Natural origin arsenic in aquatic organisms from a deep oligotrophic lake under the influence of volcanic eruptions

Romina Juncos [a, b, *], Marina Arcagni [a], Andrea Rizzo [a, b], Linda Campbell [c], María Arribére [a], Sergio Ribeiro Guevara [a]

[a] Laboratorio de Análisis por Activación Neutrónica (LAAN), Centro Atómico Bariloche, Comisión Nacional de Energía Atómica, Av. Bustillo 9500, 8400 Bariloche, Argentina
[b] Centro Científico Tecnológico − CONICET − Patagonia Norte, Av. de los Pioneros 2350, 8400 Bariloche, Argentina
[c] Department of Environmental Science, Saint Mary's University, 923 Robie St., Halifax, NS B3H 3C3, Canada

HIGHLIGHTS

- We report volcanic origin As in the food web of Lake Nahuel Huapi.
- Highest As concentrations were found in phytoplankton and mollusks.
- As biodiluted in piscivorous fish food chains and biomagnified in the benthivorous.
- As increased after the PCCVC eruption in zooplankton and planktivorous fish.
- Habitat alteration by ash deposition might impact As accumulation in benthic biota.

GRAPHICAL ABSTRACT
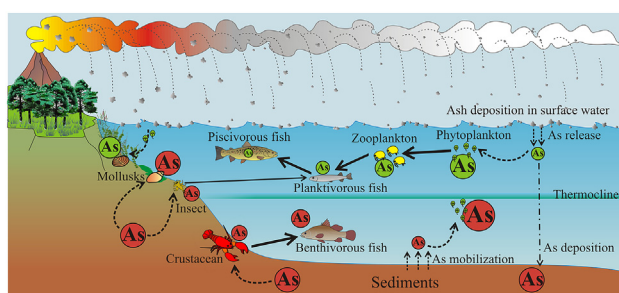
ABSTRACT

Volcanic eruptions are recognized sources of toxic elements to freshwater, including arsenic (As). In order to study the short term changes in the bioaccumulation of naturally occurring As by aquatic organisms in Lake Nahuel Huapi (Argentina), located close to the Puyehue-Cordón Caulle volcanic complex (PCCVC), we described As concentrations at different trophic levels and food web transfer patterns in three sites of the lake prior to the last PCCVC eruption (June 2011), and compared As concentrations in biota before and after the eruption. The highest As concentrations and greater variations both between sites and position in the water column, were observed in phytoplankton (3.9–64.8 µg g^{-1} dry weight, DW) and small zooplankton (4.3–22.3 µg g^{-1} DW). The pattern of As accumulation in aquatic organisms (whole body or muscle) was: primary producers (phytoplankton) > scrapper mollusks (9.3–15.3 µg g^{-1} DW) > filter feeding mollusks (5.4–15.6 µg g^{-1} DW) > omnivorous invertebrates (0.4–9.2 µg g^{-1} DW) > zooplankton (1.2–3.5 µg g^{-1} DW) > fish (0.2–1.9 µg g^{-1} DW). We observed As biodilution in the whole food web, and in salmonids food chains, feeding on fish prey; but biomagnification in the food chain of creole perch, feeding on benthic crayfish. The impact of the 2011 PCCVC eruption on the As levels of biota was more evident in pelagic-associated organisms (zooplankton and planktivorous fish), but only

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* Corresponding author. Laboratorio de Análisis por Activación Neutrónica, Centro Atómico Bariloche. Av. Bustillo 9500, 8400 Bariloche, Argentina.
E-mail address: rominajuncos@gmail.com (R. Juncos).

in the short term, suggesting a brief high bioavailability of As in water after ash deposition. In benthic organisms As variations likely responded to shift in diet due to coverage of the littoral zone with ashes.

1. Introduction

Volcanic eruptions have long been recognized as a key source of potentially toxic elements to the surroundings, including arsenic (As) (Hinkley et al., 1999; Withman et al., 2005). Arsenic is a recurrent and highly volatile constituent of volcanic gases (Symonds et al., 1992), and a highly mobile element of tephras (Ruggieri et al., 2012). Once ashes are deposited in water, As can be released by desorption or dissolution under favorable conditions (Smedley and Kinniburgh, 2002). As a result, As is an element of concern in many volcanic regions of the world (Bundschuh et al., 2012; Smedley and Kinniburgh, 2002).

Once in the aquatic environment, As can be taken up by organisms incorporating it to the food web. Unlike other elements (e.g., Hg, Rb, Se, Zn) that shown biomagnification (Campbell et al., 2005; Ikemoto et al., 2008), total As tends to consistently decrease to higher trophic levels along freshwater food chains in lakes world-wide (Chen and Folt, 2000; Chen et al., 2000; Culioli et al., 2009b; Revenga et al., 2012). Organisms can take up As through a variety of pathways: directly from solution across the entire body surface, via specialized respiratory structures (e.g., gills) or across the digestive epithelium with water or ingested food, sediments or suspended particles (Rahman et al., 2012). The direct uptake from solution tends to be highest in primary producers and organisms at lower trophic levels, as these organisms usually have a large surface to volume ratio and less developed mechanisms for metal excretion. In contrast, direct uptake from water may be of minor importance for organisms at higher trophic levels such as fish, and some crustaceans (Rahman et al., 2012). For such organisms, food is usually the main route of exposure (Culioli et al., 2009a,b; McIntyre and Linton, 2012) having low bioaccumulation factors probably due to more developed physiological mechanisms for metal regulation (McIntyre and Linton, 2012).

The uptake of nonessential trace elements as As by organisms is highly dependent on element bioavailability which varies significantly with biogeochemistry in freshwaters (Rahman et al., 2012). In oxic waters, As (as arsenate) is strongly adsorbed to the surface of several common minerals, co-precipitating with Al, Fe, and Mn (oxy) hydroxides to the sediments (Belzile and Tessier, 1990; Hamilton-Taylor and Davison, 1995). Accordingly, dissolved As concentrations in natural waters are generally low while sediments are usually highly enriched with As, being important reservoirs and also sources of As to water and biota by remobilization under anoxic conditions (e.g., in the hypolimnion during thermal stratification of lakes) (Hamilton-Taylor and Davison, 1995; Rahman et al., 2012). For all these reasons, it might be expected higher As bioavailability in lake compartments that are in close association with sediments (e.g., sediment-water interface, porewater) than in surface water.

Lake Nahuel Huapi (41°03′S, 71°25′W) is a deep oligotrophic lake from Northern Patagonia. It has been historically affected by volcanic eruptions with significant amount of tephras deposited in lake sediments and surrounding water catchment. Approximately 50 km from the western limit of the lake is the Puyehue-Cordón Caulle volcanic complex (PCCVC; 40°32′S, 72°02′W), an active volcanic centre with high historic eruptive frequency (Lara et al., 2006). Arsenic concentrations in a sedimentary sequence sampled in Brazo Rincón, the site closest to the PCCVC (Fig. 1), range

from 11 to 73 $\mu g\ g^{-1}$ with the highest peak observed in the upper sediment layers, evidencing diffusive diagenetic processes driven by redox reactions (Ribeiro Guevara et al., 2005). Farthest the volcano, in a straight line northwest-southeast, sedimentary sequences sampled in Bahía López and near the city of San Carlos de Bariloche (see Fig. 1), have As concentrations noticeably lower, ranging from 5 to 8 $\mu g\ g^{-1}$ (Ribeiro Guevara et al., 2005) and 5–7 $\mu g\ g^{-1}$ (Ribeiro Guevara, unpublished data), respectively. Reported concentrations of dissolved As in Lake Nahuel Huapi waters are below 0.7 $\mu g\ L^{-1}$ (Markert et al., 1997) that are at the lower end of the range of values reported in uncontaminated lakes around the world (Rodie et al., 1995).

On June 4th 2011 the PCCVC began an eruptive process that generated a column of gases and volcanic materials of different grain size (Bertrand et al., 2014). Bioindication of air pollution after the eruptive event was revealed by increases in As concentrations in epiphytic-lichens sampled nearest to the PCCVC in the Nahuel Huapi National Park (Bubach et al., 2012). The large amounts of volcanic products ejected during the PCCVC eruption blanketed the entire lake Nahuel Huapi with about 10–30 cm deposited in the north-west side, and about 3–5 cm in the south-east (Masciocchi et al., 2013). The input of tephras of different grain size affected the limnology of the surrounding lakes and rivers, having modified the ecology of fish, macroinvertebrates, and plankton (Miserendino et al., 2012; Lallement et al., 2014; Modenutti et al., 2013).

Geochemical characterization of tephras from 2011 PCCVC eruption showed that As contents in the glassy fraction are around 15 $\mu g\ g^{-1}$ (Daga et al., 2014), while direct release of As from the deposited ashes to water was estimated to be less than 0.21% of the total As measured (Bia et al., 2015). Since As is rapidly released from surface volcanic tephra during the first ash–water interaction (Bia et al., 2015; Ruggieri et al., 2012), it could be expected a brief increase in As bioavailability and therefore modifications in As concentrations in aquatic biota, especially in primary producers and primary consumers, immediately after tephra deposition.

Just before the PCCVC eruption, an extensive food web sampling in Lake Nahuel Huapi was carried out. Therefore, the 2011 PCCVC eruption provides a natural experiment for studying the short term changes in the bioaccumulation of naturally occurring As by aquatic organisms in a deep oligotrophic lake subjected to the influence of past and present volcanic activity. Our objectives were: (1) to determine As concentrations of aquatic organisms of Lake Nahuel Huapi at different trophic levels and to assess the effect of feeding habits on As accumulation; (2) to analyze the trophic transfer patterns of As in the food web of the lake through the analysis of stable isotopes of carbon and nitrogen; (3) to evaluate the influence of the volcanic complex on the accumulation of As by organisms comparing As concentrations in samples from different sites and before and after the 2011 PCCVC eruption.

