated Se lakes for similar species (See Table A5).

In general, [THg] and [Se] in muscle from fish species were similar or lower compared with fish of the same or similar species and from other non-impacted lakes from Nahuel Huapi and Los Alerces National Park (Arribère et al., 2008), and from other non-impacted freshwater systems from the Northern Hemisphere (See Table A5). Although Hg and Se are two of the most studied elements in aquatic systems worldwide, it was difficult to find published Hg and Se concentrations in muscle and liver from the same or similar species as the ones from this study and from non-impacted lakes. Of all the fish captured, only 3 specimens of creole perch exceeded the U. S. Environmental Protection Agency [Hg] threshold of  $1.2 \mu\text{g g}^{-1}$  dw for fish consumption.

Relationships between THg and Se concentrations and fish total length varied between elements. Mercury concentrations increased with increasing length in creole perch from BL ( $F = 15.0$ ,  $p < 0.01$ ) and DH ( $F = 24.3$ ,  $p < 0.05$ ); small puyen from BR ( $F = 8.67$ ,  $p < 0.05$ ), BL ( $F = 11.6$ ,  $p < 0.01$ ), DH ( $F = 8.23$ ,  $p < 0.05$ ), and big puyen from BR ( $F = 6.23$ ,  $p < 0.05$ ). However, it decreased in rainbow trout from BR ( $F = 23.8$ ,  $p < 0.05$ ). Selenium concentrations decreased with increasing length in rainbow trout from BL ( $F = 30.9$ ,  $p < 0.001$ ) and DH ( $F = 5.92$ ,  $p < 0.05$ ); brown trout from BR ( $F = 154$ ,  $p < 0.0001$ ); creole perch from DH ( $F = 43$ ,  $p < 0.01$ ); small puyen from BR ( $F = 61.7$ ,  $p < 0.0001$ ), BL ( $F = 30.7$ ,  $p < 0.001$ ), and DH ( $F = 82.4$ ,  $p < 0.0001$ , Fig. A1).

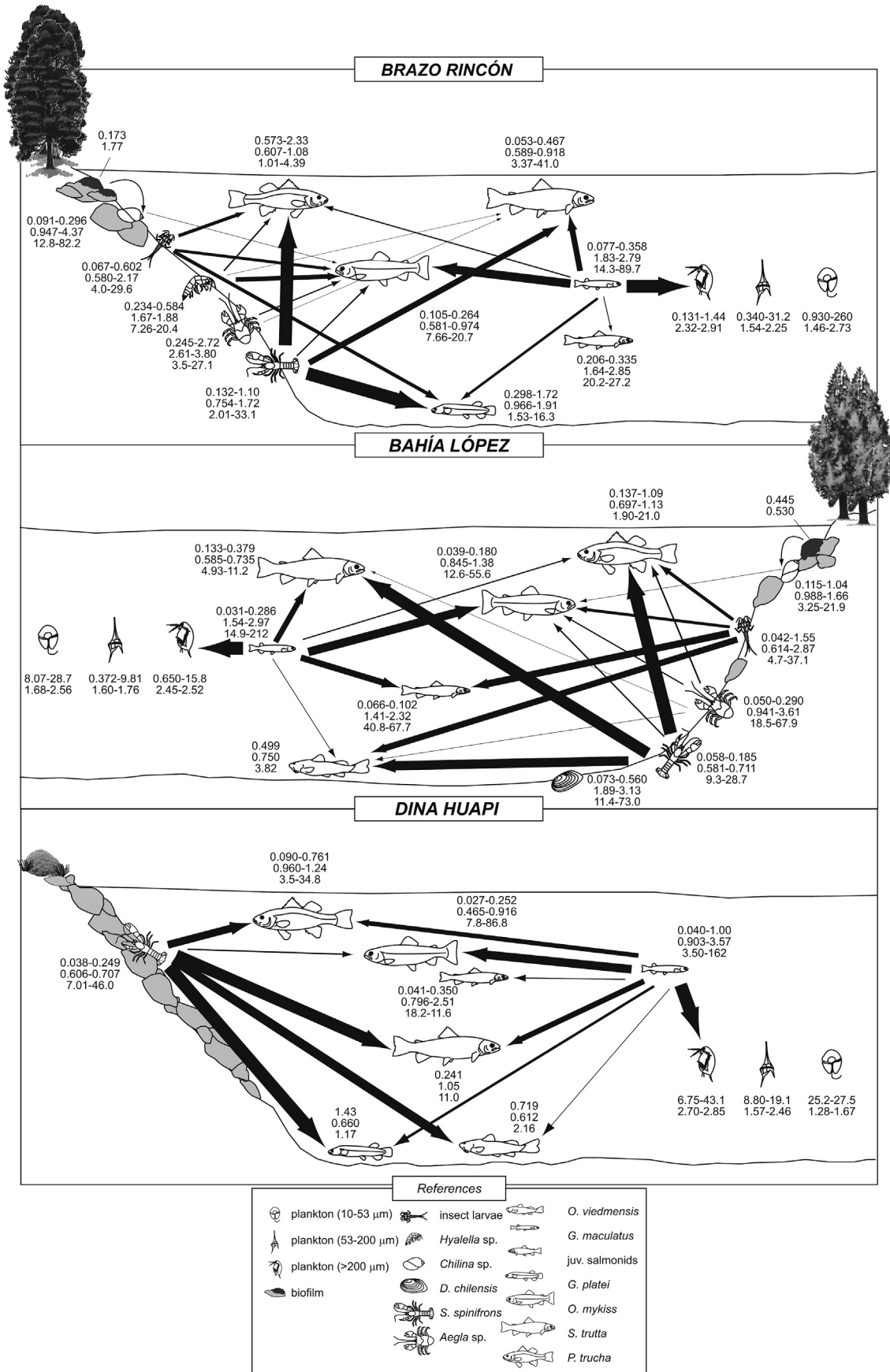
Many biological and life history characteristics affect Hg in fish (Swanson and Kidd, 2010). Mercury concentrations are influenced by age, size, trophic position, growth rate, and body condition (Dittman and Driscoll, 2009; Greenfield et al., 2001; Kidd et al., 1995; Power et al., 2002; Trudel and Rasmussen, 2006). Some studies observed a positive relationship between Hg and length in brown and rainbow trout (Jenssen et al., 2010; Robinson et al., 1995; Weech et al., 2004); however, others found no correlation between both variables in rainbow trout (Weech et al., 2004). Positive (e.g. Adams and Johnson, 1977; Belzile et al., 2009), negative (e.g. Belzile et al., 2009), and no relationship (e.g. Belzile et al., 2009; Gantner et al., 2009; Muir et al., 2005) were observed between length and Se in several fish species.

Increasing or decreasing [THg] and [Se] with fish length may indicate ontogenetic diet shifts to prey with lower or higher element concentrations. The lack of relationship between both variables is probably due to a narrow size range of fish analyzed.

#### 3.2. Selenium-mercury molar ratios

In fish muscle from Lake Nahuel Huapi, Se:Hg molar ratios vary





in a wide range, from 1.01 to 212 (Table A3). The lowest Se:Hg molar ratios were registered in native fish in the three sites: creole perch in BL (1.90) and BR (1.01), and big puyen (1.17) and velvet catfish (2.16) in DH. The highest ratios were obtained in the planktivorous fish small puyen in BL (140 and 212), BR (89 and 90), and DH (130, 161 and 162) (Table A3).

