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Variations in anthropogenic silver in a large Patagonian lake correlate with global shifts in photographic processing technology☆

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A B S T R A C T

At the beginning of the 21st century, digital imaging technology replaced the traditional silver-halide film photography which had implications in Ag contamination. Lake Nahuel Huapi is a popular Patagonia tourist destination impacted by municipal silver (Ag) contamination from photographic processing facilities since 1990's. Silver concentrations in a dated sediment core from the lake bottom showed a 10-fold increase above background levels in the second half of the 20th century, then a decrease. This trend corresponds well with published annual global photography industry demand for Ag, which clearly shows the evolution and replacement of the traditional silver-halide film photography by digital imaging technology. There were significant decreases in Ag concentrations in sediments, mussels and fish across the lake between 1998 and 2011. Lower trophic organisms had variable whole-body Ag concentrations, from 0.2–2.6 $\mu g\ g^{-1}$ dry weight (DW) in plankton to 0.02–3.1 $\mu g\ g^{-1}$ DW in benthic macroinvertebrates. Hepatic Ag concentrations in crayfish, mussels and predatory fish were significantly elevated relative to muscle which often have Ag concentrations below the detection limit (0.01–0.05 $\mu g\ g^{-1}$ DW). Trophodynamic analyses using $\delta^{15}N$ and whole-body invertebrate and muscle Ag concentrations indicated food web biodilution trends. High sedimentation rates in conjunction with the reduction of silver waste products discharged to the lake, as a result of the change to digital image processing technologies, are resulting in unplanned but welcome remediation of the Ag contamination in Lake Nahuel Huapi.

1. Introduction

Silver (Ag) is a rare element in the Earth's crust, with low background concentrations (approximately 0.1 mg/kg) (Eisler, 1996; Prucell and Peters, 1998). Elevated concentrations of this metal in surface waters are usually associated with anthropogenic activities such as mining and photographic processing (Prucell and Peters, 1998). Photographic film manufacture uses Ag in the form of Ag halides and the waste liquids from developing and washing exposed film can represent an important source of this metal to the aquatic environment (Eisler, 1996; Ratte, 1999). At the beginning of the 21st century, with the advent of digital imaging technology, the traditional film photography and its associated silver halide waste products were drastically reduced (World Silver Survey, 1990–2015). Therefore, it might be expected that the associated decline in photographic silver halide use will lead to corresponding declines in Ag concentrations in the environment (Squire et al., 2002; Flegal et al., 2007).

Ionic silver is the Ag species of greater environmental concern because of its elevated toxicity (Eisler, 1996; Ratte, 1999). However, ionic Ag is usually found at low levels in natural waters due to its rapid complexation and association with dissolved and suspended materials that are usually present in aquatic systems. Although complexed and sorbed Ag species in waters are orders of magnitude less toxic to aquatic organisms than the free Ag ion (Ratte, 1999), they are able to accumulate in freshwater invertebrates (Connell et al., 1991; Ratte, 1999; Croteau et al., 2011), and in fish (Hogstrand and Wood, 1998; Wood et al., 2012). For example, silver

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thiosulphate complexes, the main soluble waste discharged from photographic facilities (Prucell and Peters, 1998) has been seen to accumulate readily in the gills and internal tissues such as the liver (Hogstrand et al., 1996; Galvez et al., 2001).

It has been proven that particle ingestion is a significant route of Ag uptake by aquatic invertebrates, such as suspension feeders (Wang et al., 1996; Griscom et al., 2002), and especially deposit-feeding invertebrates (Lee et al., 2000; Casado-Martinez et al., 2009). Therefore, sediments can be a major route for Ag bioaccumulation for benthic organisms, entering this way to the aquatic food web. However, the trophic transfer efficiency of Ag (as measured in muscle or whole-body burden) is usually very low, so trophic transfer of Ag through the food chain is rarely reported (Huang et al., 2008; Revenga et al., 2011).

Lake Nahuel Huapi in the Nahuel Huapi National Park is a large glacial oligotrophic lake in Northern Patagonia (Fig. 1). Between 1998 and 2001, just after the municipal sewage treatment plant, which is not designed to retain heavy metals, was established nearby the City of San Carlos de Bariloche ("Bariloche"), paleolimnological analyses of a sediment core and suspended sediment were carried out. This study revealed an enrichment of Ag at the upper core layers, coincident with the period of fastest population growth around Bariloche. The highest Ag flux to sediments (380 μg m^{-2} $year^{-1}$) was observed in the sampling point located in the lake immediately in front of the city, near the site where the sewage treatment plant releases the effluents of the city, while lowest fluxes were estimated in sites further away from the city (Ribeiro Guevara and Arribére, 2002; 2005).

On the other hand, Ag concentrations in the native suspension feeder mussel, *Diplodon chilensis*, were elevated in individuals sampled near the point of discharge of the sewage treatment plant of Bariloche, while were lower in a remote site of the lake (Ribeiro Guevara et al., 2005). Moreover, very elevated Ag concentrations were measured in livers of salmonid fish (10–29 μg g^{-1} dry weight DW) sampled in 2001 in Lake Nahuel Huapi, that were well above those in the salmonid livers (0.2–3.9 μg g^{-1} DW) from a nearby reference lake (Revenga et al., 2011), and were also very elevated relative to other fish from around the world (Eisler, 1996; Wood et al., 2012). Since no other Ag contaminant activity is documented for the region, the most probable source of the Ag contamination to Lake Nahuel Huapi is waste products from the film photography processing entering the liquid effluents in the municipal sewage system.

In this study, we assessed the temporal Ag trends in Lake Nahuel Huapi from a dated sediment core and compared spatiotemporal food web data obtained in 2001 and 2011. We predicted that the presumed decline in Ag-enriched waste products after the emergence of digital photography technology would have corresponding Ag concentrations declines in sediments and in organisms. We hypothesized that Ag concentrations in Lake Nahuel Huapi would be: 1) lower in organisms sampled in 2011 than in 2001 and that a corresponding temporal trend will be seen in the dated sediment core; 2) higher in benthic-feeding organisms than in pelagic-feeding organisms; 3) higher in organisms near the city of San Carlos of Bariloche than from elsewhere in the lake; and 4) lower in organisms with higher trophic positions than those with lower trophic positions in the food web (i.e., biodilution). Therefore, the objectives of this study are: 1) identify temporal variations of Ag in sediment sequences of Lake Nahuel Huapi, 2) determine whether Ag concentrations in mussels and fish tissues have changed in the last decade (2001–2011), and 3) determine current Ag concentrations and trophic transfer patterns in organisms at different sites of the Lake Nahuel Huapi.