2. Materials and methods

2.1. Study area

Lake Nahuel Huapi (40°55′ S, 71°30′ W; Fig. 1), located within the Nahuel Huapi National Park, has a surface area of 557 km^2 and a maximum depth of 464 m. Is an oligotrophic glacial lake classified
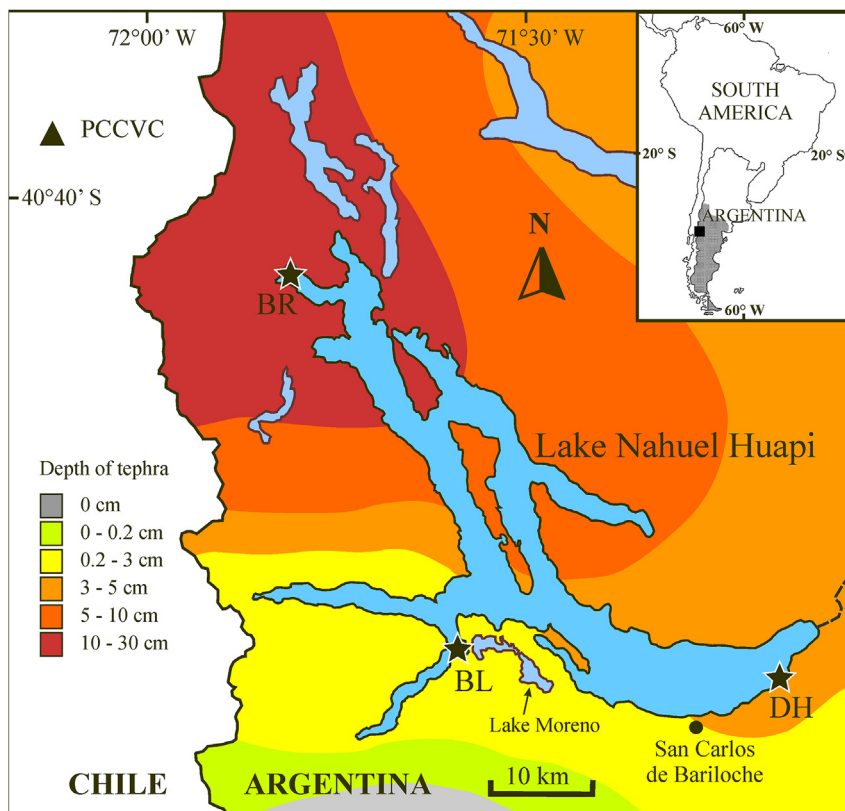
Fig. 1. Map of the study area showing the location of the three sampling sites (black stars; BR: Brazo Rincón, BL: Bahía López, DH: Dina Huapi) in Lake Nahuel Huapi, and depth (cm) of tephra deposited after the eruption of the Puyehue-Cordón Caulle volcanic complex (PCCVC) along the West-East gradient (modified from Masciocchi et al., 2013).

as warm monomictic with regular summer stratification (Díaz et al., 2007). The climate in the region is cold temperate and, as the prevailing westerly winds cross the Andes, they create a strong climatic gradient across the lake basin, with higher precipitation and moisture in the West (average precipitation: 2.800 mm y^{-1}, data provided by the Autoridad Interjurisdiccional de Cuencas (AIC)), which then transitions to more arid conditions towards the East (500 mm y^{-1} precipitation, AIC). Besides the increasing human population around the Lake Nahuel Huapi shores, there are no record of important As-generating activities (e.g., mining, metallurgical industry) in the region. It is assumed that the existence of As in the environment comes mainly from natural sources.

The sampling sites were selected from lowest to highest distance from the volcanic complex and following the West-East predominant wind direction that determine different levels of impact of the volcano on the system (Fig. 1). Brazo Rincón site (BR) is the northwestern branch of the lake with a max depth of 100 m and a summer-autumn thermocline located between 35 and 45 m depth. Bahía López site (BL) is a small and shallow closed bay (max depth 45 m), and represents the mid-point site between the humid and arid sites. The shallowness of this site does not allow an evident thermal stratification, but a decreasing temperature gradient with depth is evidenced. Dina Huapi site (DH, max depth 236 m), is in the driest region of the lake, farthest away from the PCCVC, and near the city of San Carlos de Bariloche. It has an extended thermocline that can reach 60 m depth. BR was the most affected site by the 2011 PCCVC eruption, receiving approximately 10–30 cm of coarse ash fall. DH and BL were less affected receiving 3–5 cm, and 0.2–3 cm of accumulated ash, respectively (Masciocchi et al., 2013, Fig. 1). The tephras 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.

2.2. Sampling and sample preparation

The food web compartments studied included size-fractioned plankton (including phytoplankton, mixed plankton, and zooplankton), six benthic invertebrate species, including mayfly larvae (Ephemeroptera), crayfish (Samastacus spinifrons), freshwater crabs (Aegla sp.), amphipods (Hyalella sp.), snails (Chilina sp.), and mussels (Diplodon chilensis). Six out of seven fish species were analyzed: native species, small puyen (Galaxias maculatus), big puyen (Galaxias platei), velvet catfish (Olivaichthys viedmensis), and creole perch (Percichthys trucha), and the introduced salmonids, rainbow trout (Oncorhynchus mykiss), and brown trout (Salmo trutta).

Plankton were collected on February and May 2011 (summer-fall prior to the volcanic eruption) and on July and November 2011 and February 2012 (winter, spring and summer after the eruption), by vertical hauls using a large winch system and 1-m diameter nets of three different mesh sizes (10, 53, and 200 μm). Because the composition of the planktonic communities can vary with lake depth due to strong changes in light intensity, temperature profiles and other limnological parameters, to keep hauls consistent, we divided them into two depths: between 85 m and 45 m deep (below the thermocline) and between 40 m and the lake surface (above the thermocline) in the deepest BR and DH sites. In shallower BL, plankton were sampled only from 40 m to the lake surface. The plankton net samples were subsequently filtered as detailed by Rizzo et al. (2014) to obtain three concentrated plankton fractions: P1 (10–53 μm) composed by phytoplankton (Dinophycean algae) and small mixotrophic ciliates (Ophrydium

naumanni and *Stentor araucanus*), P2 (53–200 μm) formed by mixotrophic ciliates and small zooplankton (rotifers), and P3 (>200 μm) represented by large zooplankton, i.e., copepods (*Boeckella gracilipes* and cyclopoids) and cladocerans (*Ceriodaphnia dubia*, *Daphnia* sp., and *Bosmina longirostris*) (Arcagni et al., 2015). After using samarium concentrations to subtract tephra and other geological particulate contributions to plankton samples (see Rizzo et al., 2014), P1 and P2 fractions sampled after the eruption had to be discarded because of the high proportion of ash in the samples, so the before-and-after eruption comparisons only were made for P3. To see the temporal progression of As in zooplankton after the eruptive event, all sample dates were analyzed separately.

Benthic macroinvertebrates were hand-picked from submerged logs and stones on February 2011 (except crayfish from DH which were sampled on April) and February 2012 (summer before and summer after the PCCVC eruption). Decapods and mollusks were removed from their carapaces/shells and muscle tissue and hepatopancreas were analyzed separately. Whole bodies were analyzed for the remaining macroinvertebrates. When individual sample masses were not sufficient for analyses homogenate samples of pooled individuals, grouped by species and similar size, were prepared.

Fish were sampled on May 2011 (autumn before PCCVC eruption) and one year later, on May 2012 (after the PCCVC eruption). Larger fish (i.e., salmonid adults, creole perch, velvet catfish, and big puyen) were captured using gill nets made of six 10-m long panels of different mesh size, set at dusk perpendicular to the shore from 2 m down to 40 m deep, and raised early in the morning. Small fish (i.e., native small puyen and juvenile salmonid) were collected using double-funnel baited cylinder fish traps left at each site for 24 h and by using seine nets of 12 m long and 1 mm mesh size. Small puyen individuals were also accidentally captured in BR during plankton sampling three months after the eruption (winter 2011). These samples were used to assess the short effect of the eruption in the most affected site, together with zooplankton. Fish were separated by species and their total length and weight were recorded. Muscle and liver tissue were extracted, and homogenized individually in the case of larger specimens, or pooled with individuals of similar size, in the case of smaller fish (<70 mm). The small size of small puyen did not allow to remove sufficient muscle tissue for all analyses, so the head and the guts were separated from each individual, and homogenates of 4–10 fish were made with individuals from four size classes (10 mm range each) from 30 mm to 70 mm.

2.3. Analytical procedures

Total As concentration were determined by Instrumental Neutron Activation Analysis (INAA). Aliquots ranging from 1 to 200 mg of dried homogenized sample were sealed in SUPRASIL-AN quartz ampoules and irradiated for 24 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 percent relative efficiency and a 4096-channel analyzer. The concentrations are reported in dry weight (DW) basis. The specific methodology is described in Arribére et al. (2008). Certified reference materials (CRMs) NRCC TORT-2 and DORM-2 were analyzed together with tissues samples for analytical quality control; the results of the CRMs analysis match with certified values, considering uncertainties.

Stable carbon (C) and nitrogen (N) isotopes ratios were analyzed for the samples collected before the 2011 PCCVC eruption via DELTAplusXP continuous flow stable isotope ratio mass spectrometer at the Queen's Facility for Isotope Research (QFIR), Queen's University, Kingston, ON, Canada. Stable isotope (SI) values

(δ) were expressed in parts per thousand (‰) relative to the C and N reference materials (Pee Dee Belemnite limestone and atmospheric nitrogen standard respectively). Duplicates and standard reference materials were analyzed to check the quality of analysis. Due to logistical reasons, only samples collected prior to the eruption were analyzed for SI.

2.4. Statistics and data analysis

To describe general food web As transfer patterns, regressions between $\delta^{15}N$ (‰) and $\log_{10}$ As (μg g^{-1} DW) of all sampled organisms were performed. Because of the different feeding habits of fish, not all the sampled organisms have the potential to transfer As to fish. As a result, we also examined "short food chains" for each predator fish in this lake. To describe specific trophic transfer of As to most important predator fish species, regressions were performed considering only the portion of the fish food chain that includes the main prey for the fish sizes analyzed in this study, according to Juncos et al. (2015). Here, we used the term "food web" to refer to all the organisms interactions, while "food chain" was used to refer to a specific section of the whole food web (e.g., the "creole perch food chain" was referring to the creole perch and its main prey trophic interactions). As the main prey for salmonids, small puyen pelagic- (planktonic prey) and benthic- (insect larvae) food chains were also analyzed.

Organisms were classified into six major trophic groups (TG) (Tables 1–3), based on $\delta^{15}N$ and $\delta^{13}C$ values of samples collected before the eruption, and information on diet and trophic relationships taken from literature (Estebenet et al., 2002; Lara et al., 2002; Barriga et al., 2012; Juncos et al., 2013, 2015; Arcagni et al., 2015). To assess the relationship between feeding habits and As accumulation, we performed a non-metric multidimensional scaling (NMDS) based on Bray–Curtis similarity matrix computed on the $\delta^{15}N$, $\delta^{13}C$ and As concentrations determined for each consumer, excluding mixed plankton (P2) (because they are not formed strictly by consumers) and big puyen (due to the great variability exhibited in its $\delta^{15}N$ values) at each site. A one-way analysis of similarity (ANOSIM) was used to test for differences in As concentrations among trophic groups of organisms. Post-hoc pairwise comparisons were computed when the Global-R was significant with α < 0.05. Multivariate analysis was performed using PRIMER-E 6 statistical software (Clarke and Warwick, 2001). NMDS results were considered to be sufficiently described in two dimensions when the stress value, a measure of the goodness of fit, was <0.2 (Clarke and Warwick, 2001).

Student's t-test was performed for comparisons of As concentrations before and after volcanic eruption in different organisms when sample size allowed. Statistical comparisons among means of more than two groups (e.g., among sampling sites) were performed by one-way ANOVA, or non-parametric Kruskal–Wallis, when data were no normally distributed. When ANOVA was significant, the Student–Newman–Keuls (S–N–K) test was employed for the comparison. Differences were considered significant at $p \leq 0.05$. SigmaStat software version 3.5 was used for statistical analysis.