This variation depends mainly on [THg] as [Se] does not vary significantly since it is an essential trace element regulated by the organism (Polak-Juszczak, 2015). On the contrary, [THg] varied in a wide range depending on the species. The fish with the lowest [THg], small puyen and the introduced salmonids, had the highest Se:Hg molar ratios. The natives creole perch, big puyen and velvet catfish, with the highest [THg], had the lowest Se:Hg molar ratios (Table A3). As expected, there were no differences in fish Se:Hg molar ratios of the same size range between the three sites, as Hg and Se in fish muscle do not vary between sites.

Se:Hg molar ratios higher than 1 indicate that Se is in molar excess over Hg, increasing the possibility to play a protective role against Hg toxicity by sequestering it and reducing its biological availability in organisms (Sørmo et al., 2011). On the other hand, the formation of Se-Hg stable compounds reduces the bioavailability of Se, disturbing the activity of Se-dependent functions such as redox control and preventing and reversing oxidative damage in the brain, among other important biological functions (Ralston and Raymond, 2010; Sørmo et al., 2011). The loss of these selenoenzymes has adverse effects and ultimately lethal consequences for the organisms, thus having Se in excess would guarantee there is available Se to replace the ones lost to Hg sequestration (Ralston and Raymond, 2010).

Consumption of fish is important because of their high Se and other nutrient contents. The high Se concentration in fish muscle, may offer abundant natural protection against the Hg also present in this organ (Squadrone et al., 2015). Consequently, in Lake Nahuel Huapi, there might be higher toxicological risk when consuming fish with higher Hg concentrations and lower Se:THg molar ratios such as creole perch, than when consuming salmonids, with lower Hg and higher Se:THg molar ratios.

### 3.3. Mercury trophodynamics

The trophic structure of Lake Nahuel Huapi was thoroughly described by Arcagni et al. (2015) using  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ . Native creole perch, which shares the highest trophic level of the food web with the introduced salmonids, had higher [THg] than the latter. Other native fish such as velvet catfish and the galaxiids big puyen and small puyen, all positioned in lower trophic levels, also had higher [THg] than the introduced fish (Fig. 2). Macroinvertebrates, with a lower trophic level than fish, presented a broad range of [THg], with some values being higher than some fish (Fig. 2). Although having a similar trophic level as forage fish (small puyen) and some macroinvertebrates, all plankton fractions had the highest [THg] in the food web. Biofilm, a food source for some primary consumer macroinvertebrates such as snails had [THg] similar to some fish and macroinvertebrates (Fig. 2). The most important prey items for large fish, insect larvae, crayfish and small puyen did not differ in their [THg] in BR (ANOVA  $F = 2.05$ ,  $p > 0.05$ ) and DH (ANOVA  $F = 1.46$ ,  $p > 0.05$ ), but [THg] in insect larvae from BL were higher than in crayfish and small puyen (ANOVA  $F = 4.89$ ,  $p < 0.05$ ) (Fig. 2, Tables A3 and A4).

There was no relationship between trophic level ( $\delta^{15}\text{N}$ ) and log [THg] when all the food web was considered in BR and BL (Figs. 3a

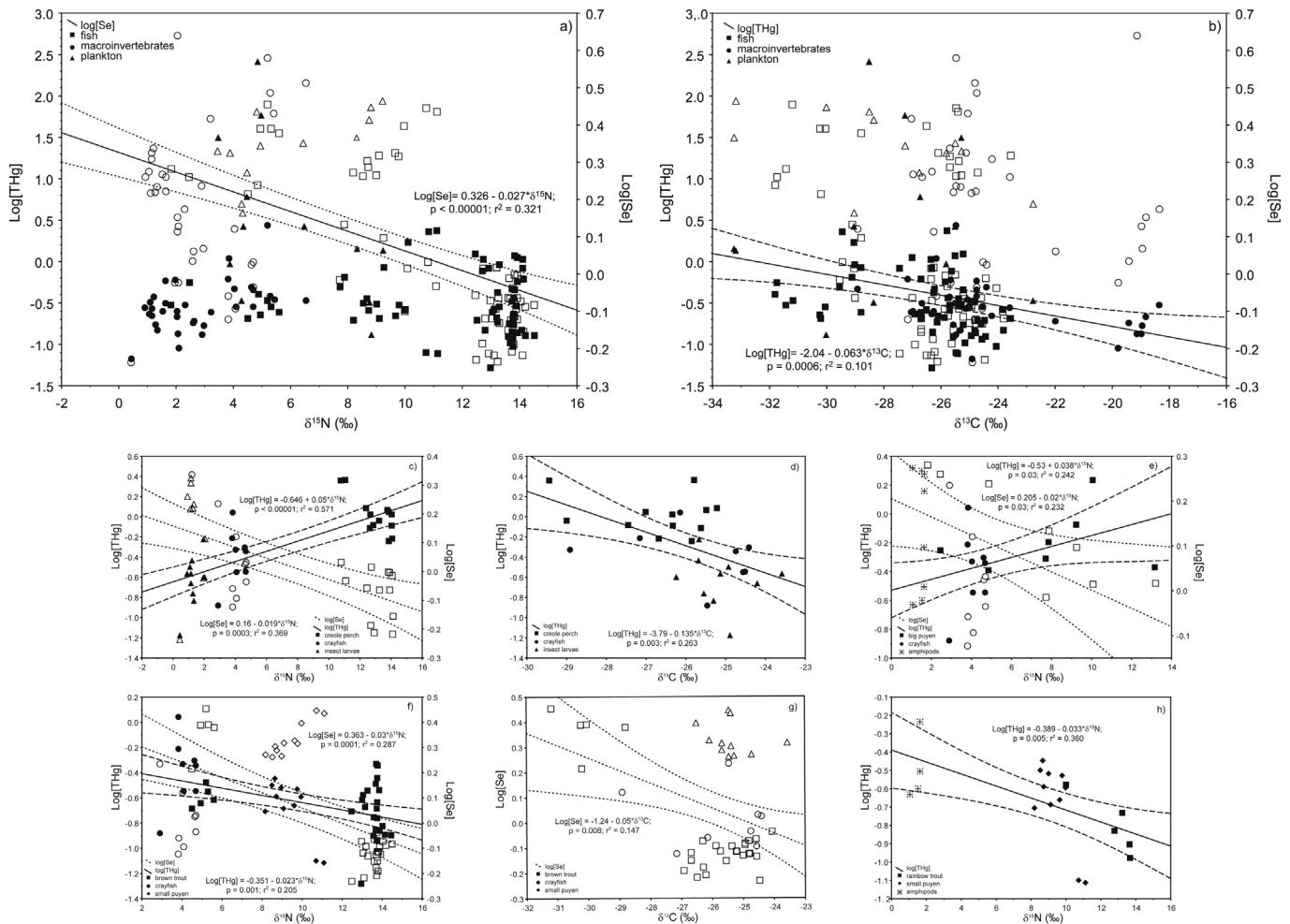
and 4a) but there was a significant negative trend in DH (Fig. 5a).

Although the organic form of Hg, methylmercury (MeHg), is the one that usually biomagnifies in aquatic food webs as it is efficiently taken up by the microorganisms at the base of the food web, retained, and passed to their predators (Morel et al., 1998), THg also tends to biomagnify in aquatic ecosystems, being the biomagnification rate higher in cold-low productive systems (Lavoie et al., 2013) such as Lake Nahuel Huapi. Many works have reported THg biomagnification trends in food webs containing plankton, macroinvertebrates and fish in a variety of ecosystems (e.g. Campbell et al., 2008; Eagles-Smith et al., 2008; Gentès et al., 2013; Omara et al., 2015; Verburg et al., 2014; Zhang et al., 2012), but we found no reports of biodilution as in DH, or of a lack of trend as in BL and BR, besides the work of Arcagni et al. (2013) in Lake Moreno. The biodilution of THg or the lack of biomagnification observed in Lake Nahuel Huapi, might be caused by the high [THg] observed in the planktonic community. The smaller plankton fraction (10–53  $\mu\text{m}$ ), which is composed by phytoplankton and small mixotrophic ciliates (Arcagni et al., 2015), and has similar  $\delta^{15}\text{N}$  values as benthic macroinvertebrates, presented very high [THg], reaching 260  $\mu\text{g g}^{-1}$  (Fig. 2, Tables A3 and A4). Despite the high [THg] measured, %MeHg in plankton are the lowest registered in the food web (0.02–7%, Rizzo et al., 2014). This means that most Hg in plankton is in the inorganic form, which in contrast to MeHg is inefficiently transferred and hence is not biomagnified (Mason et al., 1998).