2. Materials and methods

2.1. Study area

Lake Nahuel Huapi (40°50′ S, 71°30′ W), located within the Nahuel Huapi National Park (NHNP), is a large glacial oligotrophic lake in Northern Patagonia (Fig. 1). It is a monomictic ultra-oligotrophic glacial lake with a mean annual Secchi depth of 12 m,

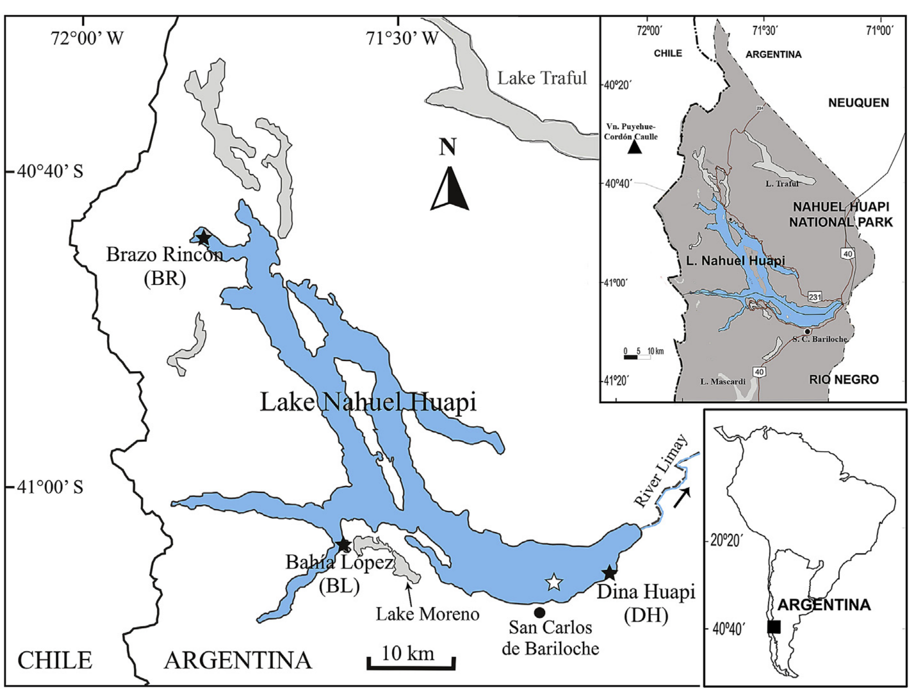

Fig. 1. Map of the study area showing the location of the biota sampling sites (black stars) and sediment core sampling site (white star) in Lake Nahuel Huapi, within the Nahuel Huapi National Park (shaded area in the right-top panel), Patagonia, Argentina.

with the euphotic zone at 49 m depth, total phosphorus of 5.1 μg L^{-1}, and chlorophyll *a* of 0.6 μg L^{-1} (Alcalde et al., 1999; Díaz et al., 2007; Caravati et al., 2010). It has a surface area of 557 km^2 and a maximum depth of 464 m.

The lake, situated at 764 m above sea level, has seven branching arms creating separate bays, resulting in a 357-km shoreline. There is a steady flow through the lake from the Andes mountain range stream runoff entering the lake in the northwest towards the River Limay in the southeast. The climate in the Andes mountains is cold temperate and due to the constant west winds, there is a strong west-east climatic gradient across the lake. As a consequence, in a stretch of less than 65 km, total annual precipitation decreases drastically from 3000 mm in the westernmost side of NHNP to less than 700 mm on the eastern side. This precipitation gradient shapes plant coverage and distribution, with the western side of the park covered by dense Andean-Patagonian *Nothofagus* forest, while the eastern borders are at the onset of the dry Patagonian steppe characterized by shrub lands.

Silver concentration trends in the food web and in biological tissues were assessed for three sites throughout the lake: Brazo Rincón (BR), Bahía López (BL), and Dina Huapi (DH) (Fig. 1). BR is situated on the northwestern part of the lake, more than 60 km far from Bariloche. BR has the highest annual precipitation (~2500 mm) and is characterized by an extended littoral zone with sandy beaches surrounded by Andino-Patagonic *Nothofagus dombeyi* (Coihue) forests. The BR basin has a regular shape with a maximum depth of approximately 100 m and an area of around 7.7 km^2. BL is a small, shallow, and semi-closed bay, 20 km upstream from Bariloche with rocky beaches, a maximum depth around 50 m and an area of approximately 1 km^2. It receives moderate precipitation (~1500 mm) and is surrounded by a mixed forest of *N. dombeyi* and *Austrocedrus chilensis* (Cordilleran cypress). In the driest southeastern region (precipitation ~ 800 mm) is the DH site, located in the main and largest branch of Lake Nahuel Huapi near River Limay mouth, the outflow of the lake, and is 10 km downstream of the city of San Carlos de Bariloche. DH has a maximum depth of 236 m, and the dominant vegetation is typical of the dry Patagonian steppe.

Bariloche is an international tourist destination located on the southeast shore of the lake (Fig. 1), and as such there has always been high demand for rapid development and photographic processing facilities in the city. With limited sewage and waste-water treatment facilities, silver contamination from on-site film processing becomes a real risk.