3. Results and discussion

3.1. Arsenic concentrations in Lake Nahuel Huapi food web

Mean total As concentration in plankton from BR and BL decreased with increasing size fraction, with highest concentrations in smaller plankton (P1, phytoplankton) and the lowest in larger plankton (P3, zooplankton) (Table 1). Plankton from DH did not follow this pattern having P2 higher As values than P1. In BR and DH, As concentrations in P1 and P2 collected below the

Table 1
Arsenic concentrations (μg g^{-1} DW), δ^{15}N (‰), and δ^{13}C (‰) in planktonic organisms from three sampling locations of Lake Nahuel Huapi before and after the PCCVC eruption (mean of Winter and Spring 2011 samples). Trophic group, sampling site, sample size (N), size range of organisms, mean values, standard deviation (s.d.), and range of values are indicated for each case. PP: Primary producer; PC: Plankton consumer; BR: Brazo Rincón; BL: Bahía López; DH: Dina Huapi; N/D: no data available.

Organism	Trophic group	Site	Before PCCVC eruption									After PCCVC (July to November 2011 samples)			
			N	Mesh size range (mm)	δ^{15}N (‰)		δ^{13}C (‰)		As (μg g^{-1} DW)		N	Size range (mm)	As (μg g^{-1} DW)	
					Mean ± s.d.	Range	Mean ± s.d.	Range	Mean ± s.d.	Range			Mean ± s.d.	Range
Plankton 1	PP	BR	2	10–53 μm[a]	4.4 ± 0.8	3.9–4.9	−26.5 ± 1.0	−25.8 to −27.2	9.4 ± 2.3	7.8–11	N/D	N/D	N/D	N/D
			2	10–53 μm[b]	4.6 ± 0.3	4.3–4.8	−28.8 ± 0.4	−28.5 to −29.1	38.2 ± 37.6	11.6–64.8	N/D	N/D	N/D	N/D
		BL	2	10–53 μm[a]	3.8 ± 0.4	3.5–4.1	−25.5 ± 1.2	−23.8 to −25.4	12.2 ± 11.8	3.9–20.6	N/D	N/D	N/D	N/D
		DH	1	10–53 μm[a]	4.3	–	−26.3	–	5.3	–	N/D	N/D	N/D	N/D
			1	10–53 μm[b]	3.8	–	−23.8	–	14.8	–	N/D	N/D	N/D	N/D
Plankton 2	PP-PC	BR	2	53–200 μm[a]	5.4 ± 1.5	4.3–6.5	−24.1 ± 1.9	−22.8 to −25.5	4.4 ± 0.2	4.3–4.6	N/D	N/D	N/D	N/D
			2	53–200 μm[b]	4.0 ± 0.7	3.5–4.5	−26.0 ± 1.0	−25.3 to −26.7	15.7 ± 9.2	9.2–22.3	N/D	N/D	N/D	N/D
		BL	2	53–200 μm[a]	4.6 ± 0.3	4.4–4.8	−23.8 ± 0.02	−23.76 to −23.75	10.2 ± 7.5	4.9–15.5	N/D	N/D	N/D	N/D
		DH	1	53–200 μm[a]	6.1	–	−24.0	–	5.5	–	N/D	N/D	N/D	N/D
			1	53–200 μm[b]	6.1	–	−23.7	–	19.1	–	N/D	N/D	N/D	N/D
Plankton 3	PC	BR	2	>200 μm[a]	8.8 ± 0.04	8.7–8.8	−29.2 ± 1.2	−28.4 to −30.0	2.1 ± 0.9	1.5–2.8	3	>200 μm[a]	3.5 ± 1.2	2.1–4.5
			2	>200 μm[b]	8.8 ± 0.6	8.3–9.2	−33.2 ± 0.04	−33.17 to −33.2	1.9 ± 0.8	1.3–2.5	3	>200 μm[b]	3.5 ± 0.3	3.1–3.7
		BL	2	>200 μm[a]	8.8 ± 0.2	8.6–8.9	−27.5 ± 0.2	−27.4 to −27.7	2.4 ± 1.6	1.2–3.5	3	>200 μm[a]	4.0 ± 1.7	2.3–5.8
		DH	1	>200 μm[a]	9.3	–	−27.0	–	2.3	–	2	>200 μm[a]	7.8 ± 1.1	7.1–8.6
			1	>200 μm[b]	10.3	–	−28.9	–	2.8	–	2	>200 μm[b]	5.1 ± 0.5	4.7–5.5

a. Plankton collected above thethermocline (40–0 m hauling).
b. Plankton collected below the thermocline (85–40 m hauling).

thermocline (85–45 m) were higher than P1 and P2 above the thermocline (Table 1). The highest concentrations were recorded in below-thermocline P1 from BR, the site closest to the volcano. Regarding, As in the surface plankton samples (40–0 m), the highest concentrations were determined in P1 and P2 fractions, and to a lesser extent in P3, from BL (Table 1). Arsenic concentrations observed in Nahuel Huapi plankton are in the range of those reported in the nearby Lake Moreno (1.73–28.17 μg g^{-1}DW; Revenga et al., 2012) and similar to concentrations in plankton from lakes with no known metal point sources of the Northeastern United States (0.1–13.4 μg g^{-1} DW; Chen et al., 2000).

The highest As concentrations and greater variations in Lake Nahuel Huapi, both between sampling sites and between position in the water column, were observed in the smallest plankton sizes P1 and P2 (phytoplankton, ciliates, and small zooplankton). This is consistent with Chen et al. (2000) that found that small zooplankton and large phytoplankton from numerous lakes in USA bioaccumulate As at higher rates than larger zooplankton. Due to its chemical and structural similarities with phosphate, arsenate (As^V) is readily and actively taken up by phytoplankton through phosphate uptake mechanisms (Levy et al., 2005; Rahman et al., 2012). Low phosphate concentrations have been related to higher As^V uptake by phytoplankton (Rahman et al., 2012), therefore phytoplankton could be an especially important pathway of As input to the food web in low nutrient water bodies, as is the case of North Patagonian lakes (Díaz et al., 2007).

The observed variations in As burden in plankton fractions could be explained by changes in aqueous As that it is known directly affect plankton burdens (Chen and Folt, 2000). Higher mean As concentrations found in phytoplankton samples collected bellow the thermocline in BR and DH, may indicate a greater availability of As to plankton in deep waters. Arsenic is stable in surface sediments under oxic conditions (Hyobu et al., 2012), but is released from sediments with further depression of dissolved oxygen (DO) levels. DO levels in the bottom of monomictic lakes, as Nahuel Huapi, decrease in summer-autumn after the development of a thermocline (Hyobu et al., 2012). In this sense, the decreasing DO concentrations through the season could be causing a remobilization of As and therefore increments in its concentrations in

phytoplankton at deeper depths under those conditions. It is noteworthy that the site closest to the volcanic complex, BR, has the highest As concentrations in bottom sediments, compared with the values recorded in BL and DH (Ribeiro Guevara et al., 2005), and also has the highest As concentrations in below-thermocline phytoplankton. Hence, sediments could be acting as suppliers of As to the aquatic food web through remobilization into water column in deep-suboxic zones.

The structure of the planktonic community (e.g., abundance, biomass, size distribution) can also influence the incorporation of trace elements to aquatic food webs (Chen and Folt, 2000; Soto Cárdenas et al., 2014). For example, the presence of mixotrophic bacterivorous organisms have been found to enhance Hg incorporation into pelagic food webs of oligotrophic lakes, because those microorganisms may incorporate this heavy metal both passively from the surrounding environment (dissolved phase) and actively through the consumption of bacteria (Soto Cárdenas et al., 2014). Bacteria are known important in the biotransformation and biogeochemical cycle of As species in aquatic systems (Rahman et al., 2012). Arcagni et al. (2015) recently described the composition of plankton factions in BR, BL and DH in Lake Nahuel Huapi founding some differences in the proportion of mixotrophic ciliates biomass among sites and seasons. For instance, the biomass of P2 in DH is highly dominated by mixotrophic ciliates, and in the present study was found to has higher As concentrations than P1. Meanwhile in BR and BL, P2 biomass is evenly distributed between rotifers and mixotrophic ciliates (Arcagni et al., 2015), so the contribution of mixotrophic organisms to As bioaccumulation is less important, and As concentrations decrease from P1 to P2.

Lastly, the high [As] recorded in plankton fractions in the 40–0 m in BL are actually intermediate values between the observed upper- and lower-thermocline values in plankton from the other two sites. Unlike BR and DH, BL is a shallower bay (max depth 45 m), without a marked thermal stratification. The presence of a thermocline in BR and DH could limit vertical mixing of As remobilized from sediments, which is then reflected in As accumulation by small plankton (P1 and P2). This behavior was also observed for Hg bioconcentration in plankton sampled below and above the thermocline in Lake Nahuel Hupai (Rizzo et al., 2014). In

Table 2
Arsenic concentrations (µg g^{-1} DW), δ^{15}N (‰), and δ^{13}C (‰) in benthic organisms from three sampling locations of Lake Nahuel Huapi before and after the PCCVC eruption. Trophic group (TG), sampling site, sample size (N), size range of organisms, mean values, standard deviation (s.d.), and range of values are indicated for each case. The numbers in parenthesis represents As concentrations in hepatopancreas. HS: herbivorous scrapper; HF: herbivorous filter feeders; OI: omnivorous organism; BR: Brazo Rincón; BL: Bahía López; DH: Dina Huapi; N/D: no data available.

