

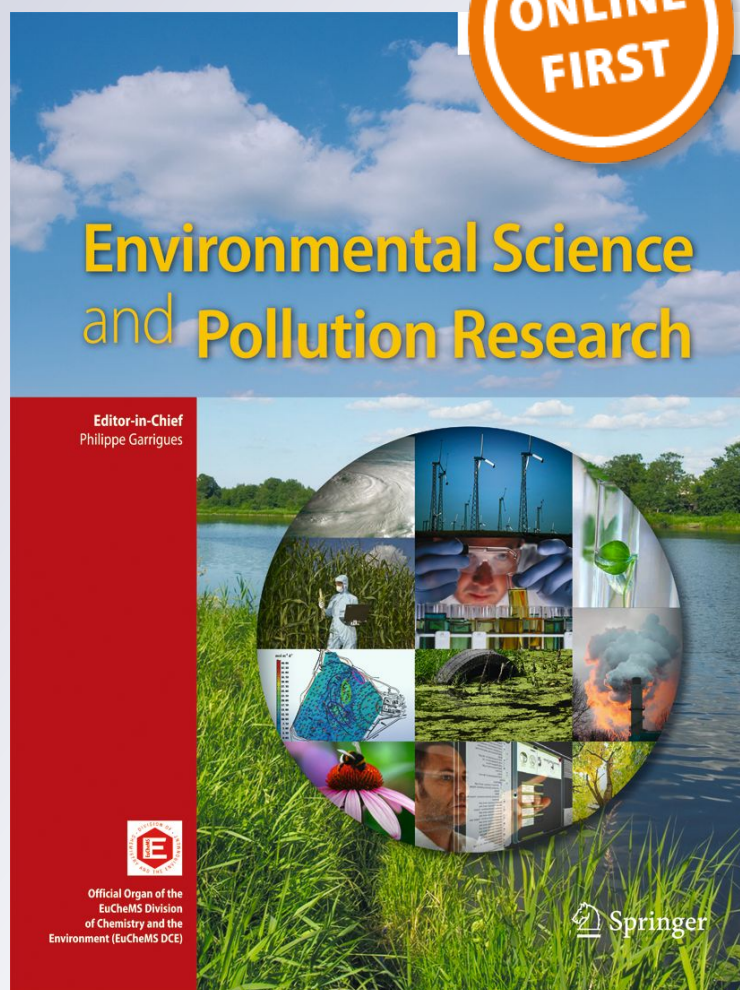
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Zinc in an ultraoligotrophic lake food web

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Abstract

Zinc (Zn) bioaccumulation and trophic transfer were analyzed in the food web of Lake Nahuel Huapi, a deep, unpolluted ultraoligotrophic system in North Patagonia. Benthic macroinvertebrates, plankton, and native and introduced fish were collected at three sites. The effect of pyroclastic inputs on Zn levels in lacustrine food webs was assessed by studying the impact of the eruption of Puyehue-Cordón Caulle volcanic complex (PCCVC) in 2011, by performing three sampling campaigns immediately before and after the PCCVC eruption, and after 2 years of recovery of the ecosystem. Zinc trophodynamics in L. Nahuel Huapi food web was assessed using nitrogen stable isotopes ($\delta^{15}\text{N}$). There was no significant increase of Zn concentrations ([Zn]) in L. Nahuel Huapi biota after the PCCVC eruption, despite the evidence of [Zn] increase in lake water that could be associated with volcanic ash leaching. The organisms studied exhibited [Zn] above the threshold level considered for dietary deficiency, regulating Zn adequately even under a catastrophic situations like PCCVC 2011 eruption. Zinc concentrations exhibited a biodilution pattern in the lake's food web. To the best of our knowledge, present research is the first report of Zn biodilution in lacustrine systems, and the first to study Zn transfer in a freshwater food web including both pelagic and benthic compartments.

Keywords Plankton · Macroinvertebrate · Fish · Nitrogen stable isotopes · Lake Nahuel Huapi · North Patagonia

Introduction

Metal bioaccumulation throughout food webs could constitute a risk for different organisms and for human health (Comby et al. 2014). Their bioavailability and potential for bioaccumulation and biomagnification in all components of an eco-

system could be high, being dietary exposure the primary transfer route in aquatic food webs (Croteau et al. 2005; Jara-Marini et al. 2009). Therefore, it is critical to understand their trophic transference in aquatic environments (Mendoza-Carranza et al. 2016). Zinc (Zn) is a metal that can pollute aquatic ecosystems from anthropogenic and natural sources, and can be toxic at high concentrations; however, it is also an essential element for all living organisms. As a component of more than 200 enzymes and other metabolic compounds, Zn is ubiquitous in the tissues of plants and animals, and is essential for normal growth, reproduction, and wound healing (Alsop et al. 1999, and references therein). Due to its essentiality in many metabolic processes, organisms regulate Zn, so its bioaccumulation and biomagnification is conditioned by this regulation. Although essential, Zn in high concentrations can be harmful as some studies demonstrated that fish fed with a diet contaminated with Zn showed reduced survival and growth, and an increase in the incidence of diseases (Farag et al. 1994; Bowen et al. 2006). In addition, aquatic populations are affected in Zn-polluted waters (Solbe and Flook 1975; Overall et al. 1989). Particularly, the gills of fish, which may be an important excretory pathway of Zn in rainbow trout, can be damage by high concentrations of Zn in water

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(Hardy et al. 1987). Moreover, the potential for Zn poisoning in fish could be the highest in oligotrophic lakes with very soft and non-acid waters, as Zn accumulation and its consequential toxicity are strongly dependent on water chemistry (Hogstrand, 2012).

There is scarce published research on Zn distribution and transfer in freshwater food webs. In most studies, Zn concentrations ([Zn]) were analyzed in fish or were focused on the impact of anthropogenic pollution in freshwater biota (Alsop et al. 1999; Besser et al. 2001, 2007; Eisler 1993; Mohamed and Osman 2014; Papagiannis et al. 2004; Saiki et al. 1995). Laboratory experiments suggested that Zn can bioaccumulate in freshwater organisms (Cardwell et al. 2013), and a few field studies focused its transference between a few organisms in freshwater food webs, but no report could be found on Zn in a whole lacustrine food web (Besser et al. 2001; Chen et al. 2000; Saiki et al. 1995).

Zinc trophodynamics can be assessed by stable isotope analysis as they have been widely used to study energy flow, food web structure, to estimate trophic position, and in ecotoxicological studies in aquatic ecosystems (Jardine et al. 2006). Stable nitrogen isotope ratios ($\delta^{15}\text{N}$) increase with trophic level as consumers are enriched in ^{15}N relative to their diet; on the contrary, carbon isotope ratios ($\delta^{13}\text{C}$) change little from one trophic level to the other, and consequently, they can be used to determine the original sources of dietary carbon (Post 2002). Biomagnifying elements tend to increase in concentration with increasing trophic level, whereas biodiluting ones show the opposite trend; therefore, the correlation between these elements and $\delta^{15}\text{N}$ in organisms can be used to evaluate biomagnification or biodilution in food webs (Cabana and Rasmussen 1994).

The food web of Lake Nahuel Huapi, an ultraoligotrophic lake in North Patagonia, has been well characterized using carbon and nitrogen stable isotopes (Arcagni et al. 2015), and based on this work, we assessed the trophic transfer of Zn from the base of the food web to top predators. There are several published studies using stable nitrogen isotopes as a tool to examine the trophic transfer of Zn in marine and estuarine food webs (Asante et al. 2008, 2010; Campbell et al. 2005; Jara-Marini et al. 2009; Nfon et al. 2009). However, to the best of our knowledge, there have been no studies examining Zn transfer in freshwater food webs including both pelagic and benthic compartments.