When THg trophodynamics leading to native and introduced predator fish were analyzed, a positive trend was found between log[THg] and trophic level of native creole perch in all the sites, and big puyen in BR. On the contrary, a negative trend was observed between introduced rainbow trout in BR and BL and brown trout in BR and their preferred prey (Figs. 3c–h and 4c–e). Even though pelagic and benthic prey do not differ in their [THg], as we hypothesized, in Lake Nahuel Huapi there seems to be two main Hg transfer pathways from the base of the food web to top predators: a benthic pathway, from sediments, through crayfish, to native fish, and a less efficient benthic-pelagic pathway, from water, through plankton, and forage fish, to introduced rainbow trout. Brown trout seem to have a mixed pathway, as it preys on both pelagic (small puyen) and benthic prey (crayfish) (Juncos et al., 2015). Trophic segregation among native fish and introduced salmonids has been previously reported in the food web of Lake Nahuel Huapi (Juncos et al., 2015). Native fish, especially creole perch, have a more benthivorous diet, feeding mostly on crayfish, while salmonids are more piscivorous preying heavily on the planktivorous small puyen (Juncos et al., 2015). Crayfish live closely related to sediments, which are major repositories of various contaminants, including Hg, and are the principal location for Hg methylation (Morel et al., 1998). Their diet, detritus, macrophytes, and animal tissue (Rudolph, 2002), and desirability as a food item for fish make them an important link in the transfer of Hg in the food webs of aquatic systems (Pennuto et al., 2005). Hence, in Lake Nahuel Huapi, crayfish may transfer Hg from sediments to benthivorous creole perch and big puyen resulting in the higher Hg concentrations found within fish from this habitat (Fig. 2).

The planktivorous small puyen is the main prey in the opportunistic diet of rainbow trout (Juncos et al., 2015), representing the pelagic pathway of Hg transfer to top predators. As mentioned before, most THg in plankton is in the inorganic form and its transfer to higher trophic levels is inefficient as small puyen, had lower [THg] but higher [MeHg] (Rizzo et al., 2014). In this way, and

Fig. 2. Diagram of trophic links and [THg] (upper values), [Se] (middle values), and Se:Hg molar ratios (lower values) in the sites sampled. The width of the arrows indicates proportion of prey consumed.



**Fig. 3.** Linear regression between log[THg] (black symbols) and log[Se] (white symbols) vs  $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}$  in the whole food web of Brazo Rincón (a and b), and in the food chain of creole perch (c and d), big puyen (e), brown trout (f and g), and rainbow trout (e and f). Only significant regression lines are shown.

contrary to what happens in the benthic pathway, [THg] decreases with increasing trophic level from plankton, small puyen and ultimately to top predator rainbow trout (Figs. 3h and 4d).

Smaller size brown trout (<540 mm) feed mostly on small puyen but as they grow larger, switch to a diet where crayfish becomes more important (>60% IRI; Juncos et al., 2015). In general, [THg] in this species are higher than in rainbow trout and lower than in creole perch, but they increase with increasing size until [THg] in individuals larger than 700 mm are similar to the concentrations observed in creole perch (unpublished data). This observation supports the Hg benthic pathway being more efficient than the pelagic pathway.

Carbon source ( $\delta^{13}\text{C}$ ) was negatively related with log[THg] when all the food web was considered in BR and DH (Figs. 3a and 5a), indicating that the highest concentrations were recorded in the organisms with the lowest  $\delta^{13}\text{C}$ , plankton and some fish species. When dietary pathways to fish were analyzed, a negative relationship between log[THg] and  $\delta^{13}\text{C}$  was observed only in creole perch from BR (Fig. 3d), indicating that although THg bioaccumulation in predator fish seems to depend on their feeding habit, there are no differences in the  $\delta^{13}\text{C}$  values between fish and their prey.

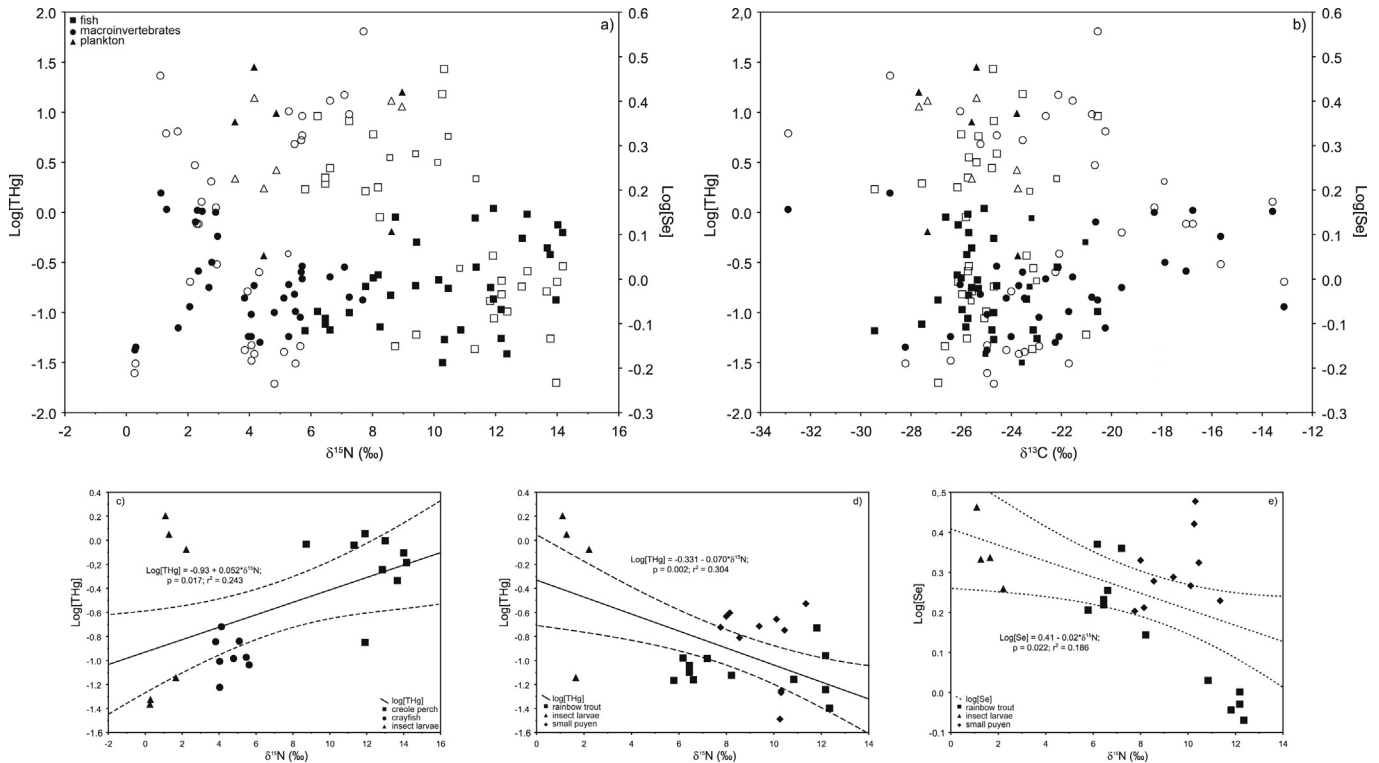
Carbon source may also be important in determining the degree of Hg bioaccumulation in food chains (Kraemer et al., 2012) and negative relationships between  $\delta^{13}\text{C}$  and Hg have been reported in

other studies (Kraemer et al., 2012; McIntyre and Beauchamp, 2007; Power et al., 2002). This would suggest that fish feeding in the pelagic zone are exposed to higher Hg concentration (Kraemer et al., 2012). However, in Lake Nahuel Huapi, this general trend in the food web of decreasing THg with increasing  $\delta^{13}\text{C}$  is due to plankton having very high inorganic Hg which is not transferred to higher trophic levels, and predator fish with higher THg (creole perch, big puyen, brown trout) being depleted in  $^{13}\text{C}$  compared with fish with lower THg (rainbow trout, small puyen) and benthic macroinvertebrates.

