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Dynamics of phosphorus in sediments of a naturally acidic lake

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Abstract

The mechanisms which controls the fixation and/or release of P in sediment of an extremely acidic lake (pH = 2.0 to 3.0) and its response to the influence of eutrophic urban waste water were investigated. The results, in the chemical composition, in the mineralogy of the sediment and in the material as obtained from sediment traps, show that the lake sediments are mainly volcanic material reflecting volcanic features of the basin. The sedimentation rate calculated for the lake (2.5×10^{-2} mg m^{-2} day^{-1}) was higher than that observed in other similar glacial lakes in both Andean Patagonia and also elsewhere in the world. The Total Phosphorus concentration in sediments was higher than figures reported by other authors for mining acid lakes, and the main fraction of P was found associated with organic matter. There was no control by Fe or Al on P, because both are in solution at pH < 3.0. It was concluded that changes in the natural input of nutrients (derivatives of Copahue volcano fluid, the discharge of sewage, or basin run-off) are responsible for a high concentration of SRP and $N\text{-}NH_4^+$ in the lake. Laboratory experiments showed that sediments have no ability to retain phosphorus and a continuous release of P from the sediments into the water column was observed. The assays where the pH was artificially increased showed that the P still remains in solution until at least pH 7.0. It was concluded that changes in the natural input of nutrients due to: 1) the volcanic fluids, 2) the increase in sewage charges, or 3) surface runoff upstream, maintain a high trophic state with high concentrations of dissolved P and $N\text{-}NH_4^+$, although the threshold of neutral pH in the lake is exceeded. This study will enable a better understanding about of the mechanism of release/fixation of phosphorus in acidic sediments in order to assist in making decisions regarding the conservation and management of this natural environment.

Key Words: Sediments, Phosphorus release, Acidic lake

1 Introduction

Lake Caviahue is located at 1,600 m a.s.l. in the Caviahue-Copahue Provincial Park (37° 53' S; 71° 02' W) Neuquén Province (Fig. 1). This lake has a horseshoe shape, with two arms: North arm (BN) and South arm (BS). The maximum length of the lake is 9.7 km, maximum width is 4.7 km, maximum depth is 95 m, the average depth is 51.4 m, the length of the coastline is 22.3 km, the lake´s total area is 9.2 km^2, the volume is 474.2 Hm^3 and the residence time is 2.6 years (Rapacioli, 1985). Lake Caviahue receives two main streams: the Upper Agrio River and the Rio Dulce. The Upper Agrio River rises on the east slope of the Copahue volcano and is characterized by a pH of 0.02, an acidity of 1.5 mM and a temperature of up to 82° C (Pedrozo et al., 2001). The Rio Dulce is a forested soil covered basin and is characterized by a pH of 6.5. Both tributaries enter the North Arm. The effluent is the Lower Agrio River. The predominant rock type in the area is andesitic lava and pyroclastic (Pesce, 1989). The lake is characterized (Pedrozo et al., 2008) by a low transparency (2.8 to 3.6 m, Secchi disk measurement), low pH (2.50; range: 1.84-2.97) and high electric conductivity (1259 μS cm^{-1}; range: 790–3,600 μS cm^{-1}). The concentration of Soluble Reactive Phosphorus (SRP) (210-240 μg L^{-1}) represents about 90-95% of total phosphorus (TP), while concentrations of $N\text{-}NH_4^+$ and $N\text{-}NO_3^-$, range between 40 and 70 μg L^{-1}. The concentrations of major ions and other elements are very high (Na = 13.5 mg L^{-1}, K = 5.5 mg L^{-1}, Ca = 22.5 mg L^{-1}, Al = 30.0 mg L^{-1}, Fe = 17.0 mg L^{-1}, S = 1,100.0 mg L^{-1}) (Pedrozo et al., 2001) when compared with neutral oligotrophic Patagonian Andean lakes. These values are similar in both arms.

On the west bank of the lake lies the town of Caviahue (500 inhabitants) with an influx of tourists, attracted mainly by the therapeutic spa and winter sports. The population can exceed 2,000 tourists during the peak summer and winter

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seasons. Although the village has a small primary sewage treatment plant, it is not always in operation. Untreated wastewater (pH = 8.0), with high concentration of phosphorus (P) and nitrogen (N), is discharged into the water column on the northern shore of the lake which causes a gradual alkalinization.