Lake Nahuel Huapi is the largest and deepest lentic water body in North Patagonia at the East of the Andes. This ultraoligotrophic lake has complex shoreline topography with seven branching arms, each with its own varying morphometric characteristics that provide opportunities to compare the range and the importance of the coupling between the pelagic and littoral habitats and food web structuring for the same species assemblage within a single large lake (Arcagni et al. 2015).

Aquatic environments receive Zn from anthropogenic and natural sources, and among the latter volcanic emissions are an important source of this metal to the environment (Nriagu 1989). Lake Nahuel Huapi has been historically affected by volcanic eruptions with significant amount of tephra deposited in the lake sediments and in the surrounding water catchment, mainly from Puyehue-Cordón Caulle volcanic complex (PCCVC) (Lara et al. 2006). On June 4, 2011, the PCCVC began an eruptive process that generated large amounts of volcanic products (ashes, gases). The volcanic deposits significantly affected the limnology of the surrounding lakes and rivers, modifying the ecology of fish, macroinvertebrates, and plankton (Lallement et al. 2014; Modenutti et al. 2013). Experimental studies have shown that volcanic ash leaching contains significant amounts of Zn that can be released to aquatic environments (Ruggieri et al. 2011). Therefore, tephra deposits in L. Nahuel Huapi may have the potential to impact Zn concentrations in biota. Although organisms can regulate their Zn levels even under conditions of Zn from anthropogenic pollution (Kraemer et al. 2005), [Zn] in lake water was a good predictor of Zn levels in fish in northeastern USA lakes (Chen et al. 2000).

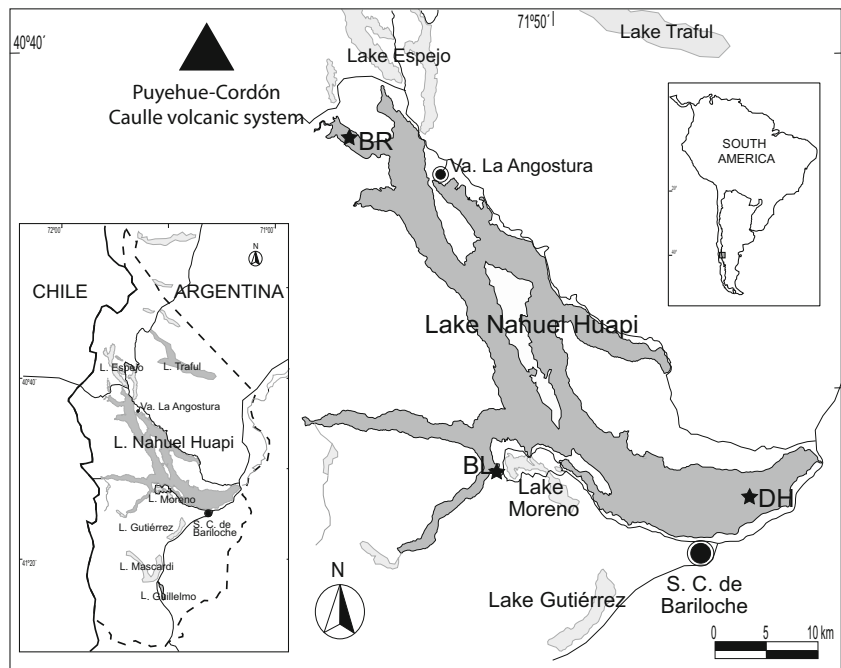
The principal aim of present work is to study the Zn distribution in the food web of L. Nahuel Huapi. We have three main objectives: (a) Assess whether the 2011 PCCVC eruption had an impact on [Zn] in aquatic biota, (b) assess the overall trends of Zn in various freshwater species for L. Nahuel Huapi, and (c) study the potential for bioaccumulation and biomagnification of Zn in the food web of L. Nahuel Huapi using previously published $\delta^{15}\text{N}$ data.

Methodology

Study site

Lake Nahuel Huapi (41°03' S, 71°25' W), located in Nahuel Huapi National Park (NHNP, Fig. 1), is an ultraoligotrophic system with a mean annual Secchi depth of 12 m, euphotic zone ($Z_{1\%}$) extended up to 48.8 m deep, total phosphorus of $5.1 \mu\text{g L}^{-1}$, and Chlorophyll *a* of $0.6 \mu\text{g L}^{-1}$ (Caravati et al. 2010), is of glacial origin, and has been classified as warm monomictic with summer stratification (Díaz et al. 2007). Because of the constant west winds and the Andes mountain range that play a crucial role in determining the precipitation regime of the area, there is a strong west-east climatic gradient. As a result, between the westernmost and easternmost margins of L. Nahuel Huapi, precipitations shift from 3000 mm to less than 700 mm, influencing plant distribution. Hence, while mountain slopes on the west are covered by dense forest, on the east, the vegetation is characterized by grass and shrub species typical of the Patagonian steppe (Arcagni et al. 2015, and references therein).

Fig. 1 Lake Nahuel Huapi, Nahuel Huapi National Park, North Patagonia Andean range. Sampling sites Brazo Rincón (BR), Bahía López (BL), and Dina Huapi (DH)



Sampling was performed at three sites, *Brazo Rincón*, *Bahía López*, and *Dina Huapi*, which represent typical L. Nahuel Huapi environmental conditions arising from the west-east precipitation gradient. Those sampling sites were over a transect from the PCCVC, following the west-east predominant wind direction, receiving a differential direct impact of the eruption due to different distance from the volcanic complex (Fig. 1).

Brazo Rincón (BR) is the northwestern branch of the lake, roughly 40 km from the PCCVC, located in the rainiest region (2800 mm year⁻¹) of NHNP (Fig. 1). The key vegetation is the Andino-Patagonian forest characterized by *Nothofagus dombeyi* (coihue), *Chusquea culeou* (caña colihue) in the understory, and other native tree and shrub species. Brazo Rincón has an extended littoral zone with sandy beaches. The regular basin has a maximum depth of approximately 100 m and an area of around 7.7 km², with a summer-autumn thermocline located 35–45 m deep (Arcagni et al. 2015).

Bahía López (BL) is a small, shallow, and nearly closed bay, 80 km from PCCVC (Fig. 1). The BL area has relatively high rainfall (1200 mm year⁻¹) and is surrounded by a mixed forest of *N. dombeyi* and *Austrocedrus chilensis* (cordilleran cypress). The basin has a maximum depth around 50 m and an area of approximately 1 km². There are a few rocky beaches around the bay which is connected to Lake Moreno on the south-east margin of the basin.

Dina Huapi (DH) is located in the main and largest branch of L. Nahuel Huapi, farthest away from the PCCVC (100 km), and is the source of River Limay, the outflow of the lake. It is the only site downstream of the City of San Carlos de

Bariloche (population 130,000) (Fig. 1) and is located in the driest region of the lake (500 mm year⁻¹), with a vegetation typical of the Patagonian steppe (Arcagni et al. 2015). The site has a maximum depth of 236 m, and a deep thermocline that can reach 60 m.

Brazo Rincón was the most affected site by the PCCVC 2011 eruption, receiving approximately 10 to 30 cm of coarse ash fall. Dina Huapi and BL were less affected receiving 3 to 5 and 0.2 to 3 cm of accumulated ash, respectively (Masciocchi et al. 2013). The tephra floated on the lake surface for about 18 months, gradually settling on the lake bottom, or were removed from the lake through the River Limay.