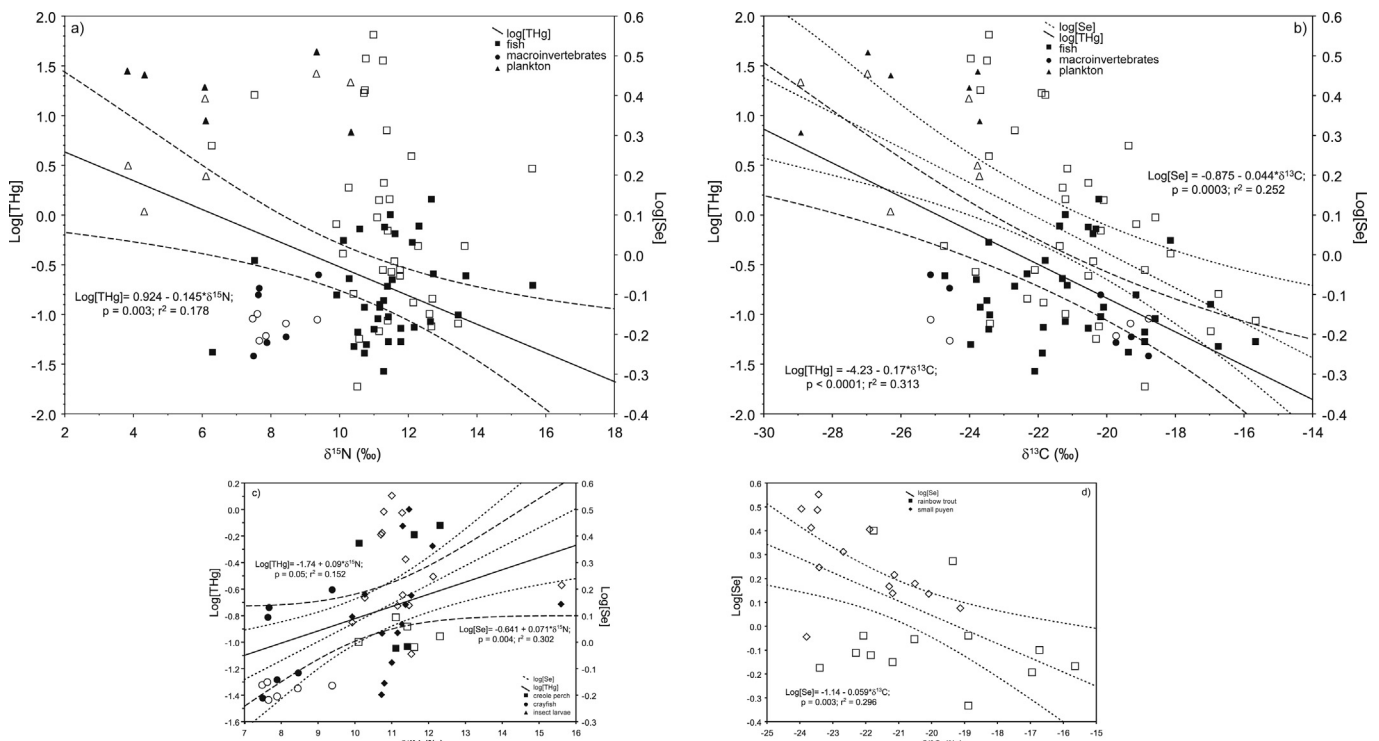
Because of the lake's morphometry, in DH the benthic-littoral habitat seems to be reduced compared to BL and BR. Hence, a higher reliance on pelagic prey was expected, as well as depleted  $^{13}\text{C}$  values in top predator fish. However, the opposite trend was observed, with fish from DH being  $^{13}\text{C}$ -enriched compared with fish from BL and BR (Arcagni et al., 2015). This shows that at least for Lake Nahuel Huapi,  $\delta^{13}\text{C}$  values are not good indicators of carbon source.

### 3.4. Selenium trophodynamics

In general, [Se] were higher in plankton and macroinvertebrates than in fish, and among that community the concentrations were higher in small forage fish, such as small puyen and juvenile salmonids. No trend regarding [Se] between native and introduced



**Fig. 4.** Linear regression between log[THg] (black symbols) and log[Se] (white symbols) vs  $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}$  in the whole food web of Bahía López (a and b), and in the food chain of creole perch (c) and rainbow trout (d and e). Only significant regression lines are shown.



**Fig. 5.** Linear regression between log[THg] (black symbols) and log[Se] (white symbols) vs  $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}$  in the whole food web of Dina Huapi (a and b), and in the food chain of creole perch (c) and rainbow trout (d). Only significant regression lines are shown.

larger fish was observed as with Hg (Fig. 2). There was a negative relationship between log[Se] and trophic level ( $\delta^{15}\text{N}$ ) in BR when all the food web was considered (Fig. 3a) but no trend in BL and DH

(Figs. 4a and 5a). As in these sites, Se showed no relationship with trophic level in the neighboring Lake Moreno (Arcagni et al., 2013). Some studies have reported that selenium concentrations increase



between successive trophic levels (e.g. Jasonsmith et al., 2008; Kehrig et al., 2013; Schneider et al., 2015) but others show no predictable trend (e.g. Campbell et al., 2005; Ouédraogo et al., 2015). The reason for this discrepancy could be that the magnitude of Se enrichment can differ among species within the same trophic level caused by different diets and varying assimilation and elimination efficiencies (Presser and Luoma, 2010).

When different dietary pathways to top predator fish are considered, log[Se] decreased with increasing  $\delta^{15}\text{N}$  in rainbow trout from BL and creole perch, brown trout, and big puyen from BR (Figs. 3c, e, f and 4e). On the contrary, there was a positive relationship between  $\delta^{15}\text{N}$  and log[Se] in creole perch from DH (Fig. 5c). Schneider et al. (2015) observed that both habitat and feeding zone are important factors that influence Se concentrations in invertebrates, which then can be transferred to fish. According to these authors, pelagic invertebrates feeding from the water column had lower Se than benthic invertebrates feeding on benthos. In Lake Nahuel Huapi, the opposite situation was observed, as plankton presents higher Se concentrations than macroinvertebrates in the three sites. Similarly to what happens with Hg, the feeding zone seems to affect Se concentrations in fish. Although Se concentrations in muscle are similar among fish species, rainbow trout which relies more on planktonic energy sources as previously stated, presents higher Se concentrations in liver than creole perch and big puyen which prey more on benthic prey (Juncos et al., 2015). Brown trout, with a mixed diet on forage fish and benthic crayfish, had intermediate Se concentrations between the native fish and rainbow trout. This effect of feeding zone on Se concentration affects its trophodynamics in the food chain as it decreases with increasing trophic level in fish feeding on benthic organisms (creole perch, big puyen and brown trout) and increases with  $\delta^{15}\text{N}$  in rainbow trout which feeds on pelagic organisms.