2.2. Sediment sampling and global photography industry trends

Temporal trends in Ag which might be associated with changes in the film photography in the city of Bariloche, were assessed in a 31-cm long sediment core collected directly in front of the city (41.11°S, 71.29 W, Fig. 1) at 200 m depth, with a short Uwitec messenger-activated gravity type corer, on February 2012. As the lake is situated in a geologically-active region, sediment cores were carefully inspected prior to laboratory analyses. The sedimentary sequence registered two high impact events: the eruption of Puyehye-Cordón Caulle volcanic complex (PCCVC) in 2011 (Daga et al., 2014), and a major earthquake in 1960 (Chapron et al., 2006). Given that our objective was to examine the potential sources of Ag from the city in sediments, it was important to separate the potential diluting contribution of volcanic tephras, in which Ag was not detected (quantification limit: 0.03 μg g^{-1}). The 2 upper cm of the PCCVC tephra were removed from the analysis, while the subsequent layer (2–3 cm), also composed mostly by volcanic ash but with a contribution of regular sediment, was the first considered in the analysis, separating bulk sediment from coarse volcanic components. The sequence section between the 2011 volcanic eruption and the 1960 earthquake events corresponds to regular sedimentation during the period 1960–2011, and can be considered as natural environmental archives. The sedimentary sequence was dated by ^{210}Pb and ^{137}Cs techniques (Ribeiro Guevara and Arribére, 2002). Total ^{210}Pb, ^{226}Ra (representing supported ^{210}Pb) and ^{137}Cs specific activity profiles were measured by high-resolution gamma-ray spectrometry using a well-type HPGe detector, with self-shielding corrections according to Furci et al. (2013). More information on sediment core analysis and ^{137}Cs specific activity profiles is provided in Supporting Information (SI).

To ascertain whether there was a relationships between the decline in the use of film-based photography and silver contamination in Lake Nahuel Huapi, we obtained annual industry reports from the Silver Institute's World Silver Surveys (1990–2015) which breaks down annual global silver demand by industry sector (e.g. jewelry, currency, photography and so on). The total annual world silver demand by the photography sector from 1950 to 2015 was extracted from the World Silver Survey reports, but only the information between 1964 and 2012 was used, which is the temporal sequence covered by the sediment core. As multinational photographic film manufacturers are not based in every country, but ship their products world-wide, we summarized the global silver demand data (million ounces/year). We note that the Silver Institute changed their reporting format and their regional break-downs between 1990 and 1991. There may be slight differences in their data collection methods before and after that year, although it was difficult to ascertain from the report methodology. However, we did not see any major differences in the world silver demand trends during this change-over in their reporting methods and this occurred before any significant trends occurred in the photography industry around 1998–1999, so we have reported the data as a single dataset.

2.3. Biota sampling and food web Ag trends

To track Ag contamination in the lake and to assess whether this potentially toxic element is being transferred to biota we examined individual compartments of the Lake Nahuel Huapi food web. Trophic relationships and food web structure in this lake have been previously described (Juncos et al., 2011, 2015; Arcagni et al., 2015).

The food web compartments analyzed included size-fractioned plankton (including phytoplankton 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*), four fish species: the natives small puyen (*Galaxias maculatus*) and creole perch (*Percichthys trucha*), and the introduced salmonids, rainbow trout (*Oncorhynchus mykiss*), and brown trout (*Salmo trutta*).

Plankton samples were collected on February and May 2011 by vertical hauls using a winch system and nets of three different mesh sizes (10, 53, and 200 μm) at two discrete depth ranges: 0 m–40 m (BR, BL, DH) and 45 m–85 m (BR, DH). Plankton hauls were sieved into three size classes: P1 (10–53 μm, i.e. phytoplankton and small mixotrophic ciliates), P2 (53–200 μm, i.e. mixotrophic ciliates and small zooplankton), and P3 (>200 μm, i.e. large zooplankton) (Rizzo et al., 2014). The phytoplankton community is dominated by Dinophycean algae and mixotrophic ciliates (*Ophridium naumanni* and *Stentor araucanus*). The zooplankton community is composed mainly by copepods (*Boeckella gracilipes* and cyclopoids) and cladocerans (*Ceriodaphnia dubia*, *Daphnia* sp., and *Bosmina longirostris*), which feed on ciliates, phytoflagellates, and bacteria (Modenutti et al., 2010), that are components of the P1 fraction (Arcagni et al., 2015).

Benthic macroinvertebrates were hand-picked from submerged logs and stones at BR and BL on February 2011 and crayfish at DH on April 2011. Most of the benthic organisms were obtained from BR and BL, and no mollusks, insects or crabs were found in DH. Snails, mussels, and crustacean decapods (*Aegla* sp. and *S. spinifrons*), were removed from their carapaces/shells. Their muscle tissue and hepatopancreas were analyzed separately. The remaining macroinvertebrates, i.e., mayflies and amphipods, were analyzed whole. 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. Small fish, including small puyen and juvenile salmonids (e.g., rainbow trout), were collected using double-funnel baited cylinder fish traps left at each site for 24 h and by using 1-mm mesh seine nets. Larger individuals, as final link in the Ag transfer chain, including creole perch rainbow trout, and brown trout, were captured using six connected 10-m gillnet panels of different mesh size, set overnight perpendicular to the shore from 2 m down to 40 m deep. 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 the small puyen (30–70 mm) did not allow to remove sufficient muscle tissue for all analyses, so the head and the guts were removed from each individual, and skin-on, bone-in homogenates of 4–10 individuals were made, obtaining four size classes (10 mm range each).

To establish whether the change in photographic technology had influence on the aquatic organisms, mean Ag concentrations in mussels from BL and in rainbow trout, brown trout and creole perch from BR, BL and DH, sampled in 2001, were compared with current concentrations.

To assess the potential for trophic transfer of Ag from lower trophic species to predatory species, Ag concentrations at each trophic level were compared. Trophic level was estimated using stable nitrogen isotopes ratios ($\delta^{15}N$) previously calculated for the Lake Nahuel Huapi organisms (Arcagni et al., 2015). Because of the below-detection Ag concentrations of top predator fish, trophic transfer trends (trophodynamics) could not be tested by regression analysis.

2.4. Analytical procedures

Total Ag concentrations were determined by Instrumental Neutron Activation Analysis (INAA) as detailed in Arribére et al. (2008) and Ribeiro Guevara et al. (2005). In summary, aliquots of 1–200 mg of lyophilized homogenized biota samples were sealed in quartz ampoules and irradiated for 20 h in the RA-6 nuclear research reactor (Centro Atómico Bariloche, Argentina). Sediment samples of 100 mg were irradiated in plastic vials for 10 h. 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. INAA detection limits depend strongly on the sample composition, and on the analytical conditions, particularly irradiation, measurement, and decay times. Total Ag concentrations were determined by measuring three gamma-ray emissions (657.76, 1383.30 and 1505.04 keV) of the long lived activation product Ag^{110m} ($T_{½} = 249.76$ d). The long Ag^{110m} half-life allows adjusting decay and measurement times according to the characteristics of each sample, after decay of most activation products generating spectral background and interferences. The concentrations are reported in dry weight (DW) basis. Certified reference materials (CRMs) NRCC DORM-2 and IAEA-140/TM were analyzed for analytical quality control; the results of the CRMs analysis match with certified values, considering uncertainties (Ribeiro Guevara et al., 2005; Arribére et al., 2008) (SI Table S1).

