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Iron buffer system in the water column and partitioning in the sediments of the naturally acidic Lake Caviahue, Neuquén, Argentina

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ABSTRACT

Sedimentary iron partitioning was studied for five sediment strata (16 cm depth) at three sampling sites of the naturally-occurring acidic Lake Caviahue (Patagonia, Argentina). Additionally, water column iron was modeled based on five-year period input loadings to study a possible iron buffer system. The partition coefficient between the water column and the total iron content of the sediments was also addressed. Sedimentary iron was found to be distributed, on average, in the following forms: exchangeable (6%), iron oxides (4%), pyrite and reactive organic matter (38%) and residual (non-andesitic) materials with a high content of humic acids (52%). Furthermore, we found that the dissolved iron in the lake was nearly constant throughout the five year period we studied. This is consistent with the existence of an iron buffer system in the lake at pH between 2.0 and 3.0, which may cause differential iron precipitation at the delta of the volcanic river with respect to the deeper northern and southern arms. Sedimentary iron measurements taken at the delta further support the existence of a buffer system, where it was found that the iron content in the sub-superficial stratum (2 cm) was double that of the remainder of the vertical profile at the same site.

1. Introduction

Strong acids may be introduced into surface waters through at least three pathways: volcanic activity, acidic mine drainage (AMD) and natural weathering of pyrite rich rocks (natural equivalent of AMD). Contributions from acid rain, while present, are negligible compared with the first two. Both natural and anthropogenic sources may lead to strongly acidic lakes and rivers ($pH < 4.0$). Due to the increase in the solubility of metals at lower pH, very high concentrations can often be found of a wide spectrum of elements such as iron and aluminum (Stumm and Morgan, 1996; Geller et al., 1998).

Hydrochemical, geochemical and limnological effects of acidification have been described most extensively for anthropogenically acidified surface water bodies (Dillon et al., 1984). In recent years much work has been done to better understand waters that are highly acidic naturally due to volcanic activity (Pedrozo et al., 2001; Wendt-Potthoff and Koschorreck, 2002; Marini et al., 2003; Gammons et al., 2005; Beamud et al., 2007; Llames and Vinocur, 2007; Koschorreck et al., 2008; Pedrozo et al., 2008; Varekamp, 2008; Varekamp et al., 2009; Beamud et al., 2010; Chiacchiarini et al., 2010, among many others).

Patagonian lakes and reservoirs span a wide pH gradient. Andean lakes are neutral, deep and ultra-oligotrophic, while those of the Patagonian plateau are alkaline, shallow, eutrophic and hyperhaline (Pedrozo et al., 1993). Lake Caviahue, the subject of the present study, is very acid, deep oligotrophic with low planktonic diversity and is unique in South America (Pedrozo et al., 2001; Pedrozo et al., 2008). Located deep in the Andean Mountains (Fig. 1), the special characteristics that differentiate it from the other lakes of the region are due primarily to the activity of the Copahue Volcano (Delpino et al., 1997; Diaz et al., 2007; Varekamp, 2008).

Sedimentary iron and trace metals are often found associated to different chemical phases, such as the exchangeable fraction, carbonates, iron and manganese oxides, monosulfides (FeS), pyrite (FeS_2), mineral rocks and in organic matter (OM). In organic matter, iron can be found in tissue or cell walls of living organisms, detritus, soluble humic substances (HS) with low molecular weight as well as in HS coatings on mineral particles (Tessier et al., 1979). The distribution of iron is governed by local physico-chemical conditions such as pH and electric potential, Eh (Butler and Rickard, 2000).