#### 4. Conclusions

In this work we showed that in Lake Nahuel Huapi, THg did not follow the biomagnification trend usually observed in most aquatic systems worldwide. This phenomenon might be explained by the very high THg concentrations found in plankton, most of it in the inorganic form, which is not efficiently transferred to successive trophic levels. Selenium did not biomagnify in the food either, but this is not an unusual trend. Pelagic carbon sources were related with high THg concentrations in two sites and with Se in one site, indicating that the highest concentrations were from plankton and some fish species.

As we hypothesized, in Lake Nahuel Huapi, there was also a clear pattern of differential THg bioaccumulation between benthic and pelagic taxa which was strongly revealed by the difference in Hg concentrations between introduced and native fish. Total Hg in muscle of benthic-littoral native fish increased with increasing trophic level. On the contrary, rainbow and brown trout, both introduced salmonids to these environments which feeds on planktonic organisms, presented lower THg concentrations than their diet, and than native fish.

Se:THg molar ratios were higher than one in all the fish species, indicating that Se might be offering a natural protection against Hg toxicity.

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#### Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.chemosphere.2016.09.085>.

#### References

- Adams, W.J., Johnson, H.E., 1977. Survey of the selenium content in the aquatic biota of eastern Lake Erie. *J. Gt. Lakes. Res.* 3, 10–14. [http://dx.doi.org/10.1016/S0380-1330\(77\)72223-3](http://dx.doi.org/10.1016/S0380-1330(77)72223-3).
- Arcagni, M., Campbell, L.M., Arribère, M.A., Marvin-DiPasquale, M., Rizzo, A.P., Ribeiro Guevara, S., 2013. Differential mercury transfer in the aquatic food web of a double basined lake associated with selenium and habitat. *Sci. Total Environ.* 454–455, 170–180. <http://dx.doi.org/10.1016/j.scitotenv.2013.03.008>.
- Arcagni, M., Rizzo, A.P., Campbell, L.M., Arribère, M.A., Juncos, R., Reissig, M., Kyser, K., Barriga, J.P., Battini, M.A., Ribeiro Guevara, S., 2015. Stable isotope analysis of trophic structure, energy flow and spatial variability in a large ultraoligotrophic lake in Northwest Patagonia. *J. Gt. Lakes. Res.* 41, 916–925. <http://dx.doi.org/10.1016/j.jglr.2015.05.008>.
- Arribère, M.A., Campbell, L.M., Rizzo, A.P., Arcagni, M., Revenga, J.E., Ribeiro Guevara, S., 2010. Trace elements in plankton, benthic organisms, and forage fish of Lake Moreno, Northern Patagonia, Argentina. *Water. Air. Soil Pollut.* 212, 167–182. <http://dx.doi.org/10.1007/s11270-010-0330-3>.
- Arribère, M.A., Ribeiro Guevara, S., Bubach, D.F., Arcagni, M., Vigliano, P.H., 2008. Selenium and mercury in native and introduced fish species of Patagonian lakes, Argentina. *Biol. Trace Elem. Res.* 122, 42–63. <http://dx.doi.org/10.1007/s12011-007-8059-6>.
- Arteel, G.E., Sies, H., 2001. The biochemistry of selenium and the glutathione system. *Environ. Toxicol. Pharmacol.* 10, 153–158. [http://dx.doi.org/10.1016/S1382-6689\(01\)00078-3](http://dx.doi.org/10.1016/S1382-6689(01)00078-3).
- Belzile, N., Chen, Y.-W., Yang, D.-Y., Truong, H.-Y.T., Zhao, Q.-X., 2009. Selenium bioaccumulation in freshwater organisms and antagonistic effect against mercury assimilation. *Environ. Bioindic.* 4, 203–221. <http://dx.doi.org/10.1080/1555270903143408>.
- Cabana, G., Tremblay, A., Kalff, J., Rasmussen, J.B., 1994. Pelagic food chain structure in Ontario lakes: a determinant of mercury levels in lake trout (*Salvelinus namaycush*). *Can. J. Fish. Aquat. Sci.* 51, 381–389. <http://dx.doi.org/10.1139/f94-039>.
- Campbell, L.M., Norstrom, R.J., Hobson, K.A., Muir, D.C.G., Backus, S.M., Fisk, A.T., 2005. Mercury and other trace elements in a pelagic Arctic marine food web (Northwater Polynya, Baffin Bay). *Sci. Total Environ.* 351–352, 247–263. <http://dx.doi.org/10.1016/j.scitotenv.2005.02.043>.
- Campbell, L.M., Verburg, P., Dixon, D.G., Hecky, R.E., 2008. Mercury biomagnification in the food web of Lake Tanganyika (Tanzania, East Africa). *Sci. Total Environ.* 402, 184–191. <http://dx.doi.org/10.1016/j.scitotenv.2008.04.017>.
- Ciardullo, S., Aurelli, F., Coni, E., Guandalini, E., Iosi, F., Raggi, A., Rufo, G., Cubadda, F., 2008. Bioaccumulation potential of dietary arsenic, cadmium, lead, mercury, and selenium in organs and tissues of rainbow trout (*Oncorhynchus mykiss*) as a function of fish growth. *J. Agric. Food Chem.* 56, 2442–2451. <http://dx.doi.org/10.1021/jf703572t>.
- Cizdziel, J.V., Hinners, T.A., Cross, C.L., Pollard, J.E., 2003. Distribution of mercury in the tissues of five species of freshwater fish from Lake Mead, USA. *J. Environ. Monit.* 5, 802. <http://dx.doi.org/10.1039/b307641p>.
- Cuvin-Aralar, M.L.A., Furness, R.W., 1991. Mercury and selenium interaction: a review. *Ecotoxicol. Environ. Saf.* 21, 348–364. [http://dx.doi.org/10.1016/0147-6513\(91\)90074-Y](http://dx.doi.org/10.1016/0147-6513(91)90074-Y).
- DeNiro, M.J., Epstein, S., 1981. Influence of diet on the distribution of nitrogen isotopes in animals. *Geochim. Cosmochim. Acta* 45, 341–351. [http://dx.doi.org/10.1016/0016-7037\(81\)90244-1](http://dx.doi.org/10.1016/0016-7037(81)90244-1).
- DeNiro, M.J., Epstein, S., 1978. Influence of diet on the distribution of carbon isotopes in animals. *Geochim. Cosmochim. Acta* 42, 495–506. [http://dx.doi.org/10.1016/0016-7037\(78\)90199-0](http://dx.doi.org/10.1016/0016-7037(78)90199-0).
- Diaz, M.M., Pedrozo, F.L., Reynolds, C.S., Temporetti, P.F., 2007. Chemical composition and the nitrogen - regulated trophic state of Patagonian lakes. *Limnologia* 37, 17–27. <http://dx.doi.org/10.1016/j.limno.2006.08.006>.
- Dittman, J.A., Driscoll, C.T., 2009. Factors influencing changes in mercury concentrations in lake water and yellow perch (*Perca flavescens*) in Adirondack lakes. *Biogeochemistry* 93, 179–196. <http://dx.doi.org/10.1007/s10533-009-9289-9>.
- Drevnick, P.E., Roberts, A.P., Otter, R.R., Hammerschmidt, C.R., Klaper, R., Oris, J.T., 2008. Mercury toxicity in livers of northern pike (*Esox lucius*) from Isle Royale, USA. *Comp. Biochem. Physiol. Part C. Toxicol. Pharmacol.* 147, 331–338. <http://dx.doi.org/10.1016/j.cbpc.2007.12.003>.
- Eagles-Smith, C.A., Suchanek, T.H., Colwell, A.E., Anderson, N.L., 2008. Mercury trophic transfer in a eutrophic lake: the importance of habitat-specific foraging. *Ecol. Appl.* 18, 196–212. <http://dx.doi.org/10.1890/06-1476.1>.
- Eisler, R., 1985. *Selenium Hazards to Fish, Wildlife, and Invertebrates: a Synoptic*

