

## Dynamics of phosphorus in sediments of a naturally acidic lake

Temporetti PEDRO<sup>1</sup>, Snodgrass KIMBERLEY<sup>2</sup>, and Pedrozo FERNANDO<sup>3</sup>

### 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 ( $2.5 \times 10^{-2} \text{ mg m}^{-2} \text{ day}^{-1}$ ) 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  $\text{N-NH}_4^+$  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  $\text{N-NH}_4^+$ , 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 Cavihue is located at 1,600 m a.s.l. in the Cavihue-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<sup>2</sup>, the volume is 474.2 Hm<sup>3</sup> and the residence time is 2.6 years (Rapacioli, 1985). Lake Cavihue 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  $\mu\text{S cm}^{-1}$ ; range: 790–3,600  $\mu\text{S cm}^{-1}$ ). The concentration of Soluble Reactive Phosphorus (SRP) (210–240  $\mu\text{g L}^{-1}$ ) represents about 90–95% of total phosphorus (TP), while concentrations of  $\text{N-NH}_4^+$  and  $\text{N-NO}_3^-$ , range between 40 and 70  $\mu\text{g L}^{-1}$ . The concentrations of major ions and other elements are very high ( $\text{Na} = 13.5 \text{ mg L}^{-1}$ ,  $\text{K} = 5.5 \text{ mg L}^{-1}$ ,  $\text{Ca} = 22.5 \text{ mg L}^{-1}$ ,  $\text{Al} = 30.0 \text{ mg L}^{-1}$ ,  $\text{Fe} = 17.0 \text{ mg L}^{-1}$ ,  $\text{S} = 1,100.0 \text{ mg L}^{-1}$ ) (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 Cavihue (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

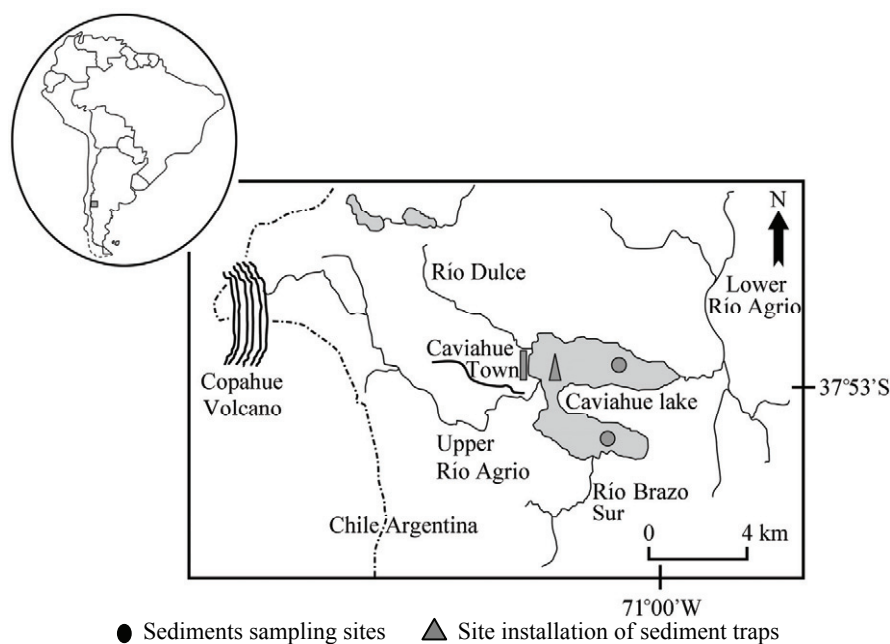
<sup>1</sup> Dr. INIBIOMA, Centro Regional Universitario Bariloche, Universidad Nacional del Comahue, CONICET, Quintral 1250, 8400 Bariloche, Argentina, E-mail: [pedro.temporetti@crub.uncoma.edu.ar](mailto:pedro.temporetti@crub.uncoma.edu.ar) or [ptempore@yahoo.com](mailto:ptempore@yahoo.com)

<sup>2</sup> Ing., Staff Environmental Engineer, Water and Environmental Technologies 480 East Park Street, Suite 200 Butte, MT59701, Montana, EEUU, E-mail: [kdraper@wet-llc.com](mailto:kdraper@wet-llc.com)

<sup>3</sup> Dr., INIBIOMA, Centro Regional Universitario Bariloche, Universidad Nacional del Comahue, CONICET, Quintral 1250, 8400 Bariloche, Argentina, E-mail: [Fernando.pedrozo@crub.uncoma.edu.ar](mailto:Fernando.pedrozo@crub.uncoma.edu.ar) or [fpedrozo@yahoo.com](mailto:fpedrozo@yahoo.com)

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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 alkalization.