| Organims | TG | Site | Before PCCVC eruption | | | | | | | | After PCCVC eruption | | | |
| | | | N | Size range (mm) | δ^{15}N (‰) | | δ^{13}C (‰) | | As (µg g^{-1} DW) | | N | Size range (mm) | As (µg g^{-1} DW) | |
					Mean ± s.d.	Range	Mean ± s.d.	Range	Mean ± s.d.	Range			Mean ± s.d.	Range
Chilina sp. (snail)	HS	BR	8	11–27	2.4 ± 0.3	2.0–3.0	−19.4 ± 1.1	−22.0 to −18.3	11.9 ± 1.7	9.3–14.4	9	9–23	13.4 ± 2.2	9.9–16.9
			8		N/D	N/D	N/D	N/D	(17.4 ± 2.0)	(14.5–21.1)	9		(17.5 ± 2.9)	(14.3–23.6)
		BL	8	11–26	2.5 ± 0.3	2.0–2.9	−16.5 ± 2.3	−19.6 to −13.1	13.6 ± 1.3	11.3–15.3	8	8–27	10.0 ± 3.3	7.1–15.2
			8		N/D	N/D	N/D	N/D	(21.3 ± 3.5)	(15.2–24.6)	7		(12.7 ± 3.7)	(10.1–19.9)
		DH	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	7	9–17	6.9 ± 1.3	5.4–8.6
					N/D	N/D	N/D	N/D	N/D	N/D	6		(11.1 ± 1.0)	(10.0–12.4)
Diplodon chilensis (mussel)	HF	BL	15	35–79	5.7 ± 0.3	5.3–6.5	−25.8 ± 0.3	−26.2 to −25.2	9.9 ± 2.4	5.4–15.6	N/D	N/D	N/D	N/D
			15		N/D	N/D	N/D	N/D	(32.3 ± 14.1)	(12.6–67.6)	N/D	N/D	N/D	N/D
Hyalella sp. (amphipod)[a]	OI	BR	4	–	1.5 ± 0.3	1.1–1.6	−26.2 ± 1.0	−27.0 to −24.8	3.8 ± 0.08	3.7–3.9	N/D	N/D	N/D	N/D
Samastacus spinifrons (crayfish)	OI	BR	9	22–96	4.1 ± 0.6	2.9–4.7	−25.7 ± 1.6	−28.9 to −24.4	1.0 ± 0.7	0.5–2.5	3	53–73	1.0 ± 0.4	0.6–1.5
			6		N/D	N/D	N/D	N/D	(3.4 ± 1.9)	(2.0–6.4)	3		(2.1 ± 1.2)	(1.2–3.5)
		BL	6	43–77	4.6 ± 0.7	3.8–5.6	−24.0 ± 1.4	−26.5 to −21.7	0.7 ± 0.3	0.4–1.2	4	36–68	0.7 ± 0.2	0.5–0.9
			6		N/D	N/D	N/D	N/D	(2.0 ± 0.8)	(1.0–3.2)	4		(1.7 ± 1.1)	(0.4–3.3)
		DH	6	57–100	8.1 ± 0.7	7.5–9.4	−21.3 ± 2.8	−25.1 to −18.8	1.4 ± 0.3	0.9–1.6	1	68	1.01	
			1		N/D	N/D	N/D	N/D	(0.9)	–	1		(4.65)	
Aegla sp. (crab)	OI	BR	5	8–40	5.1 ± 1.2	3.2–6.5	−25.4 ± 0.9	−27.0 to −24.7	4.1 ± 1.9	2.3–7.2	7	9–36	3.7 ± 1.7	1.6–5.8
			4		N/D	N/D	N/D	N/D	(3.5 ± 1.1)	(2.6–5.1)	4		(7.7 ± 1.2)	(6.1–9.1)
		BL	12	3–40	5.8 ± 1.1	3.9–7.7	−23.0 ± 1.7	−26.1 to −20.6	4.6 ± 2.2	1.5–9.2	4	14–32	4.4 ± 1.6	2.1–5.8
			9		N/D	N/D	N/D	N/D	(7.1 ± 2.6)	(4.3–12.4)	3		(7.2 ± 3.3)	(4.9–11.0)
		DH	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	9	16–31	5.1 ± 1.5	1.8–6.9
			N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	8		(8.1 ± 1.0)	(6.1–9.2)
Insects (Ephemeroptera)[a]	OI	BR	7	–	1.2 ± 0.1	0.9–1.3	−24.9 ± 0.8	−25.7 to −23.6	1.2 ± 0.2	0.96–1.5	3	–	2.3 ± 1.8	1.1–4.3
		BL	4	–	1.6 ± 0.5	1.1–2.2	−25.7 ± 6.2	−32.9 to −20.3	2.8 ± 1.9	0.6–4.3	6	–	2.8 ± 1.2	0.8–4.1
		DH	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	4	–	3.8 ± 0.9	2.9–4.7

a. Concentrations are for whole body.

Table 3

Arsenic contents(µg g^{-1} DW), δ^{15}N (‰), and δ^{13}C (‰) in fish from three sampling locations of Lake Nahuel Huapi before and after the PCCVC eruption. Trophic group (TG), sampling site, sample size (N), size range of organisms, mean values, standard deviation (s.d.), and range of values are indicated for each case. The numbers in parenthesis represents [As] in liver. CF: carnivorous fish. BR: Brazo Rincón; BL: Bahía López; DH: Dina Huapi; N/D: no data available.

Organims	TG	Site	Before PCCVC eruption								After PCCVC eruption			
			N	Size range (mm)	δ^{15}N (‰) Mean ± s.d.	Range	δ^{13}C (‰) Mean ± s.d.	Range	As (µg g^{-1} DW) Mean ± s.d.	Range	N	Size range (mm)	As (µg g^{-1} DW) Mean ± s.d.	Range
Galaxias maculatus (small puyen)[a]	CF	BR	12	33–56	9.4 ± 0.9	8.2–11.1	−25.4 ± 0.8	−26.5 to −23.6	0.8 ± 0.2	0.4–1.3	28[b]	33–65	0.8 ± 0.6	0.2–2.3
		BL	10	35–61	9.4 ± 1.2	7.7–11.4	−24.7 ± 1.3	−26.2 to −22.2	0.6 ± 0.3	0.2–1.1	31	35–58	0.6 ± 0.2	0.2–1.1
		DH	18	30–56	11.4 ± 1.3	9.9–15.6	−22.1 ± 1.6	−24.0 to −19.1	0.8 ± 0.3	0.3–1.3	17	34–61	0.5 ± 0.2	0.3–0.9
Olivaichthys viedmensis (velvet catfish)	CF	BL	1	266	9.4	−	−21.0	−	0.31 (<0.5)	−	N/D N/D	N/D	N/D	N/D
		DH	1	395	10.6	−	−20.3	−	0.29 (0.21)	−	2 2	114–242	0.2 ± 0.02 (0.4 ± 0.01)	0.18–0.21 (0.4–0.42)
Galaxias platei (big puyen)	CF	BR	8 9	190–232	7.2 ± 3.9	1.8–13.2	−29.7 ± 1.9	−26.3 to 31.8	0.4 ± 0.2 (2.1 ± 1.1)	0.1–0.7 (0.6–3.8)	1	80	0.4 N/D	N/D
		DH	1	230	12.7	−	−20.2	−	0.7 (1.3)	−	N/D N/D	N/D	N/D	N/D
Percichthys trucha A (creole perch)	CF	BR	13 13	429–511	13.1 ± 1.1	10.8–14.1	−26.7 ± 1.3	−29.4 to −25.2	1.2 ± 0.3 (3.79 ± 0.98)	0.7–1.9 (2.59–5.88)	1 1	460	0.6 (0.3.38)	
		BL	9 9	325–490	12.4 ± 1.7	8.7–14.2	−25.1 ± 1.2	−26.7 to −23.2	0.9 ± 0.2 (2.61 ± 1.2)	0.4–1.3 (0.83–3.99)	6 6	230–497	0.5 ± 0.2 (2.2 ± 2.2)	0.3–0.7 (0.4–5.2)
		DH	5 5	180–450	11.3 ± 0.8	10.1–12.3	−19.7 ± 1.3	−21.4 to −18.1	0.5 ± 0.3 (2.31 ± 1.42)	0.4–0.8 (0.8–5.88)	13 13	255–474	0.5 ± 0.2 (2.2 ± 1.0)	0.2–0.8 (0.6–4.4)
Oncorhynchus mykiss J (rainbow trout)	CF	BL	8 8	72–167	7.2 ± 1.6	5.8–10.8	−25.2 ± 2.7	−29.5 to −20.6	0.1 ± 0.1 (0.4 ± 0.2)	0.05–0.2 (0.2–0.6)	N/D N/D	N/D	N/D	N/D
		DH	3 1	53–92	8.1 ± 2.1	6.3–10.4	−19.3 ± 2.5	−21.8 to −16.7	0.2 ± 0.02 (0.3)	0.1–0.2 −	8 8	173–234	<0.3 (0.03–<0.3)	<0.8 (0.15–<0.8)
Oncorhynchus mykiss A	CF	BR	5 5	500–627	12.7 ± 1.5	10.0–13.7	−24.7 ± 1.0	−26.1 to −23.8	0.5 ± 0.3 (0.5 ± 0.11)	0.2–0.9 (0.38–0.62)	22 22	254–740	0.4 ± 0.2 (0.6 ± 0.3)	0.1–0.7 (0.2–1.4)
		BL	4 4	341–584	12.1 ± 0.2	11.8–12.3	−24.9 ± 1.3	−26.0 to −23.0	0.5 ± 0.3 (0.44 ± 0.08)	0.3–1.0 (0.34–0.53)	10 10	260–634	0.4 ± 0.2 (0.5 ± 0.1)	0.1–0.7 (0.4–0.7)
		DH	10 9	240–652	11.9 ± 0.9	10.5–13.5	−20.2 ± 2.5	−23.4 to −15.6	0.2 ± 0.1 (0.36 ± 0.11)	0.1–0.4 (0.26–0.55)	26 26	240–672	0.3 ± 0.2 (0.5 ± 0.2)	0.8–0.8 (0.2–1.1)
Salmo trutta J (brown trout)	CF	BR	5	40–84	5.1 ± 0.4	4.5–5.6	−30.1 ± 0.9	−31.2 to −28.8	0.2 ± 0.05 −	0.2–0.3 −	N/D N/D	N/D	N/D	N/D
Salmo trutta A	CF	BR	23 23	468–713	13.6 ± 0.4	12.5–14.5	−25.5 ± 0.8	−26.9 to −24.1	0.6 ± 0.2 (0.37 ± 0.19)	0.2–1.3 (0.14–0.9)	11 11	520–780	0.5 ± 0.4 (0.5 ± 0.2)	0.2–1.7 (0.3–1.0)
		BL	2 2	532–661	13.8 ± 0.1	13.7–13.9	−26.4 ± 0.8	−27.0 to −25.8	0.7 ± 0.05 (0.42)	0.7–0.8 (0.42–<1)	5 5	520–712	0.5 ± 0.3 (0.5 ± 0.1)	0.3–0.8 (0.4–0.7)
		DH	1	584	13.7	−	−24.7	−	0.78 N/D	− N/D	5 5	536–671	0.3 ± 0.1 (0.5 ± 0.3)	0.2–0.4 (0.2–0.7)

a. Concentrations are for whole body without head and guts.
b. Includes individuals captured in winter 2011 (three month after the eruption) and in autumn 2012 (a year after the eruption).

the absence of a thermocline, as is the case of BL, As released from sediments could be redistributed along the water column, being available to phytoplankton uptake until re-oxidation and co-precipitation occur. Therefore, the dynamics of As in BL, and therefore, its bioaccumulation, seems to be different from that of stratified BR and DH.

The NMDS analysis allowed the identification of four significant trophic groups (ANOSIM; Global-R = 0.87; $p < 0.01$), according to differential As concentrations and $\delta^{15}N$ and $\delta^{13}C$ values (Fig. 2). The group of the herbivorous scrapers (HS), e.g., littoral snails, was separated at one extreme of the graph due to higher As concentrations and lower $\delta^{13}C$ values (Table 2). The filter-herbivorous (HF), i.e. pelagic-feeding mussels, formed a group with lower As concentrations and lower $\delta^{13}C$ than the snails, but higher values than the other groups (Table 2). An intermediate group formed by mayfly larvae, amphipods, crayfish, and crabs, with a more diverse omnivorous diet (OI), was differentiated due to lower As values than herbivorous, and lower $\delta^{15}N$ than zooplankton (plankton consumers, PC) and carnivorous fish (CF) (Fig. 2, Tables 1 and 2). All fish species, which feed on animal species, were grouped due to their lower As concentrations and higher $\delta^{15}N$ (Table 3). In view of everything mentioned so far, the pattern of As accumulation in organisms in Lake Nahuel Huapi could be described as follows: primary producers (phytoplankton) > scrapper mollusks > filter feeding mollusks > omnivorous invertebrates > zooplankton > fish. Although no data of As for periphyton was obtained for this lake, As concentrations measured in periphyton from the nearby Lake Moreno (10 µg g^{-1} DW) indicated elevated As accumulation also at the base of the benthic food web (Revenga et al., 2012).