The phytoplanktonic community of L. Nahuel Huapi is dominated by the Bacillariophycean *Cyclotella steligera*, *Rhizosolenia eriensis*, and *Synedra ulna*, the Dinophycean *Gymnodinium* sp., the Prymnesiophycean *Chrysochromulina parva*, and the Cyanophycean *Dactylococcopsis raphidioides* (Díaz et al. 1998), whereas the zooplanktonic community includes the cladocerans *Bosmina longirostris*, *Bosmina chilensis*, and *Ceriodaphnia dubia* and the copepod *Boeckella gracilipes* (Arcagni et al. 2015). The macroinvertebrate community of L. Nahuel Huapi includes crustacean decapods (freshwater crabs *Aegla* sp., and freshwater crayfish *Samastacus spinifrons*), amphipods (*Hyalella* sp.), snails (*Chilina* sp.), mussels (*Diplodon chilensis*), and insect larvae such as Trichoptera (caddisflies), Ephemeroptera (mayflies), Plecoptera (stoneflies), and Chironomidae (non-biting midges), all important dietary items for littoral-feeding fish. The fish community includes five native species: creole perch (*Percichthys trucha*), small puyen (*Galaxias maculatus*), big puyen (*Galaxias platei*), velvet catfish (*Oliveichthys*

viademensis), and Patagonian silverside (*Odontesthes hatcheri*), and three introduced salmonid species: rainbow trout (*Oncorhynchus mykiss*), brown trout (*Salmo trutta*), and brook trout (*Salvelinus fontinalis*) (Arcagni et al. 2015).

Sampling and sample preparation

Three sampling campaigns were performed: (1) during January–April 2011 (before the PCCVC eruption), (2) during January–April 2012 (after the PCCVC eruption process ended), and (3) during January–April 2014 (after 2 years of recovery of the ecosystems from the impact of the PCCVC eruption). All samples collected were taken to the laboratory refrigerated and were processed within 24 h of sampling. The samples were rinsed with ultra-pure water, homogenized with titanium and Teflon® devices, frozen at $-40\text{ }^{\circ}\text{C}$ and freeze-dried until constant weight, then grounded to fine powder using a Teflon® pestle and mortar.

Large fish, such as the introduced salmonids and the native creole perch, velvet catfish, and big puyen, were captured using gill net gangs set at dusk perpendicular to the shore from 2 m down to 40 m deep and raised early in the morning, averaging 12 h of soak time. Nets consisted of six 10-m-long panels of 15, 20, 30, 50, 60, and 70 mm bar mesh size. Native small puyen and juvenile salmonids were collected in the lake littoral zone using double-funnel cylinder fish traps left at each site for 24 h or by using seine nets of 12 m long and 1 mm bar mesh size. Small puyen larvae were collected in the lake pelagic zone with zooplankton nets. Two of the five native species (creole perch, small puyen) and two of the three introduced fish species (rainbow trout and brown trout) were captured in all sampling sites. Fish were separated by species, and their total length and weight were recorded. Dorsal muscle tissue was dissected from fish larger than 80 mm and homogenized individually. Muscle tissue could not be removed from fish smaller than 80 mm, such as small puyen and juvenile salmonids, so head and guts were removed and pooled samples composed of specimens of similar size were analyzed.

Benthic macroinvertebrates such as insect larvae, crustaceans, and snails were hand-picked from submerged logs and stones, and the mussels were collected using scuba diving techniques at 2 to 15 m depth in BL or from sandy bottoms near the shore in BR. Decapods and mollusks were weighted and their length was measured and were removed from their carapaces/shells. Muscle samples and digestive glands were dissected using titanium tools, and pooled samples were generated with specimens classified in 1 cm length classes (from 3 to 4 cm, 4 to 5 cm, etc.). In the case of young specimens, when muscle tissue was not enough for analysis, the whole body was analyzed. Insect larvae and amphipods were analyzed whole, including caddis fly larvae which were removed from their cases.

Plankton samples were collected with nets of three different mesh sizes (10, 53, and 200 μm) by vertical tows from 5 m above the lake bottom to avoid interference of sediment resuspension, to 45 m depth, and from 40 m deep to the lake surface in BR and DH, and from the deepest point at 45 m depth (also 5 m above lake bottom) to the lake surface in BL (Fig. 1). Samples were filtered in the field and in the laboratory following prior published protocols (Arcagni et al. 2015; Arribère et al. 2010) to obtain three concentrated plankton fractions with differing species composition (Arcagni et al. 2015): P1 (≥ 10 and $< 53\text{ }\mu\text{m}$), P2 (≥ 53 and $< 200\text{ }\mu\text{m}$), and P3 ($\geq 200\text{ }\mu\text{m}$).

Analytical procedures

Zinc concentrations were determined by Instrumental Neutron Activation Analysis (INAA) following published protocols outlined by Arribère et al. (2010). In summary, aliquots ranging from 1 to 200 mg of dried homogenized sample were sealed in SUPRASIL-AN quartz ampoules and irradiated for 20 h in the RA-6 nuclear research reactor (Centro Atómico Bariloche, Argentina). Gamma-ray spectra were collected using an intrinsic High Purity Germanium (HPGe) n-type detector, 12.3% relative efficiency, and a 4096-channel analyzer. The concentrations are reported in dry weight (DW) basis. Certified reference materials (CRMs) NRCC TORT-2 (lobster hepatopancreas) and NRCC DORM-2 (dogfish muscle), IAEA 140/TM (*Fucus* sp.), and IAEA MA-A-1/TM (copepoda) were also analyzed (Table S1, in Supplementary Material files).

Whole organisms collected from benthic substrates and netted plankton samples (e.g., plankton, insect larvae, amphipods) may include fine geological particulate remains from the volcanic eruptions and sediments, although they were carefully cleaned with trace-element quality laboratory water. In order to obtain representative biological [Zn] it is necessary to correct the elemental concentration of the biota samples by subtracting the geological particulate contributions. This geological contribution can be estimated by the determination of lithophile elements, such as rare earth elements (REEs). In this case, the correction was implemented by the determination of the REE samarium (Sm) which was consistently found at very low concentrations in all samples. The methodology is described in the [Supplementary Material](#) files.

Nitrogen stable isotope $\delta^{15}\text{N}$ was analyzed in the samples collected in 2011 before the PCCVC eruption. This sampling campaign represents a steady state of the system that allows the study of the food web structure and Zn trophodynamics, whereas the eruption may modify trophic relations in a dynamic evolution, and consequently 2012 and 2014 sample sets could not represent steady state situations of the lake food web. Nitrogen stable isotope $\delta^{15}\text{N}$ was analyzed via a DELTA^{plus}XP continuous flow stable isotope ratio mass

spectrometer at Queen's University, Kingston, ON, Canada (Arcagni et al. 2015). To study Zn trophodynamics we considered those tissues which represent the main transference pathway of energy in the food web; muscle in the case of fish, large crustaceans and mollusks, whole body without head and guts for small fish, whole body for small invertebrates, and bulk plankton. Nitrogen stable isotope values were expressed in parts per thousand (‰) relative to the $\delta^{15}\text{N}$ reference materials (atmospheric nitrogen standard).

Data analyses

Graphical and statistical analyses were performed with R v3.2.4 software for Windows. The parametric tests ANOVA and post hoc tests were used. When the data was not normal distributed or the number of samples was small, the non-parametric Kruskal-Wallis test followed by Steel-Dwass-Critchlow-Fligner (pSDCFlig) test was performed using the Monte Carlo method with a number of iterations set at 150,000, whereas the 50,000 initial iterations were discarded. The variation of [Zn] with specimen length was evaluated by linear regressions. Significance level was set in 0.05 for p values.