**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

bodies, and its influence on trophic evolution.

The overall objective of this study was to evaluate the mechanisms controlling the fixation and/or release of P in the sediments of an extremely acidic lake, and the influence of urban waste water on the trophic condition, in order to assist in making decisions for conservation and management of this natural environment. Four specific objectives were raised: 1) characterize the chemical composition of pore water, bottom sediments and the sedimentary material collected by traps, 2) determine the changes in dissolved phosphorus concentrations due to the experimental variation of pH, 3) determine if under anoxic conditions, the control mechanisms of phosphorus in neutral lakes govern in acidic conditions, and 4) establish the existence of internal P loading processes similar to those described for the neutral lakes.

## 2 Materials and methods

Sediment cores were collected during austral summer season (02/14/2008) in the BN ( $z = 90$  m) and BS ( $z = 70$  m) (Fig. 1) with an Uwitec type corer of 6 cm in diameter. Sediment cores were sliced in 6 layers of 2 cm thickness until a depth of 12 cm. The pore water was extracted by centrifugation at 4000 rpm for 15 minutes from each sediment layer. Subsequently, each sample of sediment was transported in cold conditions to the laboratory where it was dried at 60°C and sieved through a mesh of 500  $\mu\text{m}$  (Newark, ASTM N° 36 U.S.A. Standard Series Sieves) to remove the less reactive coarse fraction. The pH and redox potential (Eh) (pH meter Orion 256) were measured *in situ* in each sample by using specific electrodes with temperature correction.

In order to evaluate the sedimentation rates, and the chemical and the mineralogical composition of the suspension sediment, four sediment traps were installed at the BN (70 m depth) directly in front of the delta of the Rio Agrio Superior (RAS) ( $37^{\circ} 52' 23.1''\text{S}$ ;  $71^{\circ} 02' 04.8''\text{W}$ ), the main tributary of the lake (Fig. 1). Each trap consisted of two acrylic tubes 60 cm long and 6 cm in external diameter (Blomquist and Håkanson, 1981). Sediment traps were located at 4 depths (10 m, 20 m, 55 m, 65 m) within the water column, taking into account the lake areas of erosion, transport and accumulation as defined by Håkanson and Jansson (1983). The sediment traps were installed between April and June 2008. After 70 days, the traps were removed and transported to the laboratory without exposure to light. The supernatant of each tube was extracted with a syringe, and the sediment was transported to the laboratory in cold and dark conditions. In the laboratory the material was dried in an oven at 60°C, the samples were weighed and stored in plastic containers until analysis.

### 2.1 Laboratory Analysis of pore water, sediment and sediment trap samples

#### 2.1.1 Pore water

Dissolved nutrients: Soluble reactive phosphorus (SRP), Ammonium ( $\text{N-NH}_4^+$ ) and Nitrate ( $\text{N-NO}_3^-$ ) were measured for each subsample of sediment pore water as filtered through 0.2 micron membrane filters. In all cases the methodology proposed by APHA (1992) was followed. Total elements: Ca,  $\text{SO}_4^{2-}$ , Al and Fe were analyzed on unfiltered subsamples by atomic absorption using a Perkin Elmer Analyst 100.

#### 2.1.2 Sediment and sediment trap samples

On the dried and sieved sediment samples, the following parameters were analyzed: Particle size analysis using the equipment Mastersizer 2000 optical unit, Hydro 2000 MV. Total Phosphorus (TP): a portion of sediment was digested with  $\text{SO}_4\text{H}_2$  and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) 30% (Carter, 1993). After digestion, the content of dissolved P was determined according to Murphy and Riley (1962). Total Carbon (TC): using an automatic analyzer Thermo Flash 1112. The mineralogy of settled material was determined by Rx mineralogy spectrometry (Phillips X Ray Generator PW 3719). The chemical characterization of sediments (Si, Al, Fe, Na, K, Mg, Ca, S, and P) was carried out by SEM-EDAX methodology. The different fractions of P were determined (only in sediment cores samples) according to the fractionation scheme proposed by Hietjes and Lijklema (1980) discriminating labile fractions (extraction  $\text{ClNH}_4$ ), together with the P bound to Fe/Al (NaOH extraction), P bound to Ca (HCl extraction) and P bound to organic matter (such as  $\text{TP} - \Sigma\text{P}\sim\text{Labil} + \text{P}\sim\text{Fe/Al} + \text{P}\sim\text{Ca}$ ). All chemical tests were performed in triplicate.