Most geochemical studies of the metal partitioning of sediments in acidic environments have focused on AMD, for example in the Iberian Pyrite Belt, the Mining Lakes District in Germany or massive sulfide deposits in the Yukon Territory, Canada (Geller et al., 1998; Friese et al., 1998; Kwong and Lawrence, 1998; Bachmann et al., 2001; Torres and Auleda, 2013). Investigations of sediments of naturally acidic water bodies have mainly analyzed total metal content and mineralogy rather than partitioning. Several methods have been used to determine total metal content including digestion with strong acids and other oxidant mixtures (HF, HCl, $HClO_4$, HNO_3, HSO_4, H_2O_2), energy dispersive spectroscopy, total reflexion X-ray fluorescence and X-ray diffraction (Delmelle and Bernard, 1994; McKenzie et al., 2001; Ruiz-Fernández et al., 2007; Ma et al., 2011).

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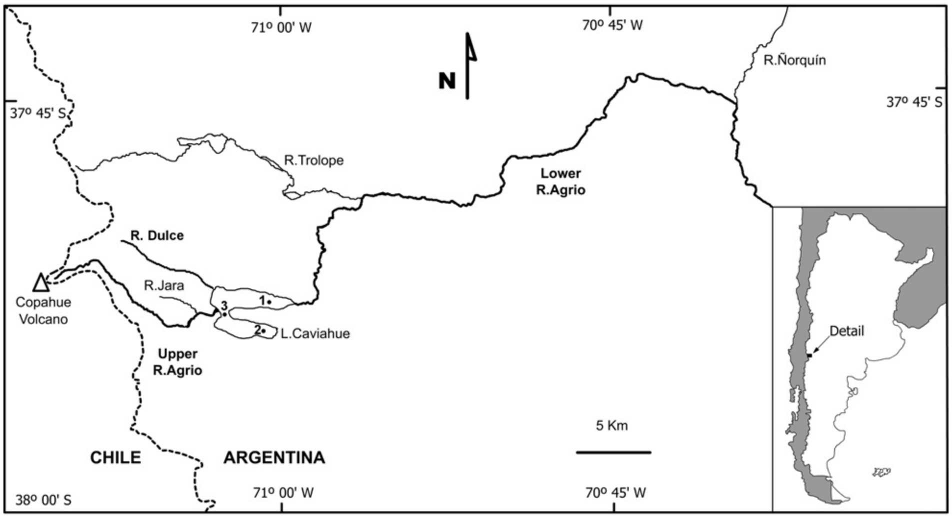

Fig. 1. Study area: Copahue Volcano, Lake Caviahue, URA, Dulce and LRA rivers. Sampling stations were located in the deeper sites of the northern (1) and southern (2) arms, and in the union of both arms at the Agrio River delta, the Center of the lake (3).

Objectives of the present study are to determine and analyze the distribution of iron in the highly acidic sediments of Lake Caviahue, and the relation between this distribution and the iron concentration in the water column.

Our findings will allow for the prediction of new scenarios in iron cycling if, due to volcanic activity, changes occur in the acidity of the lake or redox conditions (Eggleton and Thomas, 2004).

2. Study area

Lake Caviahue is located 1600 m.a.s.l. in the Copahue-Caviahue Provincial Park (37° 53′ S; 71° 02′ W), Neuquén, Argentina (Fig. 1). The lake is a naturally-occurring glaciated water body with a maximum length of 9.7 km, maximum width of 4.7 km, coastline of 22.3 km, total area of 9.2 km^2 and total volume of 0.47 km^3. The water residence time (R) has been estimated by two authors in two different ways: Rapacioli (1985) estimated 31.2 months based on hydrological calculations while Varekamp (2003, 2008) predicted 42 months based on conservative element loadings and concentration. It has a horseshoe shape with two arms (northern and southern) 90 m and 70 m deep, respectively, and the two mayor influxes are the Dulce River (average flow of 1.23 $m^3\ s^{-1}$) and the Upper Rio Agrio (URA, average flow of 1.10 $m^3\ s^{-1}$). The former is a scrubby forested, soil-covered basin with a pH of 6.5, while the latter is born on the east slope of the Copahue Volcano caldera and has an initial pH of 0.8, a temperature of 56 to 82 °C, a conductivity of 560 mS cm^{-1} (Pedrozo et al., 2001; Pedrozo et al., 2008) and flows into the lake with a pH of 1.9 to 2.5. While both tributaries discharge into the northern arm, the URA joins the lake at a point closer to the union of the arms. Caviahue has a pH of 2.2 to 3.0, high electric conductivity (560 to 1600 μS cm^{-1}) and high concentrations of PO_4^{-3} (210 to 240 μg L^{-1}), Fe (20 mg L^{-1}), Al (27 mg L^{-1}), Mn (1 mg L^{-1}), Cl (95 mg L^{-1}), F (6.7 mg L^{-1}), Si (17 mg L^{-1}), SO_4^{-2} (400 mg L^{-1}), Na (14 mg L^{-1}), K (6 mg L^{-1}), Ca (22 mg L^{-1}) and other trace elements (Pedrozo et al., 2001; Pedrozo et al., 2008; Varekamp, 2008) and this is why Lake Caviahue is unique among Andean lakes, which are usually circumneutral and oligotrophic (Diaz et al., 2007).

