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

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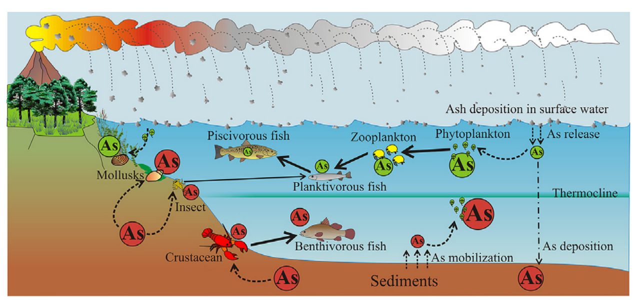
HIGHLIGHTS

- 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



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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 $\mu g\ g^{-1}$ dry weight, DW) and small zooplankton (4.3–22.3 $\mu g\ g^{-1}$ DW). The pattern of As accumulation in aquatic organisms (whole body or muscle) was: primary producers (phytoplankton) > scrapper mollusks (9.3–15.3 $\mu g\ g^{-1}$ DW) > filter feeding mollusks (5.4–15.6 $\mu g\ g^{-1}$ DW) > omnivorous invertebrates (0.4–9.2 $\mu g\ g^{-1}$ DW) > zooplankton (1.2–3.5 $\mu g\ g^{-1}$ DW) > fish (0.2–1.9 $\mu g\ g^{-1}$ 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 in the short

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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 worldwide (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 μg 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 μg g^{-1} (Ribeiro Guevara et al., 2005) and 5–7 μg g^{-1} (Ribeiro Guevara, unpublished data), respectively. Reported concentrations of dissolved As in Lake Nahuel Huapi waters are below 0.7 μg 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 μg 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 as warm monomictic with regular summer stratification