Results

There were no significant differences in [Zn] in several organisms studied when comparing 2011, 2012, and 2014 samples from each sampling site. These organisms were rainbow trout, brown trout, small puyen, crabs (Kruskal-Wallis test), brook trout (ANOVA test), and snails (ANOVA test) (see [Zn] measured for each sampling campaign and site in Tables S2, S3, and S4 in Supplementary Material files). There was a significant increase in [Zn] in mayflies after the eruption (pSDCFlig test). Zinc concentrations decreased slightly between 2011 and 2014 in creole perch (pSDCFlig test), whereas [Zn] in crayfish was similar when comparing 2011 and 2012 sampling but decreased slightly in 2014 (pSDCFlig test) (Tables S2, S3, and S4 in Supplementary Material files). No statistical analyses were possible for the other organisms analyzed due to the limited number of samples; however, [Zn] decreased in the P2 and P3 plankton fractions when comparing samples from 2011 with 2012 and 2014 (several P1 plankton samples collected after PCCVC 2011 eruption showed no significant [Zn] after correction by particulate contamination due to fine volcanic ash in suspension when sampling). Other organisms showed similar values in 2011, 2012, and 2014 sampling at the three sampling sites (Tables S2, S3, and S4, Supplementary Material files). Zinc concentrations in the organisms studied are shown in Fig. 2.

Zinc concentrations were consistent between the three sites in L. Nahuel Huapi (Table 1) for brown trout, crabs, crayfish

(Kruskal-Wallis test), brook trout (ANOVA test), and snails (ANOVA test). Conversely, other organisms showed significant differences among samplings sites. This is the case of small puyen, with increasing values in the BR, DH, and BL sequence (pSDCFlig test; this analysis excluded the pelagic specimens: Table 1). Rainbow trout showed higher values in DH (pSDCFlig test), but creole perch showed the opposite trend (pSDCFlig test). Mayflies exhibited higher values in BL ($302 \mu\text{g g}^{-1}$ average; Table 1) compared to BR and DH (234 and $255 \mu\text{g g}^{-1}$ average, respectively; Table 1) (pSDCFlig test). Other insect larvae taxa ranged around similar values, but, as well as for other organisms, there were not enough samples to search for a concentration trend. Considering that [Zn] was consistent between the three sites for most organisms, and for the others there was not a general trend, we will consider the three sites together for further data discussion.

The variation of [Zn] in muscle and in the digestive gland of snails is presented in Fig. 3 for further discussion of the hepatopancreas role in Zn dynamics in benthic macroinvertebrates. The variation of [Zn] with specimen length is presented for freshwater crabs (Fig. 4), for salmonids (Fig. 5), and for creole perch (Fig. 6), for further discussion of the age incidence on Zn accumulation ([Zn] is reported in Tables S2, S3, and S4 in Supplementary Material files).

Discussion

Zinc background published data in aquatic ecosystems is scarce in the study region, limiting the possibility of comparing our data with different lacustrine food webs. Published [Zn] in primary producers, such as riparian and aquatic plants, reported that aquatic plants had higher [Zn] ($55\text{--}98 \mu\text{g g}^{-1}$) than decomposing leaves from riparian plants ($12\text{--}39 \mu\text{g g}^{-1}$) (Juárez et al. 2016). Furthermore, unpublished and published [Zn] in sediment across L. Nahuel Huapi before the PCCVC eruption ranged between 90 and $120 \mu\text{g g}^{-1}$ (Ribeiro Guevara et al. 2005). In PCCVC volcanic ash, [Zn] ranged from 95 to $105 \mu\text{g g}^{-1}$ (Daga et al. 2014). Prior to the eruption, [Zn] in L. Nahuel Huapi water column (< 1.5 to $9.6 \mu\text{g L}^{-1}$) were consistent with global [Zn] values (Markert et al. 1997), increasing immediately after the PCCVC 2011 eruption, with values from 10 to $600 \mu\text{g L}^{-1}$ in the water column, and from 50 to $900 \mu\text{g L}^{-1}$ in pore water (Perez Catán et al. 2016).

Impact of Puyehue-Cordón Caulle eruption

The PCCVC eruption in June 2011 affected significantly L. Nahuel Huapi ecosystems as a consequence of the large ash deposits. This natural event altered the ecology of fish, macroinvertebrates, and plankton (Lallement et al. 2014; Modenutti et al. 2013; Wolinski et al. 2013). Brazo Rincón, the nearest site to PCCVC, was the most affected site of all L. Nahuel Huapi.

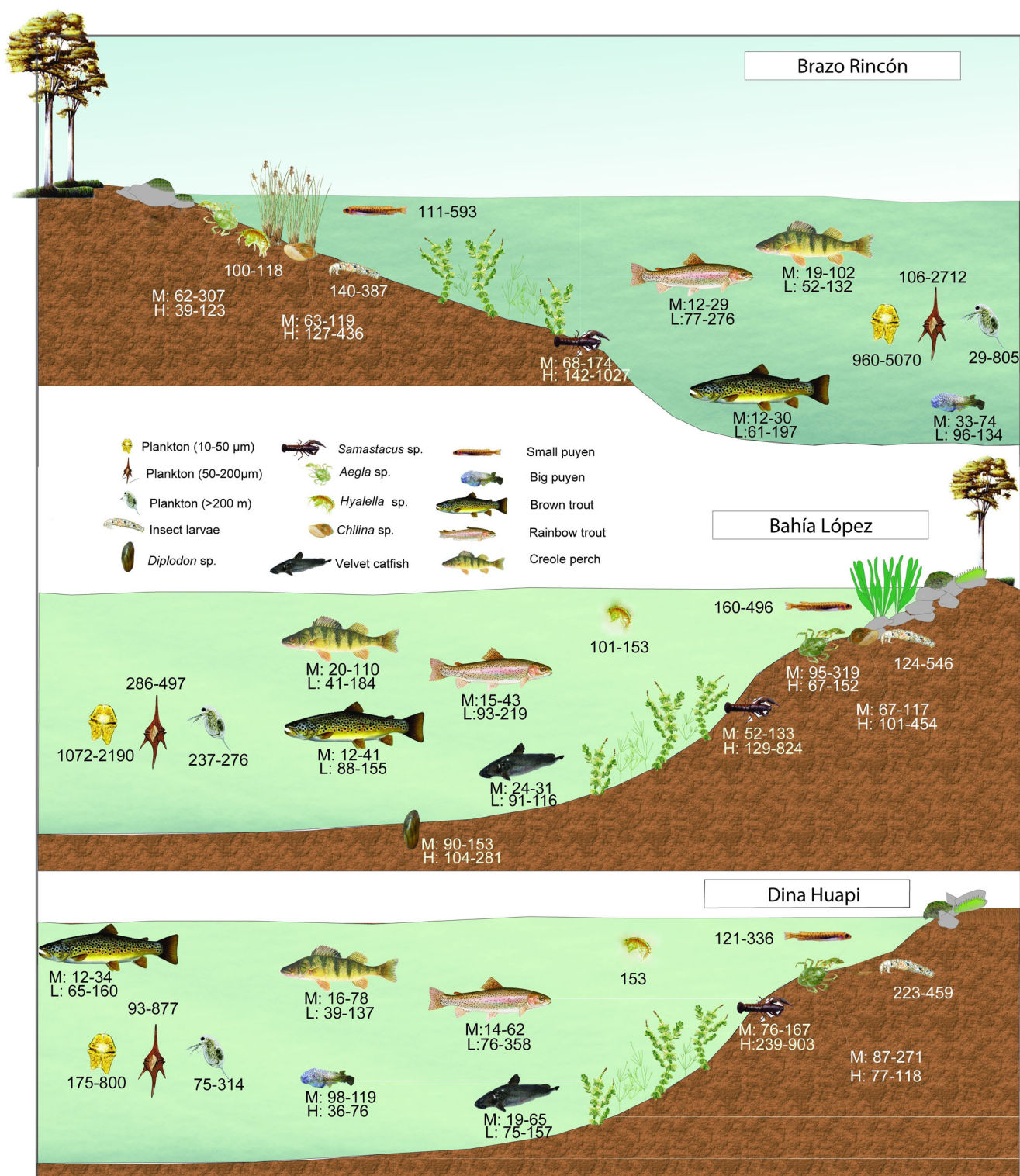


Fig. 2 Minimum and maximum [Zn] ($\mu\text{g g}^{-1}$ dry weight) in organisms from Lake Nahuel Huapi food web collected from Brazo Rincón, Bahía López, and Dina Huapi (2011–2014). The whole body was analyzed for plankton, insect larvae, and *Hyaella* sp. For small puyen, the analysis was

on the whole body without head and guts. Muscle (M) and hepatopancreas or liver (H/L) were analyzed for *Chilina* sp., *S. spinifrons*, *Aegla* sp., *Diplodon* sp., and fishes