Inorganic particulates of geological origin may contaminate biota samples, biasing Ag determinations. Geological particulate remains were detected in plankton samples and benthic organisms by the determination of lithophile elements such as the Rare Earth Element (REE) samarium (Sm). INAA is a multielemental technique which allows to simultaneously determine up to 35 elements, including the geochemical tracers Sm. Samarium showed the highest sensitivity in the biological samples analyzed among the geochemical tracers that can be determined by INAA. It was used to evaluate the contribution of geological particles in biological samples, and to perform concentration corrections (Juárez et al., 2016). Silver concentrations reported in the present study included the correction performed using Sm and Ag concentrations in sediments from the top layer of sedimentary sequences from each sampling site (Ribeiro Guevara et al., 2005).

2.5. Statistical analyses

Statistical analyses were performed using SigmaStat software version 3.5 for Windows. Unpaired Student's *t*-test (two groups), one-way ANOVA (more than two groups), or non-parametric Kruskal-Wallis (when data were not normally distributed) were used to compare the means of Ag concentrations between groups of organisms (within and between sampling sites). When ANOVA was significant, the Student–Newman–Keuls (S-N-K) test was employed for the comparison. All statistical analyses were conducted at a significance level of 0.05.

3. Results and discussion

3.1. Silver temporal trends in Lake Nahuel Huapi sediments

In the Lake Nahuel Huapi sediment core, background Ag concentrations in deep sediment layers below 6 cm, before 1960, range from 0.04 to 0.09 $\mu g\ g^{-1}$ DW (Fig. 2) and are consistent with natural baseline Ag levels in the Earth's crust (~0,1 ppm). The elevated Ag concentrations in the surface sediments of Lake Nahuel Huapi (0.6–1.1 $\mu g\ g^{1}$ DW), corresponding to the second half of the 20th century accumulation period, were 10-fold higher than background levels. This rapid increase is in agreement with similar trends found in sediments of European aquatic systems in which Ag enrichments in surface layers correspond well with anthropogenic associated pollution (0.4–0.9 $\mu g\ g^{-1}$ DW; 0.4–6.7 $\mu g\ g^{-1}$ DW; Grahn et al., 2006; Lanceleur et al., 2011). Moreover, Ag concentrations measured in Lake Nahuel Huapi second half of the 20th century sediments were even higher than the highest peaks of Ag concentrations recorded in core sediments from different locations of the high contaminated San Francisco Bay, USA (0.2–0.7 $\mu g\ g^{-1}$ DW; Hornberger et al., 1999), and close to the concentrations recorded in surface sediments from a mudflat 1 km south of a municipal discharge source in south reach of the San Francisco Bay (1.62 ± 0.42 $\mu g\ g^{-1}$ DW; Hornberger et al., 2000). Much of the Ag contamination in the South San Francisco Bay has been attributed to discharges from a water quality control plant, in which most of the discharged Ag was traced to effluents from a photographic processing plant. The extensive investment in advanced waste water treatment to reduce metal loadings to the estuary since 1970, and the closure of the photographic processing plant in the mid 80's, resulted in decreases in sediment and biota Ag concentrations in the San Francisco Bay (Flegal et al., 2007).

In Lake Nahuel Huapi, the rapid increases in Ag concentrations in recent sediments in contrast to low background concentrations, and the lack of association with volcanic deposits, points to a direct

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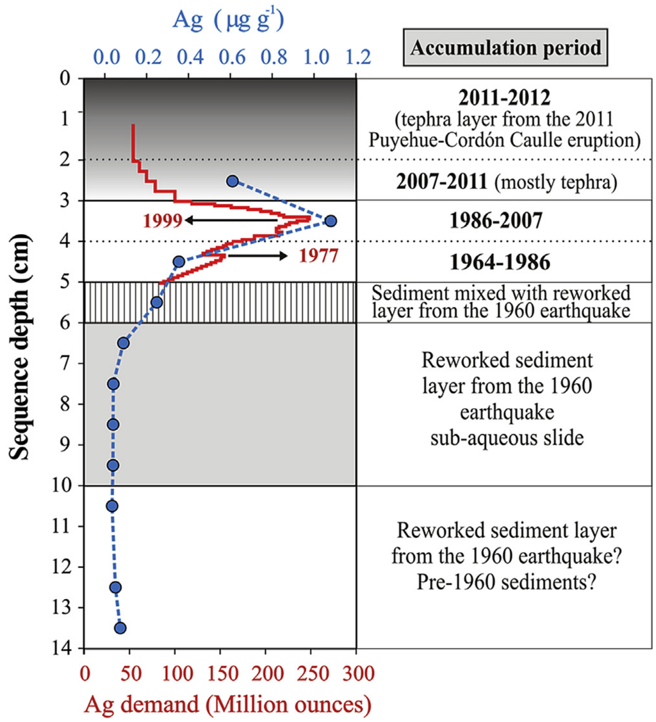

Fig. 2. Silver concentration (Ag, µg g^{-1}) profile of the sediment core sampled in Lake Nahuel Huapi in front of Bariloche city (light blue circles and dashed line), and global Ag demand for photography industry as million troy ounces (Moz) per year during the period 1964–2012 (continuous red line) (World Silver Survey, 1990–2015). Accumulation period and geological events corresponding to each sediment layer are indicated in the right side of the figure. Each Ag concentration point in the figure represents a variable time period (years), while Ag demand data are on a continuous annual basis. 1 Moz = 31.103 t (metric tones). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

anthropogenic input of Ag instead of natural sources (e.g. volcanic eruptions). Moreover, previous studies had shown the influence of Bariloche city in sediments Ag enrichments and fluxes of Ag to the lake (Ribeiro Guevara and Arribére, 2002; 2005). Here, the evolution of photographic processing technology can clearly be distinguished in the lake bottom sediments through a rapid increase of Ag concentrations after 1964 and the subsequent rapid declines. Silver concentrations in the upper layers of the sediment sequence showed a trend of increasing values in the second half of the 20th century from deep layers, with values reaching up to 1 µg g^{-1} (Fig. 2), which is consistent with our hypothesis of Ag pollution and film photographic processing wastes from the city of Bariloche prior to the increase of digital photography.