- Review. Laurel, Maryland. Biological Report.
- Fitzgerald, W.F., Engstrom, D.R., Mason, R.P., Nater, E.A., 1998. The case for atmospheric mercury contamination in remote areas. *Environ. Sci. Technol.* 32, 1–7. <http://dx.doi.org/10.1021/es970284w>.
- Floor, G.H., Román-Ross, G., 2012. Selenium in volcanic environments: a review. *Appl. Geochem.* 27, 517–531. <http://dx.doi.org/10.1016/j.apgeochem.2011.11.010>.
- France, R.L., 1995. Differentiation between littoral and pelagic food webs in lakes using stable carbon isotopes. *Limnol. Oceanogr.* 40, 1310–1313. <http://dx.doi.org/10.4319/lo.1995.40.7.1310>.
- Gantner, N., Power, M., Babaluk, J.A., Reist, J.D., Köck, G., Lockhart, L.W., Solomon, K.R., Muir, D.C.G., 2009. Temporal trends of mercury, cesium, potassium, selenium, and thallium in arctic char (*Salvelinus alpinus*) from lake Hazen, Nunavut, Canada: effects of trophic position, size, and age. *Environ. Toxicol. Chem.* 28, 254–263. <http://dx.doi.org/10.1897/08-054.1>.
- Gentès, S., Maury-Brachet, R., Guyoneaud, R., Monperrus, M., André, J.-M., Davail, S., Legeay, A., 2013. Mercury bioaccumulation along food webs in temperate aquatic ecosystems colonized by aquatic macrophytes in south western France. *Ecotoxicol. Environ. Saf.* 91, 180–187. <http://dx.doi.org/10.1016/j.ecoenv.2013.02.001>.
- Goldstein, R.M., Brigham, M.E., Stauffer, J.C., 1996. Comparison of mercury concentrations in liver, muscle, whole bodies, and composites of fish from the Red River of the North. *Can. J. Fish. Aquat. Sci.* 53, 244–252. <http://dx.doi.org/10.1139/f95-203>.
- Greenfield, B.K., Hrabik, T.R., Harvey, C.J., Carpenter, S.R., 2001. Predicting mercury levels in yellow perch: use of water chemistry, trophic ecology, and spatial traits. *Can. J. Fish. Aquat. Sci.* 58, 1419–1429. <http://dx.doi.org/10.1139/f01-088>.
- Hall, B.D., Bodaly, R.A., Fudge, R.J.P., Rudd, J.W.M., Rosenberg, D.M., 1997. Food as the dominant pathway of methylmercury uptake by fish. *Water, Air, Soil Pollut.* 100, 13–24. <http://dx.doi.org/10.1023/A:1018071406537>.
- Hammerschmidt, C.R., Fitzgerald, W.F., 2006. Methylmercury in freshwater fish linked to atmospheric mercury deposition. *Environ. Sci. Technol.* 40, 7764–7770. <http://dx.doi.org/10.1021/es061480i>.
- Havelková, M., Dusek, L., Némethová, D., Poleszczuk, G., Svobodová, Z., 2008. Comparison of mercury distribution between liver and muscle – a bio-monitoring of fish from lightly and heavily contaminated localities. *Sensors* 8, 4095–4109. <http://dx.doi.org/10.3390/s8074095>.
- Jardine, T.D., Kidd, K.A., Fisk, A.T., 2006. Applications, considerations, and sources of uncertainty when using stable isotope analysis in ecotoxicology. *Environ. Sci. Technol.* 40, 7501–7511. <http://dx.doi.org/10.1021/es061263h>.
- Jasonsmith, J.F., Maher, W.A., Roach, A.C., Krikowa, F.A., 2008. Selenium bioaccumulation and biomagnification in Lake Wallace, New South Wales, Australia. *Mar. Freshw. Res.* 59, 1048–1060. <http://dx.doi.org/10.1071/MF08197>.
- Jenssen, M.T.S., Borgström, R., Salbu, B., Rosseland, B.O., 2010. The importance of size and growth rate in determining mercury concentrations in European minnow (*Phoxinus phoxinus*) and brown trout (*Salmo trutta*) in the subalpine lake, Øvre Heimdalsvatn. *Hydrobiologia* 642, 115–126. <http://dx.doi.org/10.1007/s10750-010-0156-4>.
- Jewett, S.C., Duffy, L.K., 2007. Mercury in fishes of Alaska, with emphasis on subsistence species. *Sci. Total Environ.* 387, 3–27. <http://dx.doi.org/10.1016/j.scitotenv.2007.07.034>.
- Juncos, R., Milano, D., Macchi, P.J., Vigliano, P.H., 2015. Niche segregation facilitates coexistence between native and introduced fishes in a deep Patagonian lake. *Hydrobiologia* 747, 53–67. <http://dx.doi.org/10.1007/s10750-014-2122-z>.
- Karimi, R., Chen, C.Y., Folt, C.L., 2016. Comparing nearshore benthic and pelagic prey as mercury sources to lake fish: the importance of prey quality and mercury content lake fish: the importance of prey quality and mercury content. *Sci. Total Environ.* 565, 211–221. <http://dx.doi.org/10.1016/j.scitotenv.2016.04.162>.
- Kehrig, H.A., Palermo, E.A., Seixas, T.G., Branco, C.W.C., Moreira, I., Malm, O., 2009. Trophic transfer of methylmercury and trace elements by tropical estuarine seston and plankton. *Estuar. Coast. Shelf Sci.* 85, 36–44. <http://dx.doi.org/10.1016/j.ecss.2009.05.027>.
- Kehrig, H.A., Seixas, T.G., Malm, O., Di Benedetto, A.P.M., Rezende, C.E., 2013. Mercury and selenium biomagnification in a Brazilian coastal food web using nitrogen stable isotope analysis: a case study in an area under the influence of the Paraíba do Sul River plume. *Mar. Pollut. Bull.* 75, 283–290. <http://dx.doi.org/10.1016/j.marpolbul.2013.06.046>.
- Khan, M.A.K., Wang, F., 2009. Mercury - selenium compounds and their toxicological significance: toward a molecular understanding of the mercury - selenium antagonism. *Environ. Toxicol. Chem.* 28, 1567–1577. <http://dx.doi.org/10.1897/08-375.1>.
- Kidd, K.A., Hesslein, R.H., Fudge, R.J.P., Hallard, K.A., 1995. The influence of trophic level as measured by  $\delta^{15}N$  on mercury concentrations in freshwater organisms. *Water, Air, Soil Pollut.* 80, 1011–1015. [http://dx.doi.org/10.1007/978-94-011-0153-0\\_110](http://dx.doi.org/10.1007/978-94-011-0153-0_110).
- Kraemer, L.D., Evans, D., Dillon, P.J., 2012. The impacts of ontogenetic dietary shifts in yellow perch (*Perca flavescens*) on Zn and Hg accumulation. *Ecotoxicol. Environ. Saf.* 78, 246–252. <http://dx.doi.org/10.1016/j.ecoenv.2011.11.033>.
- Lantzy, R.J., Mackenzie, F.T., 1979. Atmospheric trace metals: global cycles and assessment of man's impact. *Geochim. Cosmochim. Acta* 43, 511–525. [http://dx.doi.org/10.1016/0016-7037\(79\)90162-5](http://dx.doi.org/10.1016/0016-7037(79)90162-5).
- Lavoie, R.A., Jardine, T.D., Chumchal, M.M., Kidd, K.A., Campbell, L.M., 2013. Biomagnification of mercury in aquatic food webs: a worldwide meta-analysis. *Environ. Sci. Technol.* 47, 13385–13394. <http://dx.doi.org/10.1021/es403103t>.
- Lemly, A.D., 2004. Aquatic selenium pollution is a global environmental safety issue. *Ecotoxicol. Environ. Saf.* 59, 44–56. [http://dx.doi.org/10.1016/S0147-6513\(03\)00095-2](http://dx.doi.org/10.1016/S0147-6513(03)00095-2).
