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

Romina Juncos [a, b, *], Linda Campbell [c], Marina Arcagni [a, b], Romina Daga [a, b], Andrea Rizzo [a, b], 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

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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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* Corresponding author. Laboratorio de Análisis por Activación Neutrónica, Centro Atómico Bariloche, Av. E. Bustillo 9500, 8400 Bariloche, Argentina.
E-mail address: romina.juncos@cab.cnea.gov.ar (R. Juncos).

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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 $\mu g\ m^{-2}\ year^{-1}$) 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 $\mu g\ g^{-1}$ dry weight DW) sampled in 2001 in Lake Nahuel Huapi, that were well above those in the salmonid livers (0.2–3.9 $\mu g\ g^{-1}$ 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,

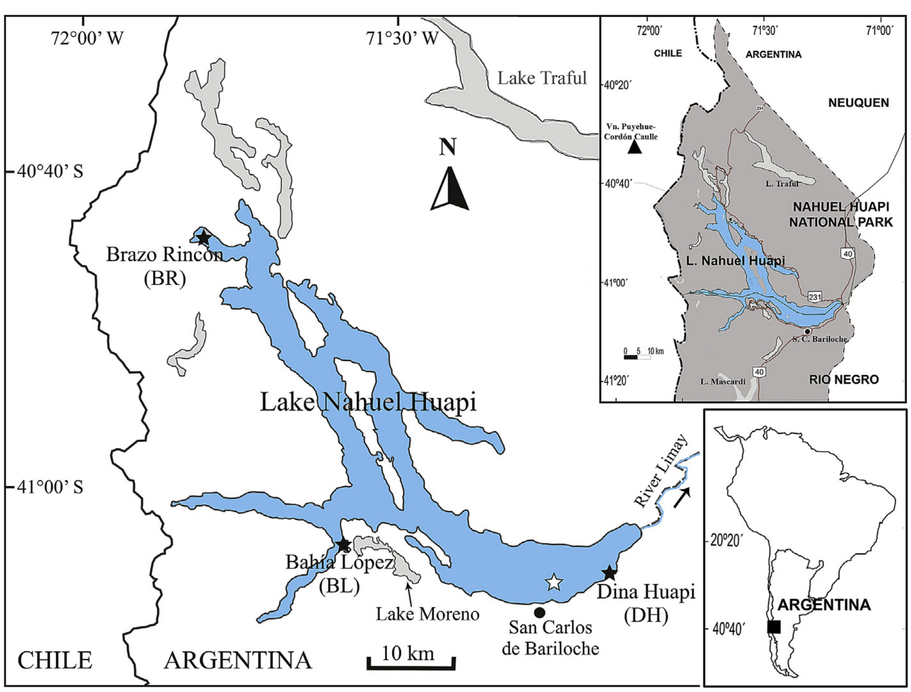

Fig. 1. Map of the study area showing the location of the biota sampling sites (black stars) and sediment core sampling site (white star) in Lake Nahuel Huapi, within the Nahuel Huapi National Park (shaded area in the right-top panel), Patagonia, Argentina.