These sedimentary trends in Ag concentrations correspond well with published annual global trends in the photography industry Ag demand (World Silver Surveys, 1990–2015) (Fig. 2). Silver demand in the world photography industry increased only slightly at an annual rate of 3–4% since 1950 until the late 1970's when inexpensive cameras and film became more accessible. Subsequently, the world photographic consumption of Ag grew almost uninterruptedly from 1970's until 1999 (Fig. 2), when the photographic market reached its peak. By then, around 50% of all Ag discharged into the environment came from the photography industry (Eisler, 1996).

Given the lack of reliable data on photographic activity for the Nahuel Huapi area, it is difficult to develop a precise estimate of Ag deposited in Lake Nahuel Huapi due to the photography industry in Bariloche. However, it is possible to generate a rough estimate based on Kodak calculations. Kodak Environmental Services (1998) has calculated that there is approximately 3 g m^2 of silver in one roll of 36-exposure 35-mm film, typical at that time and that an average of 50–70% of the coated silver is developed in an average image (depending on the exposure). As a result, the typical silver loss for an average photograph development mini-lab is approximately 280 troy ounces (8.7 kg) per year (Kodak Environmental Services, 1998). The total number of photographic processing facilities in Bariloche during this period is unknown and probably varied over time. Even so, if there were only 10 photographic processing facilities in operation in Bariloche, a reasonable number for a touristic town of less than 100,000 inhabitants at that time, it would mean that at least 87 kg of Ag could have been deposited in the lake each year. This rough estimation is in the order of the estimated total Ag loadings in 1989 (91.6 kg $year^{-1}$) in the effluents from the treatment Plant of Palo Alto City in the South San Francisco Bay, a highly urbanized estuary, before Ag and Cu source control programs were implemented (Hornberger et al., 2000). Even if all photographic processing facilities in Bariloche city practiced Ag recovery, an average of 5% is still lost, which translates to roughly 5 kg of silver being deposited in the lake from 10 photoprocessing facilities. Either way, this is a considerable amount of Ag which would result in elevated concentrations in the sediments.

After 1999, digital imaging started to be considered a potential threat to the photographic Ag market, since digital technology does not require Ag to process images (USGS, 2000). After that period, photography became dominated by the digital camera market, and consequently the global Ag demand by the photography sector rapidly contracted by 70% (Fig. 2) (World Silver Survey, 1990–2015). The close correspondence between the global photography Ag demand and Ag concentrations trends in dated sediments from Lake Nahuel Huapi support the inference that untreated Ag halide wastes from photographic facilities are the primary source of silver to the lake.

The deeper sediment layers are of interest as historical records of ecosystem activity but may also be reintroduced into the active portion of the ecosystem via dredging activities, severe storms, and hydrogeological events (Burton, 1991), or by natural sub-aqueous slumps as was historically recorded in the region (Chapron et al., 2006). The remobilization and release of Ag from the contaminated sediment layers to the water column and consequent redeposition to the surface sediment layers in Lake Nahuel Huapi, could be prevented by the thick deposition of tephras from the 2011 Puyehue-Cordón Caulle volcanic eruption which blanketed the entire lake. Therefore, a combination of high system stability (i.e., there have been no hydrogeological events causing sediment remobilization in recent times) and low anthropic impact (the point pollution source ceased and there is not relevant industrialization in the area), could have contributed to the apparently fast recovery of the ecosystem in terms of decreased Ag loads to sediment and biota.

3.2. Silver temporal trends in Lake Nahuel Huapi biota

The two time points used for analyze temporal trends in hepatic Ag concentrations for fish and mussel also corresponded with the trends for sediments and the global Ag demand by photography industries. Published data from 2001 to 2002 for rainbow trout, brown trout and creole perch sampled in BR, BL, and DH (Ribeiro Guevara et al., 2005) indicated very elevated hepatic Ag concentrations relative to current mean concentrations (Student's t-test; $p = 0.004$, 0.02, and 0.005, respectively) (Fig. 3). The same temporal trend was also observed for Ag concentrations in hepatic tissue in mussels from BL decreasing from 1.1 ± 0.2 µg g^{-1} DW in 2001 (Ribeiro Guevara et al., 2005) to 0.3 ± 0.2 µg g^{-1} DW ten years later (Table 1).

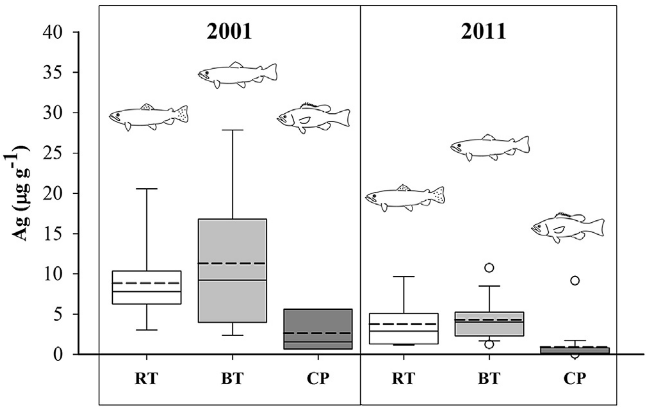

Fig. 3. Boxplot of silver concentration (Ag, μg g^{-1} DW) in liver of rainbow trout (RT, white), brown trout (BT, light gray) and creole perch (CP, dark gray) from Lake Nahuel Huapi recorded in 2001 and 2011. Solid line represents the median concentration, dashed line represents the mean concentrations, lower and upper edge of box the 25th and 75th percentiles and lower and upper whiskers the 5th and 95th percentiles respectively.