Among primary consumers, the highest As concentrations were measured in the two herbivorous mollusk species. The scraper snail *Chilina* sp., with higher $\delta^{13}C$ (indicating a more littoral isotopic value) had higher As concentrations in muscle than the algae-filtering mussel *D. chilensis* (Student's t-test, $p < 0.001$), with a more pelagic $\delta^{13}C$ (Table 2). *Chilina* sp. lives on submerged stones and logs in littoral zones, feeding on periphyton (Estebenet et al., 2002), while *D. chilensis* is an algal-organic matter filterer usually
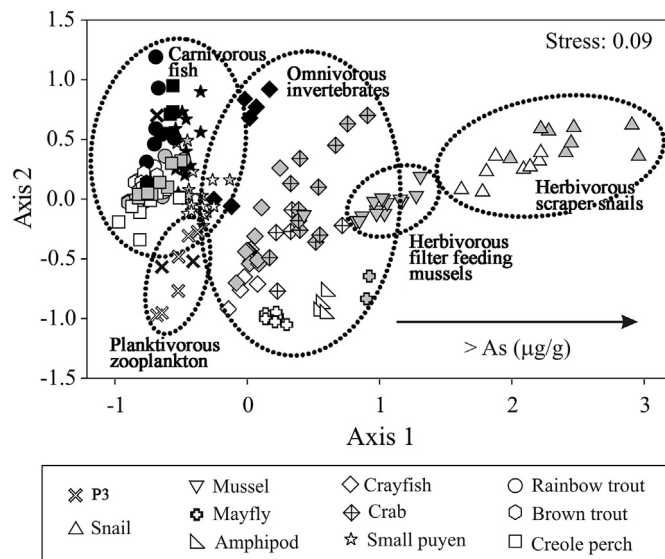
found buried in the sand (Lara et al., 2002). It has been recently found that As concentrations in leaf litter collected in coastal waters from Lake Nahuel Huapi were up to three order of magnitude higher than As in leaves collected directly from the living plant in the shores (A. Juárez, unpublished data). Allochthonous inputs as leaves and other plant litter provide substrates for bacteria and fungi colonization which are known to accumulate high amounts of metals and metalloids (Schorer and Eisele, 1997). During leaf litter decomposition, microorganisms and their exudates form a biofilm (e.g., periphyton) generating changes in the chemical properties of the substrate (e.g., redox conditions) that increase the capacity for metal fixation and thus its availability, leading to high amounts of metals in leaf litter (Schaller et al., 2011). Therefore, allochthonous inputs could be an important substrate for As remobilization and fixation, and subsequent incorporation by grazers (as the scraper snail *Chilina* sp.). Furthermore, both snails and mussels reside in direct contact with sediments. However, specific feeding habits make snails more exposed to As enriched sediments than mussels that obtain their nutrients from overlying water. Thus the differences in As burden between snails and mussels could be suggesting that periphyton and sediments are more important pathways of As entry to the food web than phytoplankton and suspended particles, and therefore that benthic organisms could be more exposed to As accumulation through phytobenthos than organisms feeding on phytoplankton. Arsenic concentrations in abiotic matrices should be measured to confirm this conclusions.

The lower As concentrations found among omnivorous compared to herbivorous groups could be attributed to a "dilution" effect caused by the incorporation of As from different food types, including plants, animals, and in many cases detritus, in the former case. In addition to food strategy, other factors may influence As concentrations in this group of organisms composed mostly by macrocrustaceans (crayfish, crabs and amphipods). For instance, it has been shown that the amphipod *Gammarus pulex* can thrive in high-As environments firstly because much of the As of the body is associated to the cuticle and secondly because As translocation from the gut to other tissues is minimized (Schaller et al., 2015). Here we measured separately the concentration of arsenic in muscle and hepatopancreas, both tissues that have been found to have the lowest As concentrations in *G. pulex* (Schaller et al., 2015). Thus, differences in food type abundance and their availability together with species-specific strategies would determine differences in As concentrations among omnivorous species within and among sampling locations.

3.2. Food web transfer of arsenic in Lake Nahuel Huapi

We were able to carry out a food web analysis on specimens collected prior to the PCCVC eruption which allowed us to characterize relationships among species and infer potential routes for As transfer through the food webs. When all sampled organisms were included in the analysis, negative and significant relationship between $\log_{10}$ As and $\delta^{15}N$ were found at the three sites ($R^2 = 0.2$, 0.14, and 0.36, respectively; $p < 0.05$; Fig. 3). These trends are consistent with total As biodilution patterns reported in the nearby Lake Moreno food web (Revenga et al., 2012) and in several marine (Asante et al., 2008) and freshwater food webs around the world (Maeda et al., 1992; Chen and Folt, 2000).

Food chain analysis for BR small puyen, including its planktonic prey and insects, showed no correlation between $\log_{10}$ As and trophic level ($\delta^{15}N$) (Fig. 4; R^2 0.06; $p = 0.16$). However, if only planktonic organisms were considered, a decreasing trend in $\log_{10}$ As can be observed. Food chain analysis for creole perch, including its preferred prey (crayfish), had a slight but significant increase in $\log_{10}$ As with increasing $\delta^{15}N$ ($R^2 = 0.47$; $p < 0.001$), indicating
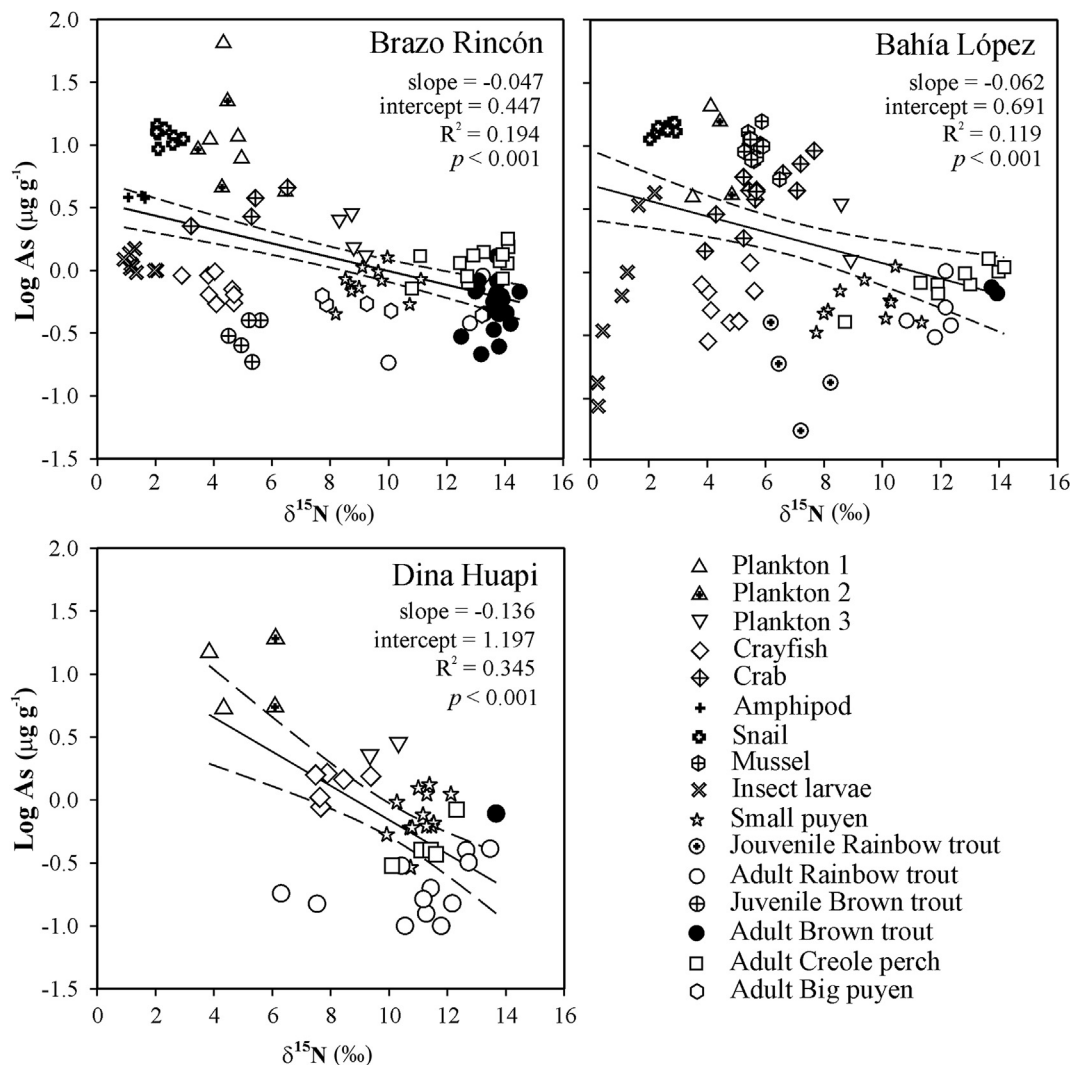

Fig. 2. Non-metric multidimensional scaling (NMDS) of the Bray–Curtis distances computed on $\delta^{15}N$, $\delta^{13}C$, and As concentrations data determined for whole body (zooplankton, mayflies, amphipods and small puyen) and muscle tissues (mollusks, decapods and fish) before PCCVC eruption. The dotted connecting lines enclose organisms of the same trophic group. White symbols correspond to organisms sampled in Brazo Rincón, grey ones are from Bahía López, and black ones are from Dina Huapi.

Fig. 3. Relationship between Log_{10} As (μg g^{-1} DW) vs δ^{15}N (‰) in biota from Brazo Rincón, Bahía López and Dina Huapi locations. Regression lines and confidence intervals are shown. Model regression parameters included.

possible As biomagnification for this species (Fig. 4). The rainbow trout food chain showed a decrease of log_{10} As from main prey to adult fish ($R^2 = 0.67$; $p < 0.001$), having the amphipods higher As concentrations than small puyen (Fig. 4). Food chain As transfer patterns for the most piscivorous brown trout could be divided into two negative regression lines: a weak one for adult individuals (LT > 400 mm), through crayfish and small puyen ($R^2 = 0.1$; $p = 0.04$), and a stronger one for juvenile individuals (LT < 100 mm), through insects and amphipods consumption ($R^2 = 0.65$; $p < 0.001$, Fig. 4).

Similar trends were found in particular fish food chains in BL (Fig. 4). Log_{10} As decreased significantly from plankton and insects to small puyen ($R^2 = 0.29$; $p = 0.01$) and a slightly significant biomagnification pattern was observed for the creole perch food chain ($R^2 = 0.32$; $p = 0.01$). Rainbow trout captured at this site included juvenile fish which have a strong biodilution pattern in As transfer through insect larvae ($R^2 = 0.9$; $p < 0.001$), contrary to the absence of correlation observed for adults ($R^2 = 0.26$; $p = 0.05$), through the consumption of small puyen as main prey (Fig. 3). No relationship between Log_{10} As and δ^{15}N was found in brown trout food chain ($R^2 = 0.03$; $p = 0.44$). At this site the crayfish exhibited the widest range of As concentrations, but only two brown trout specimens

were captured, which could be masking the presence of a pattern in this particular food chain.