As mentioned in the previous paragraph, [Zn] in water from L. Nahuel Huapi increased significantly after the PCCVC 2011 eruption, which is consistent with the results of leaching tests

that showed that significant amounts of Zn can be released from tephra to water in the lakes from the study region (Ruggieri et al. 2011). While normal Zn levels in pristine freshwaters are

Table 1 Zinc in Lake Nahuel Huapi biota. Concentrations reported in $\mu\text{g g}^{-1}$ dry weight

	Tissue	N ^a	Brazo Rincón		N ^a	Bahía López		N ^a	Dina Huapi	
			Min.-median-max.	Average (SD)		Min.-median-max.	Average (SD)		Min.-median-max.	Average (SD)
Plankton P1 (10–53 μm)	–	2	960-5070	–	2	1070-2190	–	5	175- 358 -800	400 (242)
Plankton P2 (53–200 μm)	–	4	122- 187 -2710	798 (1280)	3	198- 286 -497	327 (154)	6	131- 281 -877	376 (298)
Plankton P3 (> 200 μm)	–	6	85- 113 -258	133 (67)	3	118- 237 -276	210 (82)	6	117- 187 -314	199 (84)
Chironomidae	Whole	2 ^b	140-145	–	3 ^b	124- 136 -193	151 (37)	–	–	–
Plecoptera	Whole	–	–	–	–	247	–	1 ^b	288	–
Ephemeroptera	Whole	20 ^b	161- 240 -270	234 (29)	18 ^b	225- 296 -381	302 (53)	11 ^b	213- 247 -303	255 (29)
Trichoptera	Whole	3 ^b	166- 170 -252	198 (37)	2 ^b	162-200	–	1 ^b	459	–
<i>Hyalella</i> sp.	Whole	4 ^b	100- 104 -113	106.6 (5.4)	3 ^b	101- 112 -121	111 (10)	1 ^b	153	–
<i>Chilina</i> sp.	Whole, no shell	2 ^b	101-119	–	2 ^b	108-117	–	2 ^b	98.9-125	–
	Muscle	28 ^b	63- 95 -112	94 (12)	23 ^b	67- 88 -117	88 (13)	10 ^b	76- 89 -138	94 (18)
	DG ^c	28 ^b	127- 200 -436	222 (88)	23 ^b	101- 185 -454	217 (93)	10 ^b	112- 138 -189	143 (26)
<i>Diplodon chilensis</i>	Muscle	18 ^b	123- 136 -175	140 (14)	15 ^b	90- 125 -153	122 (16)	–	–	–
	DG ^c	18 ^b	99- 162 -203	159 (26)	15 ^b	104- 161 -281	165 (48)	–	–	–
<i>Samastacus spinifrons</i>	Whole	4 ^b	77- 112 -123	103 (20)	–	–	–	–	–	–
	Muscle	24 ^b	68- 92 -174	98 (25)	24 ^b	63- 81 -134	88 (19)	11 ^b	65- 86 -167	95 (29)
	DG ^c	24 ^b	142- 354 -1028	388 (211)	24 ^b	129- 450 -824	487 (157)	11 ^b	239- 441 -903	436 (202)
<i>Aegla</i> sp.	Whole	7 ^b	65- 94 -108	94 (15)	8 ^b	73- 94 -110	93 (13)	3 ^b	71- 81 -82	78.0 (6.1)
	Muscle	18 ^b	62- 171 -307	169 (67)	21 ^b	95- 147 -319	171 (72)	16 ^b	142- 210 -271	204 (41)
	DG ^c	17 ^b	39- 75 -123	79 (28)	21 ^b	67- 99 -152	101 (25)	16 ^b	83- 103 -117	105 (13)
Small puyen	No H&G ^d	66 ^b	112- 161 -432	173 (51)	54 ^b	160- 245 -496	256 (56)	36 ^b	121- 204 -336	203 (47)
	Pelagic	11 ^b	285- 517 -593	493 (88)	–	–	–	–	–	–
Big puyen	No H&G ^d	1 ^b	74	–	–	–	–	–	–	–
	Muscle	9 ^b	33- 50 -74	51 (13)	1 ^b	87	–	3 ^b	36- 56 -76	43 (12)
	Liver	8 ^b	96- 109 -134	112 (11)	1 ^b	97	–	3 ^b	98- 115 -119	111 (11)
Velvet catfish	Muscle	–	–	–	2	25-31	–	9	19- 29 -65	37 (18)
	Liver	–	–	–	2	98-116	–	9	75- 116 -157	117 (23)
Creole perch	Muscle	23	19- 36 -102	43 (25)	27	20- 30 -110	35 (19)	29	16- 23 -77	28 (15)
	Liver	27	52- 78 -132	79 (23)	27	42- 76 -184	80 (28)	29	39- 78 -137	84 (25)
Patagonian silverside	No H&G ^d	–	–	–	2	120-160	–	–	–	–
Rainbow trout	No H&G ^d	–	–	–	8	35- 49 -104	53 (22)	3	38- 56 -80	58 (21)
	Muscle	25	12- 18 -22	17.6 (2.2)	10	16- 17 -26	17.7 (3.4)	19	14- 19 -25	18.9 (3.0)
	Liver	39	77- 150 -276	155 (41)	22	107- 131 -187	141 (31)	64	76- 175 -392	188 (70)
Brown trout	No H&G ^d	5	94- 121 -158	125 (30)	–	–	–	–	–	–
	Muscle	49	12.3- 15.6 -29.9	16.1 (2.9)	7	12.4- 15.4 -16.4	14.8 (1.4)	24	11.9- 15.6 -19.4	15.7 (2.0)
	Liver	50	61- 105 -197	109 (26)	8	88- 95 -155	111 (27)	26	65- 98 -185	106 (30)
Brook trout	Muscle	4	13.6- 19.9 -21.8	18.8 (3.6)	–	–	–	–	–	–
	Liver	8	115- 205 -269	206 (49)	2	74-112	–	–	–	–