As many metals, once Ag is introduced into the water column, it partitions into the sediment phase, hence environmental concentrations of waterborne Ag are exceedingly low (Prucell and Peters, 1998). However, the concentrations of Ag recorded in aquatic plants and animals collected near industrialized sites are typically elevated, implying that environmental Ag is bioavailable to aquatic organisms (Eisler, 1996). Ingestion of particles may be an important metal exposure route for benthic invertebrates which have been shown to assimilate particle-bound Ag (Griscom et al., 2000; Lee et al., 2000). However, the transfer of Ag from sediments to biota may be low due to the low assimilation efficiencies reported for this element (Griscom et al., 2000), and varies depending on the physiology, life habit, and feeding type of the organism (Lee et al., 2000). For example, for some deposit feeders (e.g., the polychaetes *Arenicola marina* and *Nereis diversicolor*, and the clam *Macoma balthica*) it has been reported that the major source of bioaccumulated Ag was from ingested sediments (Griscom et al., 2002; Casado-Martinez et al., 2009; Kalman et al., 2010), but for the clam *Scrobicularia plana* was dissolved Ag the responsible for most accumulated Ag (Kalman et al., 2010). Mussels are suspension

Table 1
Silver concentrations (Ag, μg g^{-1} DW) in organisms sampled in 2011 at three locations in Lake Nahuel Huapi. 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 Ag concentrations in hepatic tissues. BR: Brazo Rincón; BL: Bahía López; DH: Dina Huapi; N/D: no data available.

Organism	Brazo Rincón				Bahía López				Dina Huapi			
	N	Size range (mm)	Ag (μg g^{-1} DW)		N	Size range (mm)	Ag (μg g^{-1} DW)		N	Size range (mm)	Ag (μg g^{-1} DW)	
			Mean ± s.d.	Range			Mean ± s.d.	Range			Mean ± s.d.	range
Plankton												
Plankton 1	4	10–53 μm[a]	2.6 ± 3.0	0.7–7.2	2	10–53 μm[a]	1.8	1.8–1.82	2	10–53 μm[a]	1.3	0.4–2.2
Plankton 2	4	53–200 μm[a]	0.7 ± 0.3	0.4–1.0	2	53–200 μm[a]	0.6	0.62–0.64	2	53–200 μm[a]	0.7	0.7–0.8
Plankton 3	4	>200 μm[a]	0.3 ± 0.1	0.2–0.5	2	>200 μm[a]	0.5	0.5–0.6	2	>200 μm[a]	0.5	0.4–0.5
Benthic macroinvertebrates												
Chilina sp. (snail)	8	11–27	0.2 ± 0.1	0.1–0.5	8	11–26	0.2 ± 0.1	0.2–0.3	N/D	N/D	N/D	N/D
	8		(4.0 ± 1.8)	(1.6–7.0)	8		(9.2 ± 3.8)	(3.6–14.7)			N/D	N/D
Diplodon chilensis (mussel)	N/D	N/D	N/D	N/D	15	35–79	0.1 ± 0.1	0.1–0.5	N/D	N/D	N/D	N/D
					15		(0.3 ± 0.2)	(0.1–1.1)				
Hyalella sp. (amphipod)[a]	4	–	0.1 ± 0.03	0.1–0.2	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D
Samastacus spinifrons (crayfish)	9	22–96	0.05 ± 0.02	0.02–0.1	8	43–77	0.1 ± 0.04	0.04–0.2	6	57–100	0.2 ± 0.1	0.1–0.3
	7		(3.1 ± 4.5)	(0.5–13.3)	8		(1.3 ± 0.5)	(0.8–2.3)	4		(7.3 ± 7.0)	(3.3–17.7)
Aegla sp. (crab)	5	8–40	0.3 ± 0.2	0.2–0.6	12	3–40	1.0 ± 0.8	0.2–3.1	N/D	N/D	N/D	N/D
	4		(1.0 ± 0.7)	(0.4–2.0)	9		(2.5 ± 2.3)	(0.7–7.0)	N/D	N/D	N/D	N/D
Mayfly larvae	10	–	0.61	<0.5–0.61	4	–	0.24	<0.1–0.24	N/D	N/D	N/D	N/D
Fish												
Galaxias maculatus (Small puyen)	8	35–55	0.03 ± 0.01	0.01–0.04	5	35–53	0.03 ± 0.01	0.02–0.04	7	32–53	0.06 ± 0.04	0.02–0.1
Adult *Percichthys trucha* (Creole perch)	13	461–511	<0.05	–	9	325–490	<0.05	–	5	180–450	<0.05	–
			(0.5 ± 0.9)	(0.01–3.0)			(0.4 ± 0.5)	(0.02–1.2)			(2.9 ± 5.8)	(0.03–13.2)
Juvenile *Oncorhynchus mykiss* (Rainbow trout)	N/D	N/D	N/D	N/D	9	500–627	<0.04	–	1	92	<0.01	–
							(0.6 ± 0.3)	(0.2–1.0)			(1.45)	–
Adult *Oncorhynchus mykiss* (Rainbow trout)	5	500–627	<0.03	–	4	341–584	<0.03	–	9	240–652	<0.03	–
			(5.4 ± 4.7)	(1.4–13.5)			(2.2 ± 1.1)	(1.3–3.8)			(3.5 ± 3.0)	(0.9–9.23)
Adult *Salmo trutta* (Brown trout)	22	468–713	<0.05		2	532–661	<0.03		1	548	0.01	
			(4.5 ± 2.6)	(1.2–11.2)			(2.3)	(2.2–2.4)			(4.6)	

[a] Mesh size of the net.

feeders and are consequently exposed to contaminants that are dissolved in water, associated with suspended particles and deposited in bottom sediments (Naimo, 1995). However, water-phase and ingestion of suspended particles has been demonstrated as the most important sources of many metal contaminants for mussels (Jenner et al., 1991; Gundaker, 2000). Ribeiro Guevara et al. (2005) concluded that most Ag present in Lake Nahuel Huapi a decade ago was adsorbed onto particulate surfaces and hence was circulating within the water column, being thus bioavailable for filtering feeder mussels. Therefore, the decrease in Ag concentrations of mussels sampled in the lake in recent years would reflect a decrease of Ag bioavailability in water and suspended phases, as a consequence of Ag reduction in waste waters discharged into the lake, following the change in photographic processing technology. In the absence of an active source of Ag, and because of its high affinity to particles, it precipitates to the bottom and therefore is likely not circulating in water or in suspended particulates at elevated concentrations.