In DH, biodilution patterns in As transfer were also distinguished (Fig. 4). The apparent absence of insect prey for small puyen could result in a more direct pelagic transfer of As to predator species (as opposed to more littoral routes for BR and BL). A negative relationship between small puyen and plankton was found ($R^2 = 0.72$; $p < 0.001$) (Fig. 4). No relationship was observed between Log_{10} As and δ^{15}N in the rainbow trout food chain ($R^2 = 0.01$; $p = 0.67$), nor in the one of brown trout ($R^2 = 0.17$; $p = 0.07$). The main difference with the other two sites was given by the higher As concentrations in the crayfish which determined a slight biodilution trend of As in the creole perch food chain ($R^2 = 0.43$; $p = 0.02$), contrary to the biomagnification patterns observed in BR and BL. In this regard it should be noted that crayfish in DH has twice δ^{15}N values than in BR and BL, whereas that δ^{15}N of perch in DH does not follow the nitrogen enrichment of crayfish, as could be expected from a prey–predator relationship. Hence, it could be a possibility that the biodilution observed in creole perch-food chain in DH is an artifact of consider as a prey an organisms that is not actually being consumed, or that is consumed in low proportions in combination with other prey (e.g., small puyen
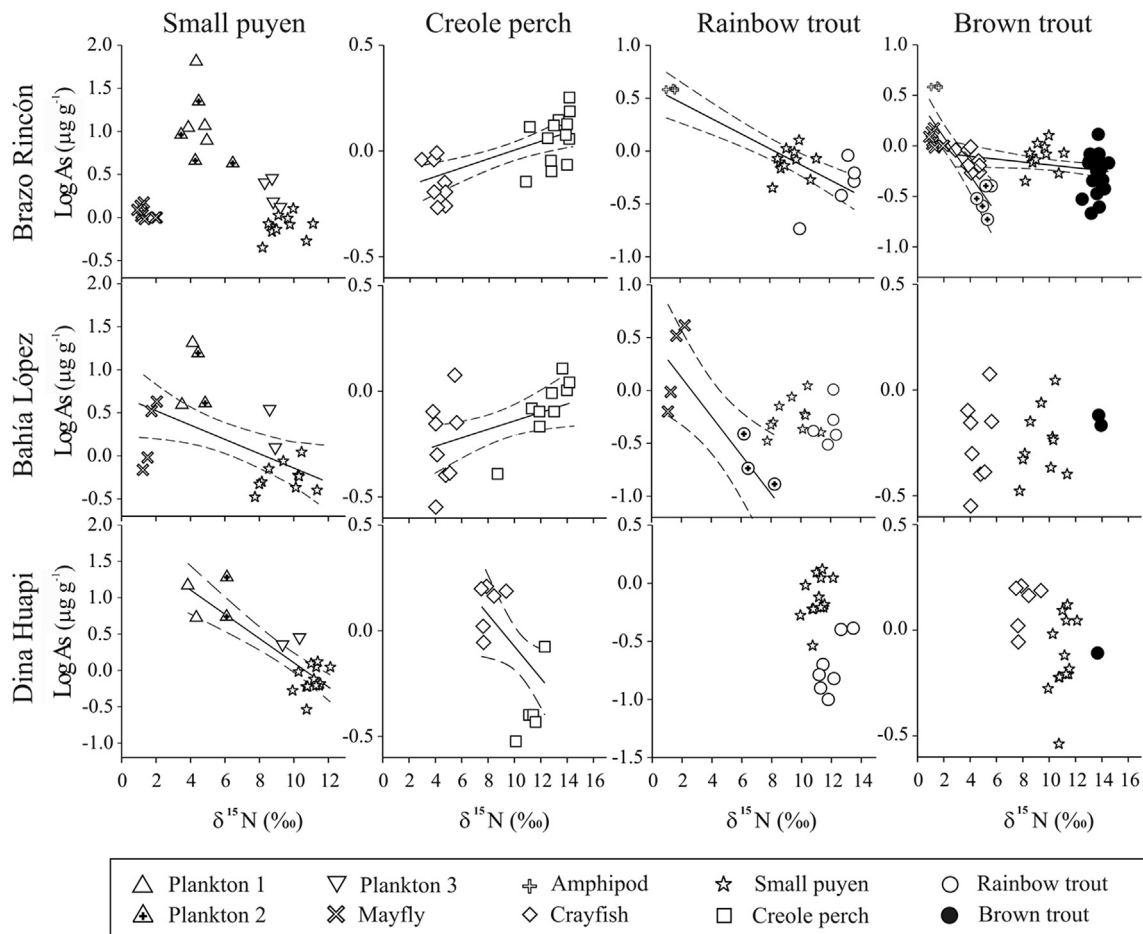
Fig. 4. Food chain regressions between Log_{10} As ($\mu g \, g^{-1}$ DW) and $\delta^{15}N$ (‰) values. The food chains (e.g., predator fish and their main prey) for small puyen, creole perch, juvenile and adult rainbow trout, and juvenile and adult brown trout from Brazo Rincón, Bahía López and Dina Huapi locations, before PCCVC eruption, are shown. Regression lines and confidence intervals are indicated only for significant relationships.

adults are heavily consumed by perch when are highly available in the environment, Juncos et al., 2013, 2015). However, more information on site-specific diet and prey availability is needed to prove this assumptions.

Several authors have reported As diminution through increasing trophic levels (Chen and Folt, 2000; Ikemoto et al., 2008; Culioli et al., 2009b). Evidence of As accumulation related to feeding strategy in fish have been reported by Chen and Folt (2000). Those authors found higher levels of As in fish feeding mostly on zooplankton compared to fish feeding on other fish in the freshwater ecosystem of Upper Mystic Lake in the US. Other authors associated the higher As accumulation in fish tissues with fewer trophic links due to low rate of As lost in simpler food webs, as pelagic ones (Stemberger and Chen, 1998). This is consistent with our results, according to which planktivorous small puyen (with fewer trophic links on its food web) had lower As concentrations than piscivorous salmonids (with more trophic links). On the other hand, Leeves (2011) found that pelagic fish had higher As concentrations compared to benthic fish, which contradicts with our results, since we found lower As concentrations in planktivorous small puyen than in benthic creole perch. Worthy of particular note is that small puyen is not a strict planktivorous along all his life in these lakes. At larval stages it exploits the pelagic habitat feeding exclusively on zooplankton, whereas that as juvenile and adults, which are the stages captured in this study, it inhabits the littoral zone consuming both littoral and pelagic prey (Reissig et al., 2003;

Barriga et al., 2012; Milano et al., 2013). Arcagni et al. (2015) found a negative relationship between $\delta^{15}N$ and small puyen biomass coincident with the mentioned diet shift. Looking at small puyen in Fig. 4, a trend of As increase with higher $\delta^{15}N$ can be observed at least in BR, indicating that a more planktivorous diet (higher $\delta^{15}N$) could favor a greater accumulation of As. Notably, maximum As concentrations in small puyen at each site (1.1–1.3 $\mu g \, g^{-1}$ DW, Table 3) were close to the mean concentrations of creole perch of BR and BL. The high As accumulation in creole perch might be related to the major interaction of perch and it prey with As-enriched sediments. Stemberger and Chen (1998) observed a positive correlation between fish tissue As and site depth that was associated to elevated As concentrations in anoxic bottom sediments. Existent analysis of diet and depth distribution of fish in Lake Nahuel Huapi established that creole perch were eating crayfish at deeper strata (Juncos et al., 2015), emphasizing a benthic route of As uptake by fish, through prey consumption and also likely by sediment ingestion.

3.3. Spatial and temporal patterns of As in relation to PCCVC

It was not possible to generalize an unifying pattern of variation in the As concentration of organisms regarding the distance to the volcano. The crabs, amphipods, and mayfly larvae from BL had the highest As concentrations (ANOVA, $p < 0.001$; Table 2), while crayfish from DH registered higher As concentration in muscle and
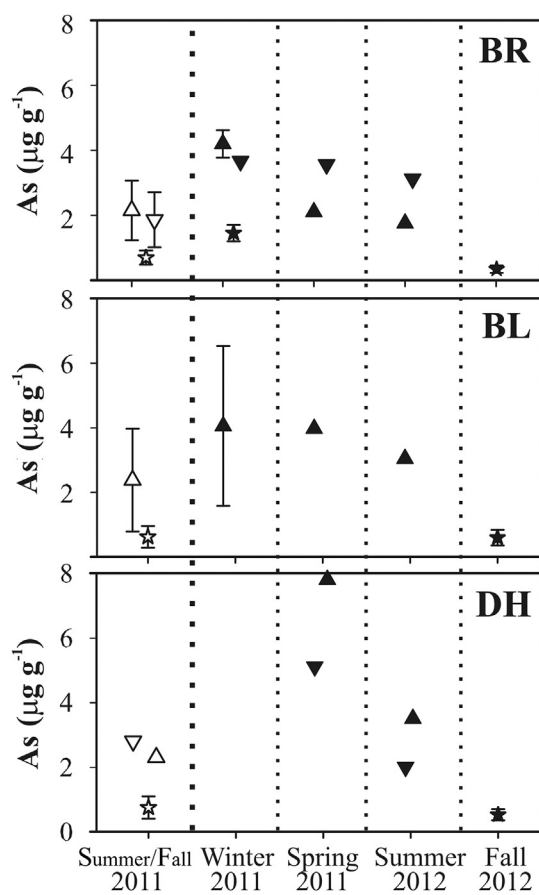
Fig. 5. Temporal variation of As concentrations ($\mu g\ g^{-1}$ DW) in zooplankton above the thermocline (triangles up) and below the thermocline (triangles down), and small puyen (stars), in the summer-fall before the PCCVC eruption (white symbols) and on dates after the volcanic eruption (black symbols), at each site. Season and year of sampling are indicated. BR: Brazo Rincón; BL: Bahía López; DH: Dina Huapi.

liver than in BR and in BL (ANOVA, $p < 0.001$; Table 2). However, as crayfish from DH were sampled in autumn (the other sites were sampled in summer), seasonal influence cannot be discarded. The snails from BL had higher As concentration than those from BR.

Regarding fish, the highest As levels, both in muscle and liver, were observed in the more benthivorous creole perch in BR and BL (Table 3). Decreasing levels were observed with increasing distance to the PCCVC, having creole perchs from DH lower As concentrations, similar to levels registered for salmonids. The more homogeneous distribution of As in tissues of salmonids may be reflecting their greater mobility and homogenous diet, while the more restricted mobility of perch and of its preferred prey (i.e., crayfish, with high As concentrations in DH) could be suggesting a different diet in DH.