Median values in bold

^a Number of samples analyzed

^b Pooled samples

^c Digestive gland

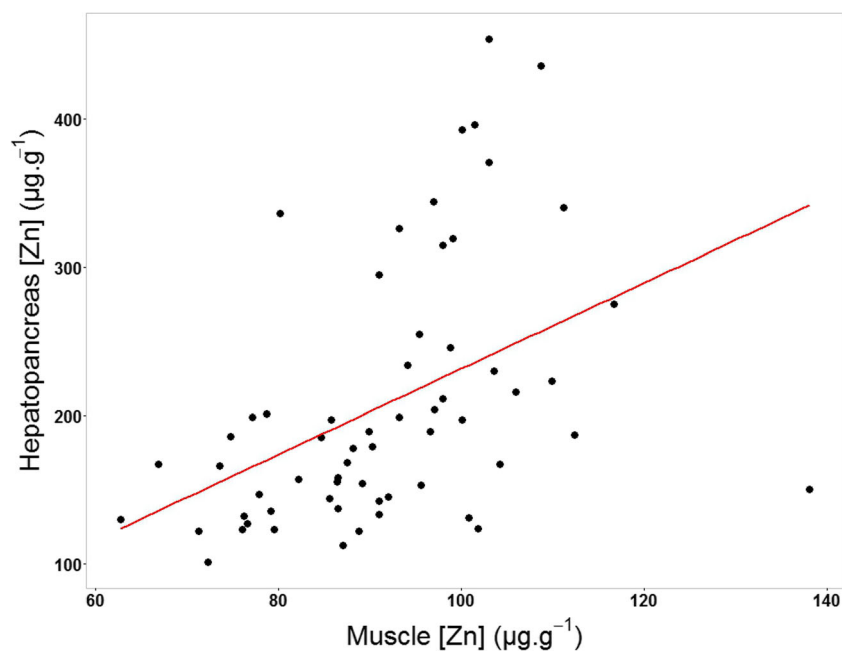
^d Whole body without head and guts

only a few micrograms per liter or less, concentrations of $50 \mu\text{g L}^{-1}$ are routine in industrialized areas. Maximum [Zn] in contaminated surface waters are reported to range from 130 to $1170 \mu\text{g L}^{-1}$ in different areas of Canada (Alsop and Wood 2000). Although [Zn] reached $600 \mu\text{g L}^{-1}$ in the water column and $900 \mu\text{g L}^{-1}$ in pore water in L. Nahuel Huapi after the PCCVC 2011 eruption (Perez Catán et al., 2016), no significant increase in [Zn] was observed in biota when comparing samples collected before and after the volcanic event (only mayflies showed a significant increase; see “Results” section). It is noteworthy the lack of significant increase of [Zn] in L. Nahuel Huapi biota after a natural and catastrophic event despite the increase in [Zn] in water associated to volcanic deposits,

considering that a significant fraction of the large extra Zn in solution could be bioavailable. This underscores the capacity of this aquatic biota to regulate Zn despite the increased [Zn] in the environment.

Studies on Zn accumulation, both in the field and in the laboratory, support Zn homeostasis in fish (Spry et al. 1988, and references therein). The increase of waterborne [Zn] to even $500 \mu\text{g L}^{-1}$ was not stressful to rainbow trout regarding growth and mortality, whereas [Zn] of $1000 \mu\text{g L}^{-1}$ was found to be in the toxic range (Spry et al. 1988). The maximum acceptable [Zn] in water from L. Superior regarding toxic effects for brook trout lied between 534 and $1360 \mu\text{g L}^{-1}$ (Holcombe et al. 1979). There are homeostatic mechanisms in fish when the Zn source is

Fig. 3 Zinc concentrations in muscle vs. digestive gland of *Chilina* sp. from three sites in Lake Nahuel Huapi (2011–2014). Linear regression equation: (digestive gland [Zn]) = $(3.22 \pm 0.68) \times (\text{muscle [Zn]}) + (88 \pm 60)$; Spearman's rank correlation, $R = 0.56$, $p < 0.05$)



limited, as Spry et al. (1988) noted that when dietary Zn was adequate, the waterborne contribution was as high as 57%, but when dietary Zn was deficient, waterborne contribution was 100%. In general metallothioneins, non-enzymatic proteins with low molecular weight, play an important role in Zn homeostasis and in the protection against Zn poisoning (Eisler 1993; Roesijadi 1992).

Zinc in Lake Nahuel Huapi biota

Zinc concentrations in fish and macroinvertebrate muscle were typically lower than in the digestive gland or liver for

all species except for crabs (Fig. 2, Table 1). This crustacean exhibited an exceptional behavior, with higher [Zn] in muscle than in the digestive gland (Table 1), unlike other decapods that presented higher accumulation in the hepatopancreas (Kouba et al. 2010). *Aegla* sp. has been poorly studied with only a few works describing its distribution, habitat, and bioenergetics (Ciancio and Pascual 2006; Lucci 2015); thus, we hypothesize that this peculiar behavior may be due to particular physiological needs of Zn of this species. On the contrary, crayfish showed higher [Zn] in the digestive gland, the highest (up to $1000 \mu\text{g g}^{-1}$) among all the fish and benthic organisms analyzed. Although [Zn] in crayfish muscle from this study

Fig. 4 Zinc concentrations in muscle tissue vs. length of *Aegla* sp. from three sites in Lake Nahuel Huapi (2011–2014). Linear regression equation: (digestive gland [Zn]) = $(9.8 \pm 1.3) \times (\text{muscle [Zn]}) + (113 \pm 34)$; Spearman's rank correlation, $R = 0.75$, $p < 0.05$)

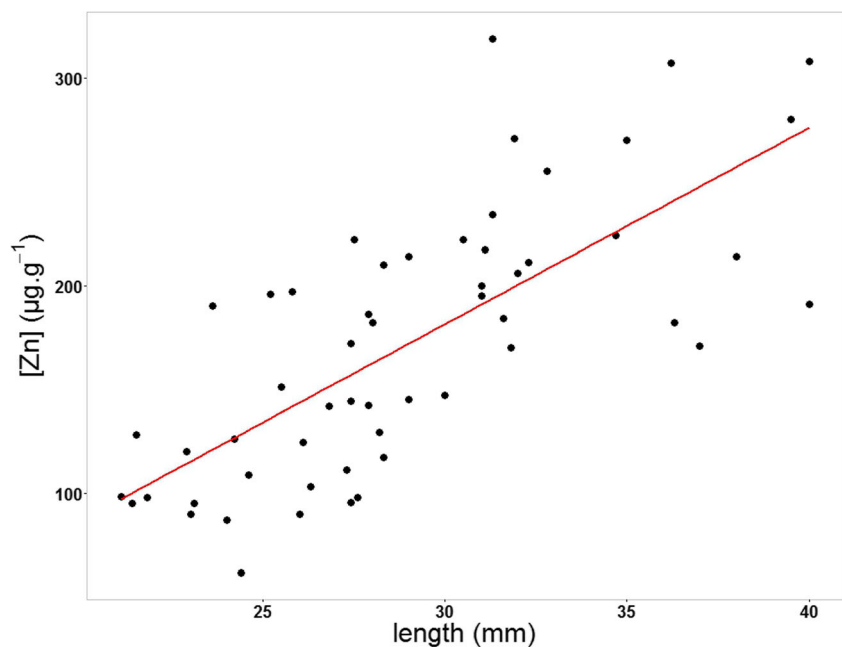
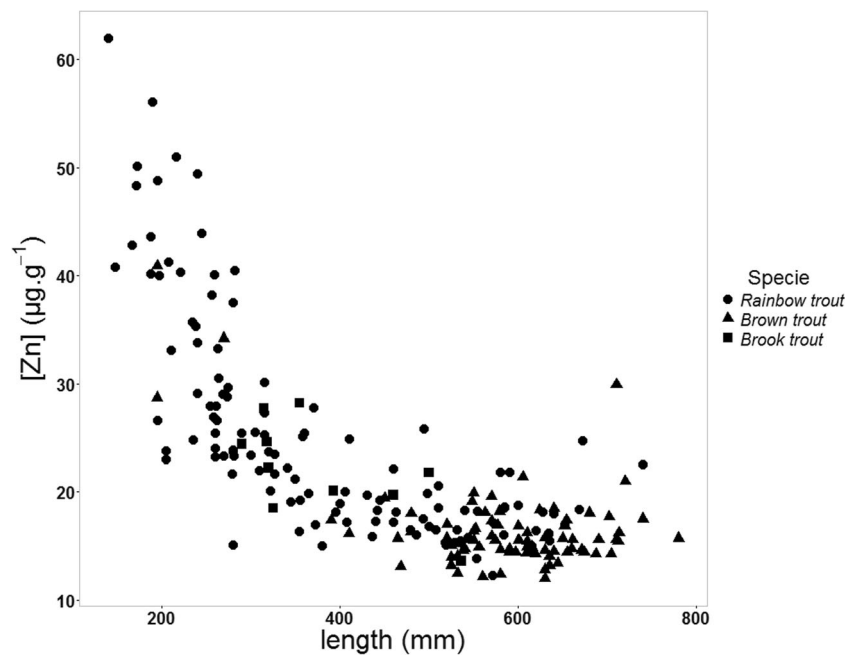