Fish can uptake Ag from water through the gills or from diet through the gastrointestinal tract (Wood et al., 2012). Due to the tendency of Ag to bind with colloidal material or to form complexes with suspended sediments, waterborne Ag concentrations are usually very low (Prucell and Peters, 1998). Consequently, the majority of Ag accumulated in pelagic organisms like fish, is likely derived from food rather than from the water column (Yamazaki et al., 1996). Bioaccumulation of Ag in trout liver fed on fish exposed to Ag thiosulphate was experimentally demonstrated (Hogstrand et al., 1996; Galvez et al., 2001). Silver thiosulphate complexes are the main soluble waste discharged from photographic facilities (Prucell and Peters, 1998), therefore, it would be expected that a reduction of Ag waste products discharged to the lake would be translated into a decrease in Ag concentrations in fish liver from Lake Nahuel Huapi with the advent of digital technology. Our results provide indirect evidence for the existence of a relationship between a known source of Ag and Ag accumulation in hepatic tissues of fish and mussels from a large Patagonian lake.

3.3. *Silver in Lake Nahuel Huapi food web*

To assess the potential for trophic transfer of Ag from lower trophic species to predatory species at the three sites, we examined individual compartments of Lake Nahuel Huapi food web. Average Ag concentrations in plankton from the three sites consistently decreased with increasing size fraction from 1.3 to 2.6 $\mu g\ g^{-1}$ DW in the P1 fraction (phytoplankton), to 0.6–0.7 $\mu g\ g^{-1}$ DW in the P2 fraction (mixed plankton), and to 0.3–0.5 $\mu g\ g^{-1}$ DW in the P3 fraction (zooplankton) (Table 1). Those were within the range of published values for plankton around the world (Eisler, 1996; Ratte, 1999). The differences in Ag concentrations between size fractions indicate that bulk Ag concentration decreased in the plankton community with both size and trophic position (considering that copepods in P3 fraction occupy the highest trophic position, Arcagni et al., 2015), and has implications for trophic transfer through the food web. Furthermore, spatially-consistent plankton Ag concentrations were found between all three sites for all three fractions (P1, P2, P3), indicating homogeneous distribution of Ag in the pelagic compartment throughout the whole lake. In addition, their primary fish predator, the planktivorous small puyen (Barriga et al., 2012; Milano et al., 2013), also did not have any significant differences between all three sites (Kruskal-Wallis; $p = 0.76$). This suggests that pelagic species in Lake Nahuel Huapi may not be important vectors of concentrated silver to larger fish and piscivorous predators.

However, benthic invertebrates have been shown to assimilate particle-bound silver, allowing the metal to enter the aquatic food chain (Ratte, 1999; Griscom et al., 2000; Lee et al., 2000). Many macroinvertebrates and other aquatic organisms are more efficient than zooplankton in terms of Ag uptake and accumulation from food, so the importance of diet as a route of uptake relative to water depends on the organism in consideration (Luoma, 2008). In Lake Nahuel Huapi, Ag concentrations in whole-body and muscle tissue from macroinvertebrates varied considerably according to the species, tissue type and sampling site (Table 1). Crabs from BL (0.2–3.1 $\mu g\ g^{-1}$ DW) and mayfly larvae from BR (<0.05–0.61 $\mu g\ g^{-1}$ DW) had the highest Ag concentrations, while crayfish from BR (0.02–0.1 $\mu g\ g^{-1}$ DW) had the lowest. These results are in agreement with Ag levels of benthic organisms from the neighbouring Lake Moreno (Revenga et al., 2011) and comparable to Ag concentrations in benthic organisms from uncontaminated streams in Turkey (Tokatli et al., 2013). Hepatic tissues generally had higher Ag concentrations than muscle tissue for decapods and mussels. The highest hepatic Ag concentrations were found in species with strongest benthic food association, e.g., the snail *Chilina* sp. from BL (9.2 ± 3.8 $\mu g\ g^{-1}$ DW) and the crayfish from DH (7.3 ± 7.0 $\mu g\ g^{-1}$ DW). This is in contrast with the lower concentrations in the pelagic filter feeding mussel (0.3 ± 0.2 $\mu g\ g^{-1}$ DW). The differences in Ag concentrations among species and tissue type could be reflective of species-specific mechanisms of metal regulation or differential distribution of Ag in the source matrix. This result also suggest a benthic uptake route of Ag (i.e., through sediment), since higher Ag concentrations were recorded in hepatic tissues of organisms that take their food from the sediment instead of filtering food from water. Lake-wide spatial distribution of Ag was only possible to analyze with the crayfish which was captured in all 3 sampling sites. Silver was observed to increase in crayfish from BR to DH, both in muscle and hepatic tissues, suggesting a relationship between tissue concentrations and the proximity to the city's municipal sewage output.

Similar to macroinvertebrates, fish Ag concentrations in 2011 were more elevated in hepatic (liver) tissue (creole perch: 0.01–13.2 $\mu g\ g^{-1}$ DW; rainbow trout: 0.2–13.5 $\mu g\ g^{-1}$ DW; brown trout: 1.2–11.2 $\mu g\ g^{-1}$ DW) relative to those in muscle tissue which was often below the detection limit (0.01–0.05 $\mu g\ g^{-1}$ DW) (Table 1). The low Ag concentrations recorded in muscle of large fish, especially salmonids, is consistent with what has been found for fish elsewhere (Wood et al., 2012). Effective processes of Ag sequestration occur in liver and other metabolic organs to store potentially toxic metals for detoxification (Hogstrand et al., 1996; Galvez et al., 2001; Wood et al., 2012). While Ag concentrations in muscle were in line with most investigations and at acceptable levels for human consumption, hepatic concentrations in fish in our study were well above values found in liver of fishes from water bodies with variable degree of human activity impact (Eisler, 1996; Yamazaki et al., 1996; Ratte, 1999; Jarić et al., 2011). Silver concentrations in livers of creole perch were lower than in salmonid livers, which might be indicating a better detoxifying capacity or lower diet transfer efficiency of Ag in the native species. Differential bioaccumulation between salmonids and creole perch in this lake has already been observed for other toxic elements such as arsenic (Juncos et al., 2016) and Hg (Arcagni et al., 2017).

Biodilution patterns of Ag in the food web have been frequently described in aquatic systems due to the low trophic transfer efficiency of Ag (Huang et al., 2008; Revenga et al., 2011). The lack of consistency between samples taken at different sites (e.g., some species were not present at all sites) and the consistently below-detection Ag concentrations in top predator fish muscle prevented the performance of regression analysis commonly used to assess the trophic transfer patterns. However, a decreasing trend with increasing trophic level (i.e., $\delta^{15}N$) could be observed when whole-body and muscle Ag concentrations of all species in Lake

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Nahuel Huapi were plotted with the mean $\delta^{15}N$, which is consistent with the global patterns of silver in aquatic food webs (Fig. 4).