Liver tissue from creole perch and big puyen presented higher As concentration than muscle tissues (ANOVA, $p < 0.001$) (Table 3), consistent with studies indicating liver efficiently concentrate As as a detoxification processes (Culioli et al., 2009a,b; Jankong et al., 2007). However, no differences were found for rainbow trout (ANOVA, $p = 0.35$), being As levels in liver of brown trout even lower than in muscle (ANOVA, $p = 0.028$). These differences could be suggesting differences in physiology or in metal sensitivity between the natives and salmonid species, or higher exposure to As through diet in the native fish. The As concentrations found in muscle and liver of salmonids ($0.1–0.8\ \mu g\ g^{-1}$ DW) were higher than the concentrations registered in fish from uncontaminated water bodies (Culioli et al., 2009a,b) and in the range of values registered for brown trout

tissues ($0.1–0.6\ \mu g\ g^{-1}$ DW) from a low As-impacted river in Corsica (Culioli et al., 2009a). Arsenic concentration in creole perch muscle ($0.4–1.3\ \mu g\ g^{-1}$ DW) and liver ($0.8–5.8\ \mu g\ g^{-1}$ DW) from BR and BL were similar to concentrations found in fish tissues from moderate to high As-polluted systems (Culioli et al., 2009a,b; Jankong et al., 2007; Rosso et al., 2013; Shah et al., 2009).

The effect of the 2011 PCCVC eruption varied depending on the organism analyzed (Tables 1–3). Mean winter–spring As concentrations increased in above- and below-thermocline zooplankton from BR and BL, almost duplicating the values in surface samples (Table 1). Although sample size did not allowed to test for differences in DH, zooplankton values after the volcanic eruption were almost four times higher above-thermocline ($7.8\ \mu g\ g^{-1}$ DW) and almost twice higher below-thermocline ($5.1\ \mu g\ g^{-1}$ DW) than before the eruption (2.3 and $2.8\ \mu g\ g^{1}$DW, respectively). When sampling dates were analyzed separately, it was possible to see the evolution of the levels of arsenic in zooplankton after the eruption and some interesting patterns showed up (Fig. 5). Arsenic increased immediately after the PCCVC eruption (three month after in BR and five month after in DH, both in above and below thermocline samples) (Fig. 5). This support our assumption that after ash deposition in surface lake water, availability of dissolved As for organisms living in the water column (e.g., phytoplankton and zooplankton) could have been increased, even though the percentage of As liberation from ashes to water is low (0.21%, Bia et al., 2015). The large amount of pyroclastic products that were deposited in this water body and surroundings, in addition with the long time that the ashes remained in the system, and the great affinity that phytoplankton shows for As (Rahman et al., 2012), likely favored the large accumulation observed in zooplankton few month after the massive ash deposition. Although phytoplankton samples after eruption were discarded because of ash interference, the high values measured in zooplankton suggest that phytoplankton As concentrations could have been much more elevated. A study on five North Andean Patagonian lakes, including Lake Nahuel Huapi, showed that phytoplankton biomass increased after the 2011 PCCVC eruption and that they moved upwards to around 20 m depth because of suspended ash ameliorate exposure of phytoplankton to excessive damaging solar radiation (Modenutti et al., 2013). This might explain the higher As concentrations observed in surface zooplankton compared to deeper zooplankton immediately after de eruption (Fig. 5). In BL, the increase in As after the eruption was also evident, albeit with high variation, which might be caused by the aforementioned particularities of the site. Notably, after the peak of As in zooplankton following the volcanic eruption in BR and BL, levels began to decrease, reaching concentrations close to pre-eruptive levels. In DH the peak of As concentrations was much higher than in the other sites, and ocurred in spring (there are no samples from winter), and finally down to previous levels. This greater and longer lasting increase could be due to the position of the site in relation to the direction of the winds and its proximity to the outlet of the lake (the Limay River). The ashes were swept westward from the lake and remained floating long time on lake waters until they finally were drained by the river. Following the changes in the As concentrations in zooplankton at the three sites it seems that the time of recovery of the system after an eruptive event is less than one year.

As concentrations significantly decreased in muscle and hepatopancreas of snails from BL (Student's t-test, $p < 0.001$), and almost duplicated in hepatopancreas of crabs from BR (Student's t-test, $p = 0.002$) (Table 2). A slight increment of As in muscle of snails and whole-body of mayfly larvae was observed in BR (Table 2). A significant increase in [As] in small puyen was observed immediately after ash deposition in BR, on early September (winter) 2011, following the increase observed in zooplankton (Fig. 5). Almost a

year later (May 2012) As concentrations significantly decreased in BR (ANOVA, $p < 0.001$) and DH (Mann—Whitney U test, $p = 0.005$), but not in BL (Table 3). Therefore, concentrations in small puyen a year after the eruption returned to values close to the recorded before the eruptive event, as observed in zooplankton. Regarding big fish, As concentrations significantly decreased in muscle of creole perchs from BL (Table 3) (Student's t-test, $p = 0.004$). In BR, the only creole perch captured after volcanic eruption had As concentrations lower than before eruption, while in DH concentrations remained unchanged. Reduction of benthic invertebrate densities and changes in trophic web structure after the PCCVC eruption have been reported in tributaries rivers of Lake Nahuel Huapi, not having those parameters fully recovery even eighteen months after the eruptive event (Lallement et al., 2014). A reduction of benthic prey in the lake could have been forced creole perch to change their more bentivorous diet to a more piscivorous one, this impacting on perch As levels. It should be noted that As concentrations in creole perch after the volcanic eruption in the three sites were in the range of concentrations recorded in DH before the event, consistent with the assumption that a different diet might explain the lower As levels recorded in perchs from DH before the volcanic eruption.

Numerous factors affect bioaccumulation of As in freshwater organisms, such as elemental speciation, passive or active uptake mechanisms, transport and distribution between tissues, physiological factors such as ingestion rates, growth rates, lipid levels, dilution and excretion. These factors are likely to be species specific and may also vary within species due to food quality, life history characteristics and environmental conditions as the biogeochemistry of the freshwater that influence the bioavailability of As and therefore its bioaccumulation (Rahman et al., 2012). Future research should certainly be directed towards the analysis of some of these factors to complete and better explain our conclusions about As accumulation and trophic transfer in this lake.

4. Conclusions

Present work analyzed As concentrations in aquatic organisms and its trophic transfer through the food web of a deep oligotrophic lake, with no known anthropogenic sources of As but with a long history of eruptive events. Different levels of As were found in different groups of organisms, at different trophic levels and according to different feeding strategies. The highest As concentrations were recorded in phytoplankton, especially in samples below the thermocline (85—45 m depth), probably associated to the lower dissolved oxygen in the hypolimnion during thermal stratification that is known to favor remobilization of As deposited in sediments. The pattern of As accumulation in the studied organisms was: primary producers (phytoplankton) > scrapper mollusks > filter feeding mollusks > omnivorous invertebrates > zooplankton > fish. Trophic relationships and feeding strategies (which in turn determines the type of habitat used) influenced As accumulation in the organisms having found that benthic feeders in close association with sediments generally had higher As concentrations than organisms directly or indirectly associated to pelagic prey. These two entry routes of As (benthic and pelagic) to the food web were reflected in As trophic transfer to fish. Benthic creole perch (feeding mainly on crayfish (Juncos et al., 2013, 2014)) and benthopelagic small puyen (feeding both on zooplankton and small littoral invertebrates (Barriga et al., 2012; Milano et al., 2013)) had higher As tissue concentrations than piscivorous salmonids. However, only creole perch from BR and BL showed evidence of biomagnification, which may be associated with a different diet at that site. The apparent biomagnification of As in creole perch, could be reflecting a major exposition of benthic organisms to bioavailable As than

pelagic organisms such as small puyen.

The impact of the 2011 PCCVC eruption and of ash deposition on the As levels of aquatic organisms was more evident in zooplankton and small puyen, but only in the short term (a few months after the eruption). This might be due to the rapid release of arsenic from the ashes when interact with water (Bia et al., 2015) and the following rapid formation of As-complex that could result in a short time high As bioavailability for planktonic organisms. In benthic organisms As increased in some tissues (muscle or hepatopancreas) of some organism (snails, crabs and mayfly larvae) only in the site closest to the PCCVC, which could respond to an effect of proximity to the volcano. On the other hand, the ashes covering large extensions of the littoral zone of the lake could have forced some benthic organisms, as could be the case of creole perch, to shift their diet to other food (e.g., small puyen), thus modifying As uptake pathways, and ultimately varying As concentrations in the organisms itself.

References

Arcagni, M., Rizzo, A., Campbell, L., Arribére, M.A., Juncos, R., Reissig, M., Kyser, K., Barriga, J.P., Battini, M., 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. http://dx.doi.org/10.1016/j.jglr.2015.05.008.

Arribére, M.A., Ribeiro Guevara, S., Bubach, D., Arcagni, M., Vigliano, P.H., 2008. Selenium and mercury in native and introduced fish species in Patagonian lakes, Argentina. Biol. Trace Elem. Res. 122, 42—63.

Asante, K.A., Agusa, T., Kubota, R., Mochizuki, H., Ramu, K., Nishida, S., Ohta, S., Yeh, H., Subramanian, A., Tanabe, S., 2008. Trace elements and stable isotope ratios (δ^{13}C and δ^{15}N) in fish from deep-waters of the Sulu Sea and the Celebes Sea. Mar. Pollut. Bull. 60, 1560—1570.

Barriga, J.P., Battini, M.A., García-Asorey, M., Carrea, C., Macchi, P.J., Cussac, V.E., 2012. Intraspecific variation in diet, growth, and morphology of landlocked Galaxias maculatus during its larval period: the role of food availability and predation risk. Hydrobiologia 679, 27—41.

Belzile, N., Tessier, A., 1990. Interactions between arsenic and iron oxyhydroxides in lacustrine sediments. Geochim. Cosmochim. Ac 54, 103—109.

Bertrand, S., Daga, R., Bedert, R., Fontijn, K., 2014. Deposition of the 2011—2012 Cordón Caulle tephra (Chile, 40°S) in lake sediments: Implications for tephrochronology and volcanology. J. Geophys. Res. 119, 2555—2573.

Bia, G., Borgnino, L., Gaiero, D., García, M.G., 2015. Arsenic-bearing phases in South Andean volcanic ashes: implications for as mobility in aquatic environments. Chem. Geol. 393—394, 26—35.

Bubach, D., Pérez Catán, S., Arribére, M., Ribeiro Guevara, S., 2012. Bioindication of volatile elements emission by the Puyehue—Cordón Caulle (North Patagonia) volcanic event in 2011. Chemosphere 88, 584—590.

Bundschuh, J., Litter, M.I., Parvez, F., Román-Ross, G., Nicolli, H.B., Jean, J.S., Liu, C.W., López, D., Armienta, M.A., Guilherme, L.R.G., Gomez Cuevas, A., Cornejo, L., Cumbal, L., Toujaguez, R., 2012. One century of arsenic exposure in Latin America: a review of history and occurrence from 14 countries. Sci. Total Environ. 429, 2—35.

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.

Chen, C.Y., Folt, C.L., 2000. Bioaccumulation and diminution of arsenic and lead in a freshwater food web. Environ. Sci. Technol. 34, 3878—3884.