Fig. 5 Zinc concentrations in muscle tissue vs. body length for rainbow trout, brown trout, and brook trout from three sites in Lake Nahuel Huapi (2011–2014)

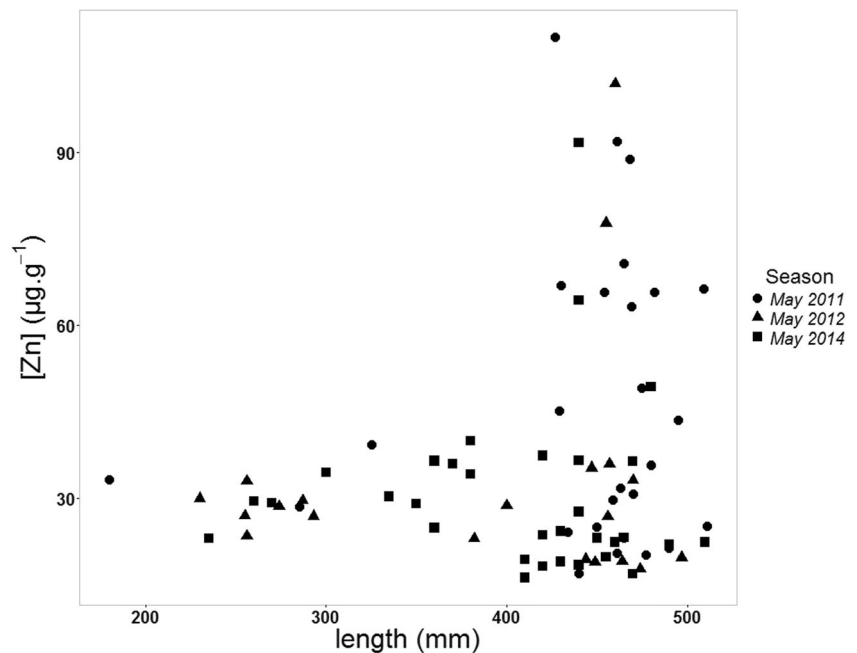


was within the average concentrations reported in the literature for crayfish from polluted and non-polluted fresh water systems (Kouba et al. 2010), [Zn] of $1000 \mu\text{g g}^{-1}$ in the digestive gland is by far the highest. Higher accumulation of metals in hepatopancreas tissues than in the abdominal muscle has been reported in the literature for crayfishes (Alcorlo et al. 2006; Anderson et al. 1997; Bellante et al. 2015; Bianchi et al. 2011; Martín-Díaz et al. 2006). Snails were the only organism in this study that showed a significant positive correlation between [Zn] in muscle and in the digestive gland (Fig. 3). Aquatic mollusks possess diverse strategies in the handling and storage of metals, including metal-rich granules

metallothioneins or metallothionein-like proteins (Roesijadi 1992). The uptake of Zn occurs primarily through the diet in freshwater systems, whereas incorporation from the aquatic media through the gills is an auxiliary pathway (Hogstrand, 2012). The liver acts as a Zn metabolizer and storage organ, which thereafter redistributes the element to muscle and other organs (Thompson et al. 2002, 2003; Hogstrand, 2012). As a result, [Zn] is likely more variable in liver due to differing inputs of Zn from the diet but is better regulated in the muscle.

In small puyen, [Zn] was one order of magnitude higher than in salmonid muscle (Fig. 2). Whole body without head and guts was analyzed in this small fish, and the inclusion of

Fig. 6 Zinc concentrations in muscle tissue vs. body length for native creole perch from three sites in Lake Nahuel Huapi (2011–2014)



skin and bones would likely increase the average [Zn] over muscle. No trend on [Zn] with small puyen length was observed. Pelagic small puyen larvae showed higher [Zn] ($489 \mu\text{g g}^{-1}$ average, $n = 10$) compared to littoral adult specimens, and also the highest of any fish sample. Pelagic larvae feeds mostly on zooplankton with high [Zn] (Table 1), whereas small puyen adults caught from the littoral zones have a mixed diet including zooplankton and insect larvae such as non-biting midges and mayflies (Rechencq et al. 2011; Reissig et al. 2015). In general, fish feeding on invertebrates have higher [Zn] than piscivorous species (Amundsen et al. 1997; Mathis and Cummings 1973; Murphy et al. 1978).

The lowest [Zn] found in biota was measured in large fish muscle. In general, [Zn] was lower in salmonids than in native perch and velvet catfish. Zn concentrations were higher in fish liver than in muscle; however, whereas [Zn] in liver from native fish was two to threefold higher than in muscle, the concentrations were higher by a factor of 10 in salmonids (Table 1).

Size-related trends in [Zn] varied among taxa; significant correlation was observed for snails and crabs only. Freshwater snails exhibited a weak negative relationship with [Zn] and shell length (Spearman's rank correlation, $R = -0.43$, $p < 0.05$). On the contrary, freshwater crabs from the three sites had a significant positive relationship of increasing [Zn] with body length, ranging from 100 to $300 \mu\text{g g}^{-1}$ (Fig. 4). This behavior is opposite to that reported in a long-term study of [Zn] in the hepatopancreas, gills, and abdominal muscle of the decapod *Cherax tenuimanus*, with the highest levels in juveniles. Higher [Zn] in juveniles was explained by the relatively larger and more permeable body surface of juveniles which renders them unable to regulate Zn content as effectively as adults (Bennet-Chambers and Knott 2002; Kouba et al. 2010).

Zinc content variation with specimen length of top predators showed a contrasting behavior between native creole perch and salmonids. In the three salmonid species, muscle tissue [Zn] decreases with length (Spearman's rank correlation, $R = -0.73$; Fig. 5), with a steeper trend for fish smaller than 300 mm (2 to 3 years old for L. Nahuel Huapi; Juncos et al. 2013) (Spearman's rank correlation, $R = -0.60$; Fig. 5). Amundsen et al. (1997) observed a similar pattern of decreasing [Zn] with increasing length, explained by differential adsorption rates across the gut or more efficient excretion in older fish (Patric and Loutit 1978). Negative correlations between metal concentrations and body size may also be a result of homeostatic regulation (Wiener and Giesy 1979). The native species Patagonian silverside and big puyen showed a similar [Zn]-length trend as salmonids, although few specimens were analyzed.

Zn concentrations in creole perch muscle exhibited a particular trend with length. For specimens smaller than 400 mm (corresponding to 5 year old perch; Juncos et al. 2013), [Zn] ranged from 22.9 to $39.9 \mu\text{g g}^{-1}$ (average $30.3 \mu\text{g g}^{-1}$, SD $4.8 \mu\text{g g}^{-1}$), but [Zn] variability increased drastically to a

tenfold range for larger specimens, with [Zn] ranging from 16.1 to $110 \mu\text{g g}^{-1}$ (average $37 \mu\text{g g}^{-1}$, SD $23 \mu\text{g g}^{-1}$) (Fig. 6). This behavior of [Zn] in this native fish is noteworthy and contrasts with that of salmonids. The concentrations of trace metals in food play a key role in determining their concentrations in fish tissue (Pentreath 1976; Singh and Ferns 1978). Creole perch diet changes ontogenetically from small prey-like insect larvae with relative low [Zn], to larger prey at older ages, feeding mainly on *S. spinifrons* (Macchi et al. 1999, 2007; Juncos et al. 2013). Crayfish exhibited the highest [Zn], particularly in the hepatopancreas, among fish and benthic organisms studied in L. Nahuel Huapi (Table 1). Therefore, the high [Zn] in muscle of creole perch in specimens older than 5 years old can be explained by the incorporation of *S. spinifrons* in their diet, and the high variability could be due to the variation in diet composition, particularly with *S. spinifrons* contributions.