A literature review indicates that there are contradictory conclusions regarding the route of Ag uptake and transfer along food webs. Some authors argue that once Ag in solution is incorporated to algae, it remains tightly bound to cell membranes and cannot be removed even by changes in pH or enzymatic activity (e.g. during digestion) (Connell et al., 1991). Therefore, assimilation by consumers is very low and thus biomagnification is unlikely (Ratte, 1999). On the contrary, other researchers have highlighted the importance of Ag bioaccumulation from contaminated food or sediments concluding that, at least for invertebrate predators, diet is a more important route of uptake than is from solution (Luoma, 2008; Croteau et al., 2011). Therefore, the importance of the dietary transfer of Ag through the food web will depend on the food web structure, the food chains being analyzed and the appropriate selection of the bioaccumulating tissue. For instance, hepatic tissues may represent a potentially significant entry pathway of Ag to the higher predators in Nahuel Huapi National Park such us the imperial cormorants *Phalacrocorax atriceps* and the southern river otters *Lontra provocax*, both of which preferably prey on whole crayfish and salmonids (not only muscle) (Medina-Vogel and Gonzalez-Lagos, 2008; Casaux et al., 2010), whose hepatic tissues recorded high Ag levels in the studied lake, and therefore this should be considered in monitoring programs.

4. Conclusions

We linked global film photography Ag demand data with local environmental Ag data, to establish a relationship between Ag contamination in Lake Nahuel Huapi with photographic activity. It was possible to observe an unequivocal trend of diminished Ag concentrations in each compartment analyzed (i.e., sediments, mussels, and fish) across Lake Nahuel Huapi through time. This decreasing trend showed a strong correspondence with worldwide film photography industrial trends (World Silver Survey, 1990–2015). Unlike the highly contaminated San Francisco Bay, in which great efforts to stop and reverse the impacts of Ag pollution had to be done (Hornberger et al., 2000; Squire et al., 2002; Flegal et al., 2007), in Lake Nahuel Huapi a significant decrease of Ag levels was observed after the unregulated reduction or cessation of the main polluting activity, i.e., film photography and film developing centers, without human intervention.

As expected, Ag concentrations were lower in organisms with higher trophic positions than those with lower trophic positions in the food web (i.e., biodilution), with higher concentrations recorded in hepatic tissues of organisms that take their food from the sediment, suggesting a benthic uptake route of Ag (i.e., through sediment).

Our results are encouraging because they show that if the Ag inputs to the lake are stopped or controlled, the contamination may naturally recede and therefore, there is a possibility that the ecosystem may recovery from Ag contamination in the short to medium term. However, even though the replacement of film-based Ag halide photography by digital photography ended an important source of Ag to the environment, other industrial uses of Ag, particularly nano-silver, and therefore its dispersal into the environmental matrices, both continue to increase (Luoma, 2008). Even if Ag from photographic uses recedes, looking backwards will allow us to anticipate and manage future environmental challenges

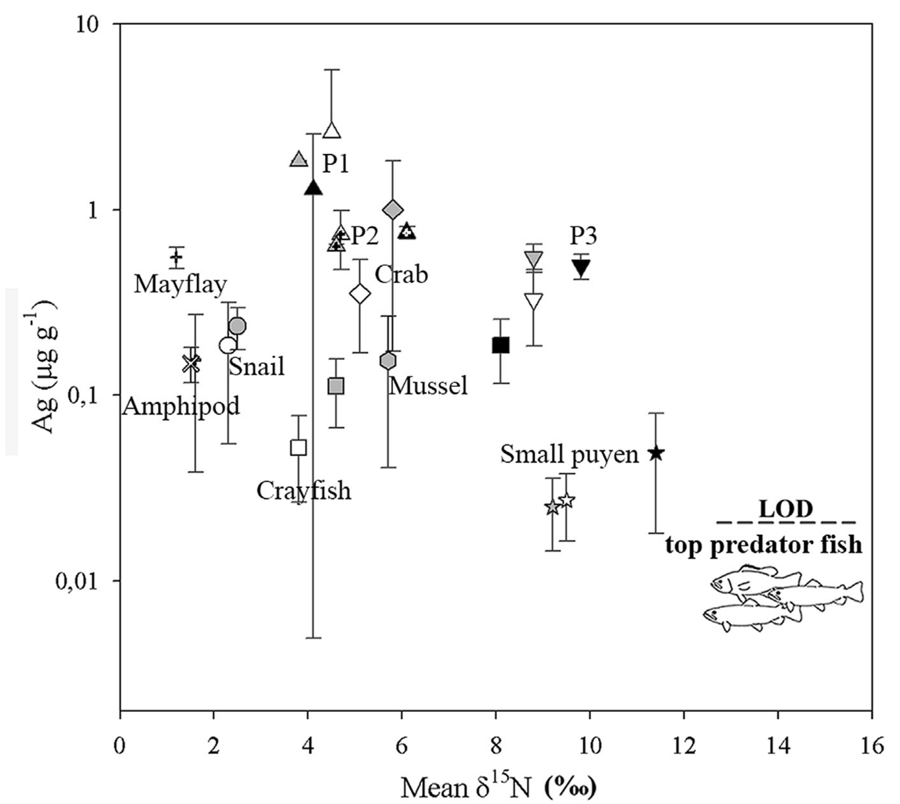

Fig. 4. Mean (±SD) silver concentrations (µg g^{-1}) in whole body of plankton, insect and amphipods, muscle of snails, crayfish and crabs, and whole body without head and gut of small puyen from Brazo Rincón (white symbols), Bahía López (grey symbols) and Dina Huapi (black symbols). Species are arranged from lowest to highest trophic position as indicated by mean $\delta^{15}N$ (‰) values (taken from Arcagni et al., 2015). Silver concentrations in top predator fish (salmonids and perch) were below detection limits (LOD, dashed line). P1: Plankton 1 (10–53 µm); P2: Plankton 2 (53–200 µm); P3: Plankton 3 (>200 µm).

associated with new uses of silver.

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Appendix A. Supplementary data

Additional information on sediment sequence sampling and analysis and Ag reference materials analyzed by INAA (Table S1).

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.envpol.2017.02.003.

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