Chen, C.Y., Stemberger, R.S., Klaue, B., Blum, J.D., Pickhardt, P.C., Folt, C.L., 2000. Accumulation of heavy metals in food web components across a gradient of lakes. Limnol. Oceanogr. 45, 1525—1536.

Clarke, K.R., Warwick, R.M., 2001. Change in Marine Communities: an Approach to Statistical Analysis and Interpretation, second ed. PRIMER-E, Plymouth.

Culioli, J.L., Calendini, S., Mori, C., Orsini, A., 2009a. Arsenic accumulation in a freshwater fish living in a contaminated river of Corsica, France. Ecotox.

Environ. Safe 72, 1440–1445.

Culioli, J.L., Fouquoire, A., Calendini, S., Mori, C., Orsini, A., 2009b. Trophic transfer of arsenic and antimony in a freshwater ecosystem: a field study. Aquat. Toxicol. 94, 286–293.

Daga, R., Ribeiro Guevara, S., Poire, D.G., Arribére, M., 2014. Characterization of tephras dispersed by the recent eruptions of volcanoes Calbuco (1961), Chaitén (2008) and Cordón Caulle Complex (1960 and 2011), in Northern Patagonia. J. S. Am. Earth. Sci. 49, 1–14.

Díaz, M., Pedrozo, F., Reynolds, C., Temporetti, P., 2007. Chemical composition and the nitrogen-regulated trophic state of Patagonian Andes. Limnologica 37, 17–27.

Estebenet, A.L., Cazzaniga, N.J., Pizani, N.V., 2002. The natural diet of the argentinean endemic snail Chilina pachappii (Basommnatophora: Chilinidae) and two other coexisting pulmonate gastropods. Veliger 45, 71–78.

Hamilton-Taylor, J., Davison, W., 1995. Redox-driven cycling of trace elements in lakes. In: Lerman, A., Imboden, D., Gat, J. (Eds.), Physics and Chemistry of Lakes. Springer-Verlag, Berlin, 334 pp.

Hinkley, T.K., Lamothe, P.J., Wilson, S.A., Finnegan, D.L., Gerlach, T.M., 1999. Metal emissions from Kilauea, and a suggested revision of the estimated worldwide metal output by quiescent degassing of volcanoes. Earth Planet Sc. Lett. 170, 315–325.

Hyobu, Y., Itai, T., Hayase, D., Kumagai, M., Tanabe, S., 2012. Mobilization of manganese and arsenic under hypoxia in the bottom of lake Biwa. In: Kawaguchi, M., Misaki, K., Sato, H., Yokokokawa, T., Itai, T., Nguyen, T.M., Ono, J., Tanabe, S. (Eds.), Interdisciplinary Studies on Environmental Chemistry - Environmental Pollution and Ecotoxicology. TERRAPUB, Tokio, pp. 133–140.

Ikemoto, T., Tu, N.P.C., Okuda, N., Iwata, A., Omori, K., Tanabe, S., Tuyen, B.C., Takeuchi, I., 2008. Biomagnification of trace elements in the aquatic food web in the Mekong Delta, South Vietnam using stable carbon and nitrogen isotope analysis. Arch. Environ. Contam. Toxicol. 54, 504–515.

Jankong, P., Chalhoub, C., Kienzl, N., Goessler, W., Francesconi, K.A., Visoottiviseth, P., 2007. Arsenic accumulation and speciation in freshwater fish living in arsenic-contaminated waters. Environ. Chem. 4, 11–17.

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.

Juncos, R., Beauchamp, D.A., Vigliano, P.H., 2013. Modeling prey consumption by native and nonnative piscivorous fishes: implications for competition and impacts on shared prey in an ultraoligotrophic lake in Patagonia. T. Am. Fish. Soc. 142, 268–281.

Lallement, M.E., Juárez, S.M., Macchi, P.J., Vigliano, P.H., 2014. Puyehue Cordón-Caulle: post-eruption analysis of changes in stream benthic fauna of Patagonia. Ecol. Austral 24, 64–74.

Lara, L.E., Moreno, H., Naranjo, J.A., Matthews, S., Pérez de Arce, C., 2006. Magmatic evolution of the Puyehue–Cordón Caulle Volcanic Complex (40 S), Southern Andean Volcanic Zone: from shield to unusual rhyolitic fissure volcanism. J. Volcanol. Geoth. Res. 157, 343–366.

Lara, G.P., Parada, E., Peredo, S., 2002. Alimentación y conducta alimentaria de la almeja de agua dulce Diplodon chilensis (Bivalvia: Hyriidae). Gayana (Concepc.) 66, 107–112.

Leeves, S., 2011. Bioaccumulation of Arsenic, Cadmium, Mercury, Lead and Selenium in the Benthic and Pelagic Food Chain of Lake Baikal (M Sc thesis). Norwegian University of Science and Technology.

Levy, J.L., Stauber, J.L., Adams, M.S., Maher, W.A., Kirby, J.K., Jolley, D.F., 2005. Toxicity, biotransformation, and mode of action of arsenic in two freshwater microalgae (Chlorella sp. and Monoraphidium arcuatum). Environ. Toxicol. Chem. 24, 2630–2639.

Maeda, S., Ohki, A., Kusadome, K., Kuroiwa, T., Yoshifuku, I., Naka, K., 1992. Bioaccumulation of arsenic and its fate in a freshwater food chain. Appl. Organomet. Chem. 6, 213–219.

Markert, B., Pedrozo, F., Geller, W., Friese, K., Korhammer, S., Baffico, G., Díaz, M., Wölfl, S., 1997. A contribution to the study of the heavy-metal and nutritional element status of some lakes in the southern Andes of Patagonia (Argentina). Sci. Total Environ. 206, 1–15.

Masciocchi, M., Pereira, A.J., Lantschner, M.V., Corley, J.C., 2013. Of volcanoes and insects: the impact of the Puyehue-Cordon Caulle ash-fall on populations of invasive social wasps, Vespula spp. Ecol. Res. 28, 199–205.

McIntyre, D.O., Linton, T.K., 2012. Arsenic. In: Wood, C.M., Farrel, A.P., Brauner, C.J. (Eds.), Homeostasis and Toxicology of Non-essential Metals, Fish Physiology, vol. 31 (PART B). Elsevier, pp. 297–349. http://dx.doi.org/10.1016/S1546-5098(11) 31028-X.

Milano, D., Aigo, J.C., Macchi, P.J., 2013. Diel patterns in space use, food and metabolic activity of Galaxias maculatus (Pisces: Galaxiidae) in the littoral zone of a shallow Patagonian lake. Aquat. Ecol. 47, 277–290.

Miserendino, M.L., Archangelsky, M., Brand, C., Beltrán Epele, L., 2012. Environmental changes and macroinvertebrate responses in Patagonian streams (Argentina) to ashfall from Chaitén Volcano (May 2008). Sci. Total Environ. 424, 202–212.

Modenutti, B.E., Balseiro, E.G., Elser, J.J., Bastidas Navarro, M., 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.

Rahman, M.A., Hasegawa, H., Lim, R.P., 2012. Bioaccumulation, biotransformation and trophic transfer of arsenic in the aquatic food chain. Environ. Res. 116, 118–135.

Reissig, M., Queimaliños, C.P., Balseiro, E.G., 2003. Effects of Galaxias maculatus on nutrient dynamics and phytoplankton biomass in a North Patagonian oligotrophic lake. Environ. Biol. Fishes 68, 15–24.

Revenga, J.E., Campbell, L.M., Arribére, M.A., Ribeiro Guevara, S., 2012. Arsenic, cobalt and chromium food web biodilution in a Patagonia mountain lake. Ecotox. Environ. Safe 81, 1–10.

Ribeiro Guevara, S., Rizzo, A., Sánchez, R., Arribére, M., 2005. Heavy metal inputs in Northern Patagonian lakes from short sediment core analysis. J. Radioan. Nucl. Ch 265, 481–493.

Rizzo, A., Arcagni, M., Campbell, L., Koron, N., Pavlin, M., Arribére, M., Horvat, M., Ribeiro Guevara, S., 2014. Source and trophic transfer mercury in plankton from an ultraoligotrophic lacustrine system (Lake Nahuel Huapi, North Patagonia). Ecotoxicology 23, 1184–1194.

Rodie, A., Gertis, J.J.P., Azcue, J.M., 1995. Biogeochemical pathways of arsenic in lakes. Environ. Rev. 3, 304–317.

Rosso, J.J., Schenone, N.F., Pérez Carrera, A., Fernández Cirelli, A., 2013. Concentrations of arsenic in water, sediments and fish species from naturally contaminated rivers. Environ. Geochem. Health 35, 201–214.

Ruggieri, F., Fernandez-Turiel, J.L., Saavedra, J., Gimeno, D., Polanco, E., Amigo, A., Galindo, G., Caselli, A., 2012. Contribution of volcanic ashes to the regional geochemical balance: the 2008 eruption of Cahitén volcano, Southern Chile. Sci. Total Environ. 425, 75–88.

Schaller, J., Brackhage, C., Mkandawire, M., Dudel, E.G., 2011. Metall/metalloid accumulation/remobilization during aquatic litter decomposition in freshwater: a review. Sci. Total Environ. 409, 4891–4898.

Schaller, J., Koch, I., Caumette, G., Nearing, M., Reimer, K.J., Planer-Friedrich, B., 2015. Strategies of Gammarus pulex L. to cope with arsenic — Results from speciation analyses by IC-ICP-MS and XAS micro-mapping. Sci. Total Environ. 530–531, 430–433.

Schorer, M., Eisele, M., 1997. Accumulation of inorganic and organic pollutants by biofilms in the aquatic environment. Water Air Soil Pollut. 99, 651–659.

Shah, A.Q., Kazi, T.G., Arain, M.B., Jamali, M.K., Afridi, H.I., Jalbani, N., Baig, J.A., Kandhro, G.A., 2009. Accumulation of arsenic in different freshwater fish species: potential contribution to high arsenic intakes. Food Chem. 112, 520–524.

Smedley, P.L., Kinniburgh, D.G., 2002. A review of the source, behavior and distribution of arsenic in natural waters. Appl. Geochem 17, 517–568.

Soto Cárdenas, C., Diéguez, M.C., Ribeiro Guevara, S., Marvin-DiPasquale, M., Queimaliños, C.P., 2014. Incorporation of inorganic mercury (Hg^{2+}) in pelagic food webs of ultraoligotrophic and oligotrophic lakes: the role of different plankton size fractions and species assemblages. Sci. Total Environ. 494–495, 65–73.

Stemberger, R.S., Chen, C.Y., 1998. Fish tissue metals and zooplankton assemblages of northeastern U.S. lakes. Can. J. Fish. Aquat. Sci. 55, 339–352.

Symonds, R.B., Reed, M.H., Rose, W.I., 1992. Origin, speciation and fluxes of trace-element gases at Augustine volcano, Alaska: insights into magma degassing and fumarolic processes. Geochim. Cosmochim. Ac 56, 633–657.

Withman, C.S., Oppenheimer, C., Horwell, C.J., 2005. Volcanic ash-leachates: a review and recommendations for sampling methods. J. Volcanol. Geoth. Res. 141, 299–326.