There is strong evidence in the literature that [Zn] decreases in all tissues with increasing age and length (Eisler and LaRoche 1972; Eisler 1981, 1984; Grady et al. 1989). This would relate to the different roles that Zn plays in metabolism and, in particular, to the fact that highly proliferating cells require more Zn (Beyersmann and Haase 2001). Negative correlations between [Zn] and fish size within a species have been attributed to a slower metabolism of older fish as, for example, Zn is necessary for the growth and differentiation of muscle fiber types (Rosser and George 1986). Salmonids from L. Nahuel Huapi showed a trend consistent with literature reports, but the native creole perch exhibited a distinctive behavior that deserves further research.

Food web transfer of Zn in L Nahuel Huapi

The organisms of the L. Nahuel Huapi food web collected before the PCCVC 2011 eruption were analyzed for $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ (Arcagni et al. 2015). Stable nitrogen values are reported in the Supplementary Material files (Table S5) along with $\delta^{13}\text{C}$ values. These values were discussed previously by Arcagni et al. (2015) and are not included in the present work according to its objectives (for methodological aspects see Arcagni et al. 2015). Zinc concentrations showed a trend of decreasing Zn with increasing trophic level (Fig. 7), evidencing Zn biodilution throughout the food web. We considered the three sites together for this analysis, since we did not find significant differences in fish [Zn] among sites. Biodilution was also observed in [Zn] if the pelagic (plankton and fish) and benthic-littoral (macroinvertebrates and fish) sub-systems are considered separately (Fig. 7), although both habitats are coupled by fish (Arcagni et al. 2015).

In general, Zn biomagnifies in the food web of natural freshwater systems according to the scarce literature available, although only the analysis of partial food web sections has been studied in those reports, but no evidence of Zn biodilution was reported (Saiki et al. 1995; Chen et al. 2000;

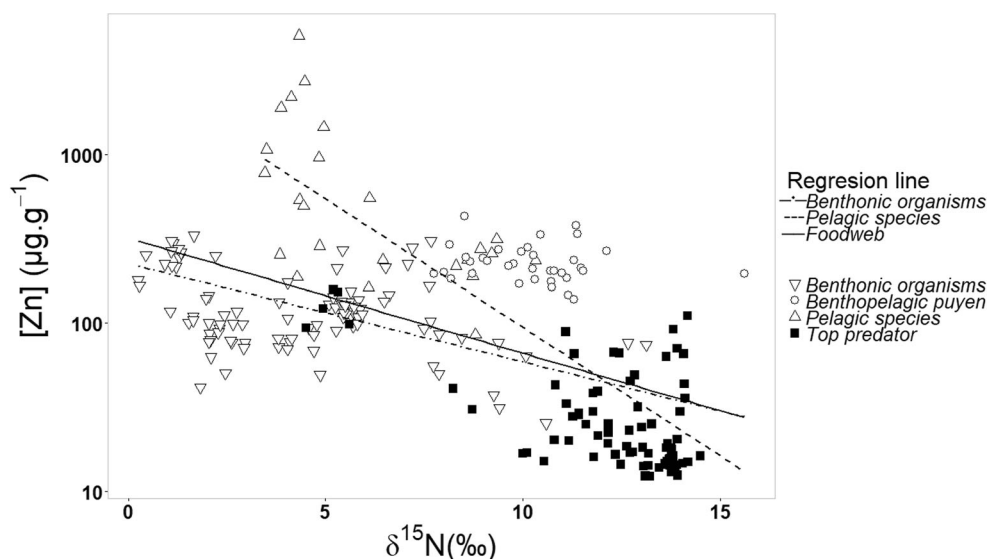


Fig. 7 Zinc concentrations vs. $\delta^{15}\text{N}$ for the whole Lake Nahuel Huapi food web, including plankton, macroinvertebrates, and fish. The 2011 sampling campaign. Linear regression equation (GLM): $\log_{10}[\text{Zn}] = -(0.078 \pm 0.06) \times \delta^{15}\text{N} + (2.59 \pm 0.07)$; $df = 232$; $p < 0.001$; (Spearman's rank correlation, $R = -0.55$, p value < 0.05). Benthonic food web (macroinvertebrates and fish; Arcagni et al. 2015) linear

regression equation (GLM): $\log_{10}[\text{Zn}] = -(0.65 \pm 0.06) \times \delta^{15}\text{N} + (2.41 \pm 0.07)$; $df = 208$; $p < 0.001$; (Spearman's rank correlation $R = -0.57$, p value < 0.05). Pelagic food web (plankton and fish; Arcagni et al. 2015) linear regression equation (GLM): $\log_{10}[\text{Zn}] = -0.153 \pm 0.013 \times \delta^{15}\text{N} + (3.51 \pm 0.17)$; $df = 136$; $p < 0.001$ (Spearman's rank correlation $R = -0.75$, p value < 0.05)

Cardwell et al. 2013). Some marine environments showed Zn biodilution like the Baltic Sea food web (Nfon et al. 2009). Zinc biomagnification was observed in fish in multiple field studies on different aquatic systems, laboratory experiments, and modeling (Cardwell et al. 2013). Campbell et al. (2005) observed Zn biomagnification in the study of a marine food web composed by ice algae, three species of zooplankton, mixed zooplankton samples, Arctic cod, ringed seals, and eight species of seabirds from the Arctic. Chen et al. (2000) also found trophic enrichment when analyzing Zn in two size fractions of zooplankton and fish from 20 lakes. To remark, to the best of our knowledge, the present research is the first report of Zn biodilution in lacustrine systems, and there has been no study examining Zn transfer in a freshwater food web including both pelagic and benthic compartments.

Moreover, Cardwell et al. (2013) stated that, from field studies, biomagnification of Zn in fish only occurred in uncontaminated reference sites where prey contained $< 105 \mu\text{g g}^{-1}$ (Campbell et al. 2005; Saiki et al. 1995). Based on this literature review, the authors suggested that Zn biomagnification is more likely to occur in waters where ambient [Zn] is deficient or less than optimal. Lake Nahuel Huapi receives limited anthropogenic impact, and most catchment area is pristine. However, our food web analysis indicated consistent biodilution of [Zn] with increasing trophic level. Zinc is an essential element; therefore, regulation by the organisms, and element source and availability are the key issues to understand its transference and distribution across food webs. Food items of all fish species in L. Nahuel Huapi food web, particularly those for top predators native perch and

salmonids (Arcagni et al. 2015), exhibited [Zn] above $105 \mu\text{g g}^{-1}$ (Table 1), a [Zn] considered as a reference for dietary Zn deficiency (Cardwell et al. 2013). Therefore, in this ultraoligotrophic freshwater system, the organisms do not appear to be stressed for Zn deficiency, regulating adequately Zn even under catastrophic situations like PCCVC 2011 eruption.

Zinc is essential for normal cellular growth and reproduction, having a primary metabolic effect on Zn-dependent enzymes that regulate biosynthesis and catabolic rate RNA and DNA (Hogstrand, 2012). In unicellular organisms like plankton, Zn is adsorbed by organic agents such as biogenic structures (i.e., cell walls of plankton; Spear 1981). In multicellular organisms, Zn exerts a protective effect on liver by inhibiting lipid peroxidation and stabilizing lysosomal membranes (Sternlieb 1988). Zinc also aids neurotransmission in the brain of fish, prolongs muscular contractions, and increases oxygen affinity of myoglobin, and it is necessary for the growth and differentiation of muscle fiber types (Eisler 1993, and references therein). Although metal trophodynamics is complex and difficult for interpretation, and is influenced by multiple routes of exposure and by differences among species (Luoma and Rainbow 2005), the consistent [Zn] biodilution appears to be the characteristic pattern in this ultraoligotrophic freshwater system.

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