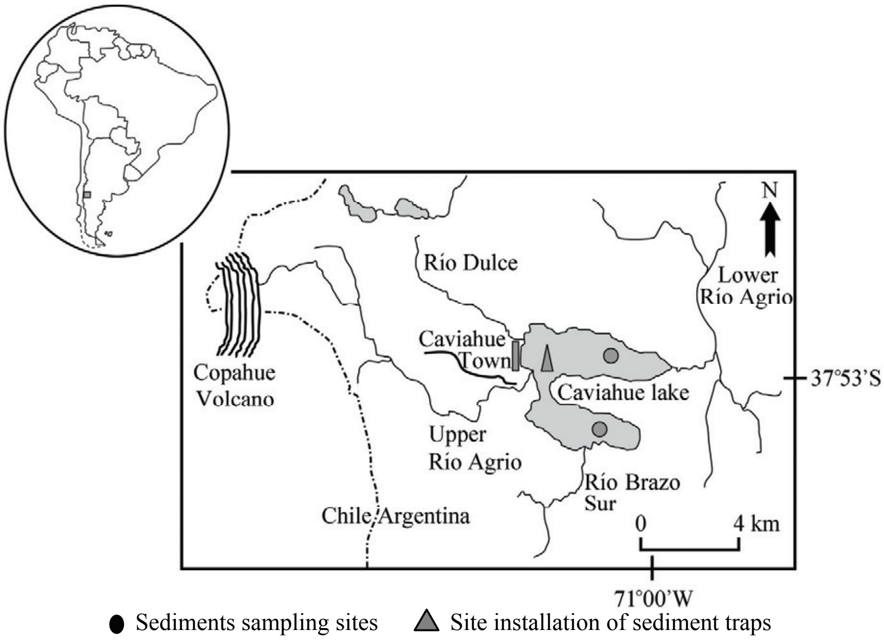

Fig. 1 Location of sampling sites

Acidic aquatic environments are scarce worldwide (Geller et al., 1998). Some of them are of natural origin, mainly caused by volcanic activity and others are anthropogenic, resulting from mine working. In Argentina, Lake Caviahue is the most important acidic natural lake (Pedrozo et al., 2008; Varekamp, 2008), due to either its extreme acidity, or its dimensions and location in a predominantly touristic area.

Phosphorus is often a growth-limiting element for aquatic organisms and plays a significant role in the eutrophication process of water bodies (Hsieh et al., 2006; Kisand, 2005). Excessive P in the water body can accelerate freshwater primary productivity, leading to eutrophication and negative impacts on ecosystem function (Wetzel, 2001; Bai et al., 2009). The amount of phosphorus present in a water body depends on both the external phosphorus load and its release and retention in the sediments (Wetzel, 2001). The relationship between nutrients and sediments provides an appropriate microbiological substrate to promote more rapid and complete transformation of certain contaminants (Golterman et al., 1983) at the expense of oxygen consumption. The recirculation of elements from sediments to the water column becomes very important when it comes to essential nutrients (P and N) (Håkanson and Jansson, 1983), and it depends on the morphological (mean depth), physical (thermal stratification), chemical (dissolved oxygen, redox potential) and biological (bioturbation) characteristic of the waterbody. In this regard, sediments play an important role in the dynamics of phosphorus in lakes. This importance is related to the ability of sediments to retain or release phosphorus (Boström et al., 1982). Understanding the fate and transport of phosphorus to and from sediment is necessary when planning the recovery of an impacted water body (Golterman, 2004).

Most studies related to the dynamics of phosphorus in the sediments are focused on so-called fresh-water bodies, i.e. predominantly carbonate-bicarbonate buffer systems. There are very few studies on this subject in extreme acidic lakes such as Lake Caviahue. According to Boström et al. (1982), the three elements of major importance in controlling the solubility of P are Fe, Al and Ca. The dominance of one or the other depends on the pH and the dominant buffer system. According to Geller et al. (1998), the molar ratio between aluminum and iron varies between 1.5 and 5.0 in acid mine lakes, and can be indicative of a dominant buffer system in lakes of low pH and high ionic concentration. When the pH range varies between 4.5 and 5.5 the dominant buffer system is controlled by aluminum, while between pH 2.0 and 4.0 iron predominates the buffer system. Geller et al. (1998) leave the hypothesis open on which buffer system is dominant in volcanic lakes of extreme pH ($\leq$ 2.0). With the pH increase, a decreased P due to the formation of ferric salts, aluminum and calcium is expected. By contrast, in the pH range 2-3 Caviahue lake, the formation of stable salts of P with Fe (strengite) and Al (variscite) (Stumm and Morgan, 1996), is expected, although a high proportion of P remains in solution. Sulfate salts can also contribute to maintaining P in solution due to the competition for adsorption sites in the sediments particles (Caraco et al., 1989). The nutrient inputs from anthropogenic sources, their eutrophicant effects and the recovery solutions in neutral lakes have been extensively studied throughout the world. In this sense, there is no literature concerning the study of factors affecting the fixation and/or release of phosphorus in sediments of acidic water