- Lemly, A.D., 1999. Selenium transport and bioaccumulation in aquatic ecosystems: a proposal for water quality criteria based on hydrological units. *Ecotoxicol. Environ. Saf.* 42, 150–156. <http://dx.doi.org/10.1006/eesa.1998.1737>.
- Lescord, G.L., Kidd, K.A., Kirk, J.L., O'Driscoll, N.J., Wang, X., Muir, D.C.G., 2015. Factors affecting biotic mercury concentrations and biomagnification through lake food webs in the Canadian high Arctic. *Sci. Total Environ.* 509–510, 195–205. <http://dx.doi.org/10.1016/j.scitotenv.2014.04.133>.
- Mason, R.P., Laporte, J.-M., Andres, S., 2000. Environmental contamination and toxicology factors controlling the bioaccumulation of mercury, methylmercury, arsenic, selenium, and cadmium by freshwater invertebrates and fish. *Arch. Environ. Contam. Toxicol.* 38, 283–297. <http://dx.doi.org/10.1007/s002449910038>.
- Mason, R.P., Rolffhus, K.R., Fitzgerald, W.F., 1998. Mercury in the North Atlantic. *Mar. Chem.* 61, 37–53. [http://dx.doi.org/10.1016/S0304-4203\(98\)00006-1](http://dx.doi.org/10.1016/S0304-4203(98)00006-1).
- McIntyre, J.K., Beauchamp, D.A., 2007. Age and trophic position dominate bioaccumulation of mercury and organochlorines in the food web of Lake Washington. *Sci. Total Environ.* 372, 571–584. <http://dx.doi.org/10.1016/j.scitotenv.2006.10.035>.
- Modenutti, B.E., Balseiro, E.G., Elser, J.J., Bastidas Navarro, M.A., Cuassolo, F., Laspoumaderes, C., Souza, M.S., Díaz Villanueva, V., 2013. Effect of volcanic eruption on nutrients, light, and phytoplankton in oligotrophic lakes. *Limnol. Oceanogr.* 58, 1165–1175. <http://dx.doi.org/10.4319/lo.2013.58.4.1165>.
- Morel, F.M.M., Kraepiel, A.M.L., Amyot, M., 1998. The chemical cycle and bioaccumulation of mercury. *Annu. Rev. Ecol. Syst.* 29, 543–566. <http://dx.doi.org/10.1146/annurev.ecolsys.29.1.543>.
- Muir, D.C.G., Wang, X., Bright, D.A., Lockhart, W.L., Köck, G., 2005. Spatial and temporal trends of mercury and other metals in landlocked char from lakes in the Canadian Arctic archipelago. *Sci. Total Environ.* 351–352, 464–478. <http://www.sciencedirect.com/science/article/pii/S004896970500433X>.
- Naranjo, J.A., Stern, C.R., 2004. Holocene tephrochronology of the southernmost part (42° 30' - 45°S) of the Andean Southern volcanic zone. *Rev. Geol. Chile* 31, 225–240. <http://dx.doi.org/10.4067/S0716-02082004000200003>.
- Nriagu, J.O., Becker, C., 2003. Volcanic emissions of mercury to the atmosphere: global and regional inventories. *Sci. Total Environ.* 304, 3–12. [http://dx.doi.org/10.1016/S0048-9697\(02\)00552-1](http://dx.doi.org/10.1016/S0048-9697(02)00552-1).
- Omara, M., Crimmins, B.S., Back, R.C., Hopke, P.K., Chang, F.-C., Holsen, T.M., 2015. Mercury biomagnification and contemporary food web dynamics in lakes Superior and Huron. *J. Gt. Lakes. Res.* 41, 473–483. <http://dx.doi.org/10.1016/j.jglr.2015.02.005>.
- Ouédraogo, O., Chételat, J., Amyot, M., 2015. Bioaccumulation and trophic transfer of mercury and selenium in African sub-tropical fluvial reservoirs food webs (Burkina Faso). *PLoS One* 10, e0123048. <http://dx.doi.org/10.1371/journal.pone.0123048>.
- Pacyna, E.G., Pacyna, J.M., Steenhuisen, F., Wilson, S., 2006. Global anthropogenic mercury emission inventory for 2000. *Atmos. Environ.* 40, 4048–4063. <http://dx.doi.org/10.1016/j.atmosenv.2006.03.041>.
- Pacyna, E.G., Pacyna, J.M., Sundseth, K., Munthe, J., Kindbom, K.A., Wilson, S.J., Steenhuisen, F., Maxson, P.A., 2010. Global emission of mercury to the atmosphere from anthropogenic sources in 2005 and projections to 2020. *Atmos. Environ.* 44, 2487–2499. <http://dx.doi.org/10.1016/j.atmosenv.2009.06.009>.
- Pelletier, E., 1985. Mercury-selenium interactions in aquatic organisms: a review. *Mar. Environ. Res.* 18, 111–132. [http://dx.doi.org/10.1016/0141-1136\(86\)90003-6](http://dx.doi.org/10.1016/0141-1136(86)90003-6).
- Pennuto, C.M., Lane, O.P., Evers, D.C., Taylor, R.J., Loukmas, J.J., 2005. Mercury in the northern crayfish, *Orconectes virilis* (Hagen), in New England, USA. *Ecotoxicology* 14, 149–162. <http://dx.doi.org/10.1007/s10646-004-6266-x>.
- Peterson, S.A., Ralston, N.V.C., Peck, D.V., Van Sickle, J., Robertson, J.D., Spate, V.L., Morris, J.S., 2009. How might selenium moderate the toxic effects of mercury in stream fish of the western U.S. *Environ. Sci. Technol.* 43, 3919–3925. <http://dx.doi.org/10.1021/es803203g>.
- Polak-Juszczak, L., 2015. Selenium and mercury molar ratios in commercial fish from the Baltic Sea: additional risk assessment criterion for mercury exposure. *Food Control* 50, 881–888. <http://dx.doi.org/10.1016/j.foodcont.2014.10.046>.
- Porcella, D.B., Bowie, G.L., Sanders, J.G., Cutter, G.A., 1991. Assessing Se cycling and toxicity in aquatic ecosystems. *Water, Air, Soil Pollut.* 57–58, 3–11. <http://dx.doi.org/10.1007/BF00282863>.
- Post, D.M., 2002. Using stable isotopes to estimate trophic position: models, methods and assumptions. *Ecology* 83, 703–718. [http://dx.doi.org/10.1890/0012-9658\(2002\)083\[0703:USITET\]2.0.CO;2](http://dx.doi.org/10.1890/0012-9658(2002)083[0703:USITET]2.0.CO;2).
- Power, M., Klein, G.M., Guiguer, K.R.A., Kwan, M.K.H., 2002. Mercury accumulation in the fish community of a sub-Arctic lake in relation to trophic position and carbon sources. *J. Appl. Ecol.* 39, 819–830. <http://dx.doi.org/10.1046/j.1365-2664.2002.00758.x>.
- Presser, T.S., Luoma, S.N., 2010. A methodology for ecosystem-scale modeling of selenium. *Integr. Environ. Assess. Manag.* 6, 685–710. <http://dx.doi.org/10.1002/ieam.101>.
- Quiros, R., Drago, E., 1985. Relaciones entre variables físicas, morfológicas y climáticas en lagos patagónicos. *Rev. la Asoc. Ciencias Nat. del Litoral* 16, 181–199.
- Ralston, N.V.C., Blackwell, J.L., Raymond, L.J., 2007. Importance of molar ratios in selenium-dependent protection against methylmercury toxicity. *Biol. Trace Elem. Res.* 119, 255–268. <http://dx.doi.org/10.1007/s12011-007-8005-7>.
- Ralston, N.V.C., Raymond, L.J., 2010. Dietary selenium's protective effects against methylmercury toxicity. *Toxicology* 278, 112–123. <http://dx.doi.org/10.1016/>