The effluent is the Lower Rio Agrio (LRA), which exits the lake with a pH near 3.0 and joins the Neuquén River approximately 200 km downstream with a pH of 8.0 due to the contribution of several dilute tributaries.

The predominant mineral throughout the basin is andesitic (Pesce, 1989; Varekamp et al., 2006) although much of the sediment input since year 2000 is probably ash from the eruption that took place that year (basaltic andesite, Varekamp, 2015). The organic matter content of the lake sediment is between 5 and 10%, and is rich in phosphorus (1 mg g^{-1} associated with the organic fraction). The average Eh is −120 mV (−20/−180 mV), and the pH ranges between 3.0 and 4.0 for both basins, and between 3.0 and 6.0 at the union of both arms (Temporetti et al., 2013 and data not published).

Located on the west side of the northern arm is the town of Caviahue. It has approximately 900 permanent inhabitants, although the population varies throughout the year due to incoming tourists that visit the thermal bath complex and the sky resort located on the Copahue Volcano.

3. Materials and methods

3.1. Sample collection, processing and in situ measurements

Sediment cores were collected with a 6 cm diameter, Uwitec-type corer in January of 2013 at three stations: the deepest sites of both arms, northern (NA) and southern (SA), and at the Center (C) (Fig. 1). Each core was sliced into five strata, 2 cm thick in the upper horizon (0 to 4 cm) and 4 cm thereafter (4 to 16 cm). Eh and pH (Orion 920A) measurements, adjusting for temperature, where take in each stratum. Samples were stored in polyethylene bags in a N_2 atmosphere at 4 °C for no longer than 24 h before being frozen. All analyses were performed within one week.

Concurrently, water samples were collected from the same sites at various depths using a 4 L Van Dorn bottle. Additional samples were taken along a transect extending into the lake from a point 50 m upstream of the URA discharge site. Measurements were made at the start point of the transect located in the river, at the coastline (discharge point) and at a distance of 5, 50, 100 and 250 m into the lake. Samples were filtered (0.45 μm acetate filters) and stored in polyethylene bottles at 4 °C for further metal analysis (water pH 2.0).

In the years 1999 and 2000, water samples were taken for the simulation of the saturation indexes following the same method as Pedrozo et al. (2001). Samples were analyzed as described in Section 3.3.3 at the Helmholtz Centre for Environmental Research in Magdeburg, Germany.

In the laboratory, sediment samples from all strata were carefully homogenized by hand inside a container bag (under a N_2 atmosphere). Aliquots with a dry weight (dw) of 1 g were stored in polypropylene tubes for metal extraction. All analyses were performed on fresh anoxic sediments under anaerobic conditions in order to preserve the metal distribution among the sediment fractions. Reagents were of analytical grade, and MilliQ water was used. Oxygen in the reagents was removed by N_2 bubbling. The extraction procedures were performed within 48 h of sub-sampling.