- j.tox.2010.06.004.
- Rasmussen, P.E., 1994. Current methods of estimating atmospheric mercury fluxes in remote areas. *Environ. Sci. Technol.* 28, 2233–2241. <http://dx.doi.org/10.1021/es00062a006>.
- Ribeiro Guevara, S., Rizzo, A.P., Sánchez, R.S., Arribére, M.A., 2005. Heavy metal inputs in Northern Patagonia lakes from short sediment core analysis. *J. Radioanal. Nucl. Chem.* 265, 481–493. <http://dx.doi.org/10.1007/s10967-005-0852-0>.
- Rizzo, A.P., Arcagni, M., Arribére, M.A., Bubach, D.F., Ribeiro Guevara, S., 2011. Mercury in the biotic compartments of Northwest Patagonia lakes, Argentina. *Chemosphere* 84, 70–79. <http://dx.doi.org/10.1016/j.chemosphere.2011.02.052>.
- Rizzo, A.P., Arcagni, M., Campbell, L.M., Koron, N., Pavlin, M., Arribére, M.A., Horvat, M., Ribeiro Guevara, S., 2014. Source and trophic transfer of mercury in plankton from an ultraoligotrophic lacustrine system (Lake Nahuel Huapi, North Patagonia). *Ecotoxicology* 23, 1184–1194. <http://dx.doi.org/10.1007/s10646-014-1260-4>.
- Robinson, B.H., Brooks, R.R., Outred, H.A., Kirkman, J.H., 1995. Mercury and arsenic in trout from the Taupo volcanic zone and Waikato river, North Island. *New Zeal. Chem. Speciat. Bioavailab.* 7, 27–32. <http://dx.doi.org/10.1080/09542299.1995.11083237>.
- Rudolph, E.H., 2002. Sobre la biología del camarón de río *Samastacus spinifrons* (Philippi 1882) (Decapoda, Parastacidae). *Gayana (Concepción)* 66, 147–159. <http://dx.doi.org/10.4067/S0717-65382002000200009>.
- Scheuhammer, A.M., Meyer, M.W., Sandheinrich, M.B., Murray, M.W., 2007. Effects of environmental methylmercury on the health of wild birds, mammals, and fish. *Ambio* 36, 12–18. [http://dx.doi.org/10.1579/0044-7447\(2007\)36\[12:EOE-MOT\]2.0.CO;2](http://dx.doi.org/10.1579/0044-7447(2007)36[12:EOE-MOT]2.0.CO;2).
- Schneider, L., Maher, W.A., Potts, J., Taylor, A.M., Batley, G.E., Krikowa, F., Chariton, A.A., Gruber, B., 2015. Modeling food web structure and selenium biomagnification in lake Macquarie, New South Wales, Australia, using stable carbon and nitrogen isotopes. *Environ. Toxicol. Chem.* 34, 608–617. <http://dx.doi.org/10.1002/etc.2847>.
- Sørmo, E.G., Ciesielski, T.M., Øverjordet, I.B., Lierhagen, S., Eggen, G.S., Berg, T., Jenssen, B.M., 2011. Selenium moderates mercury toxicity in free-ranging freshwater fish. *Environ. Sci. Technol.* 45, 6561–6566. <http://dx.doi.org/10.1021/es200478b>.
- Squadrone, S., Benedetto, A., Brizio, P., Prearo, M., Abete, M.C., 2015. Mercury and selenium in European catfish (*Silurus glanis*) from Northern Italian Rivers: can molar ratio be a predictive factor for mercury toxicity in a top predator? *Chemosphere* 119, 24–30. <http://dx.doi.org/10.1016/j.chemosphere.2014.05.052>.
- Swanson, H.K., Kidd, K.A., 2010. Mercury concentrations in arctic food fishes reflect the presence of anadromous arctic charr (*Salvelinus alpinus*), species, and life history. *Environ. Sci. Technol.* 44, 3286–3292. <http://dx.doi.org/10.1021/es100439t>.
- Swift, M.C., 2002. Stream ecosystem response to, and recovery from, experimental exposure to selenium. *J. Aquat. Ecosyst. Stress Recover* 9, 159–184. <http://dx.doi.org/10.1023/A:1021299003516>.
- Trudel, M., Rasmussen, J.B., 2006. Bioenergetics and mercury dynamics in fish: a modelling perspective. *Can. J. Fish. Aquat. Sci.* 63, 1890–1902. <http://dx.doi.org/10.1139/f06-081>.
- Verburg, P., Hickey, C.W., Phillips, N., 2014. Mercury biomagnification in three geothermally-influenced lakes differing in chemistry and algal biomass. *Sci. Total Environ.* 493, 342–354. <http://dx.doi.org/10.1016/j.scitotenv.2014.05.097>.
- Wang, W.-X., 2012. Biodynamic understanding of mercury accumulation in marine and freshwater fish. *Adv. Environ. Res.* 1, 15–35. <http://dx.doi.org/10.12989/aer.2012.1.1.015>.
- Wang, Y., Gu, B., Lee, M.K., Jiang, S., Xu, Y., 2014. Isotopic evidence for anthropogenic impacts on aquatic food web dynamics and mercury cycling in a subtropical wetland ecosystem in the US. *Sci. Total Environ.* 487, 557–564. <http://dx.doi.org/10.1016/j.scitotenv.2014.04.060>.
- Weech, S.A., Scheuhammer, A.M., Elliott, J.E., Cheng, K.M., 2004. Mercury in fish from the Pinchi Lake region, British Columbia, Canada. *Environ. Pollut.* 131, 275–286. <http://dx.doi.org/10.1016/j.envpol.2004.02.016>.
- Yang, D.-Y., Chen, Y.-W., Gunn, J.M., Belzile, N., 2008. Selenium and mercury in organisms: interactions and mechanisms. *Environ. Rev.* 16, 71–92. <http://dx.doi.org/10.1139/A08-001>.
- Yang, D.-Y., Ye, X., Chen, Y.-W., Belzile, N., 2010. Inverse relationships between selenium and mercury in tissues of young walleye (*Stizostedion vitreum*) from Canadian boreal lakes. *Sci. Total Environ.* 408, 1676–1683. <http://dx.doi.org/10.1016/j.scitotenv.2009.11.049>.
- Zhang, L., Campbell, L.M., Johnson, T.B., 2012. Seasonal variation in mercury and food web biomagnification in Lake Ontario, Canada. *Environ. Pollut.* 161, 178–184. <http://dx.doi.org/10.1016/j.envpol.2011.10.023>.