### 2.2 Laboratory experiments

In order to evaluate changes in the concentration of P in water and sediments on different conditions, the following experiments were designed.

#### 2.2.1 Influence of pH variations on dissolved phosphorus concentration

Incubations of sediment with un-filtered lake water (ratio 1:5) were carried out. The control (A) was carried out at the pH Cavihue Lake (2.9). The variation of pH was obtained in two ways. 1) By adding an alkaline standard solution ( $\text{CaCO}_3$ ): two experimental conditions, representing two different pH conditions: 6.0 (B) and 7.5 (C), were established, and 2) by adding a concentrated solution of liquid sewage (D). Throughout this process, it was only possible to define one experimental condition (pH 5.0), because of the buffering capacity produced when sewage was added to the lake water; a large volume of sewage was required to change one unit of pH. All the experiments lasted 13 days and were

performed in triplicate, in darkness at room temperature (20-21 °C). To prevent a sharp decrease in the oxygen concentration of the experiences, a manual stirring was performed once a daily. All measurements and analyses were performed once the system was stabilized. In the system water-sediment, electrical conductivity (EC), dissolved oxygen (DO), Eh, pH (specific electrodes) and TP, SRP, N-NH<sub>4</sub><sup>+</sup> concentrations (APHA, 1992) and SO<sub>4</sub><sup>2-</sup> (turbidimetry, SulfaVer 4, Method 8051, Hach commercial test), were measured at the beginning, on day 6 and at the end of the experiment.

### 2.2.2 Effect of anoxia in the control of the P in sediment

The internal load of P was studied by experiments simulating dissolved oxygen depletion: The incubations were performed, in triplicate, under two different conditions: 1) under high concentrations of DO (> 8 mg L<sup>-1</sup>) by bubbling with air and, 2) decreasing oxygen concentrations (< 1 mg L<sup>-1</sup>), to almost anoxic, by bubbling with nitrogen gas. Sediments were incubated with un-filtered lake water in a PVC tube 60 cm long and 10 cm in diameter. Each tube was filled with a sediment layer from 4 cm thick and 5 L of lake water (ratio 1.2:5.0). The diffusion of air and nitrogen in PVC tubes was performed to 50 cm above the sediment, in order to avoid disturbing the sediments with the bubbling. The duration of experience was 15 days, in darkness and room temperature (20-21 °C). In both situations, EC, DO, Eh, and pH were recorded daily. In all cases, the concentrations of SRP (APHA, 1992), SO<sub>4</sub><sup>2-</sup> (turbidimetry, SulfaVer 4, Method 8051, Hach commercial test), Total Fe (TFe) (Ferrover, Method 8008, Hach commercial test), Fe<sup>2+</sup> (1, 10 phenanthroline, Method 8146, Hach commercial test), Fe<sup>3+</sup> (calculated by difference between TFe and Fe<sup>2+</sup>) and SiO<sub>2</sub> (silicomolibdate Method 8185, Hach commercial test) were measured at the beginning and at the end of the experiment.

## 3 Results and Discussion

Table 1 shows the concentrations of nutrients and ions in the pore water measurements and comparisons with measurements in the water column (Pedrozo et al., 2008). The concentration of SRP in the pore water was similar in both lake arms (1.1 mg L<sup>-1</sup> in BN and 0.9 mg L<sup>-1</sup> in BS). On the other hand, the concentration of N-NH<sub>4</sub><sup>+</sup> was 1.6 times higher in the BN (9.6 mg L<sup>-1</sup>) than in the BS (5.9 mg L<sup>-1</sup>). The concentration of N-NO<sub>3</sub><sup>-</sup> was equal (0.2 mg L<sup>-1</sup>) in both arms. The ionic composition of both arms was SO<sub>4</sub><sup>2-</sup> >> Fe > Al > Ca, although the concentrations in the BN (458.0 mg L<sup>-1</sup>, 66.3 mg L<sup>-1</sup>, 40.2 mg L<sup>-1</sup> and 27.6 mg L<sup>-1</sup>, respectively) were between 0.7 and 0.9 times lower than in the BS (522.0 mg L<sup>-1</sup>, 92.9 mg L<sup>-1</sup>, 60.3 mg L<sup>-1</sup> and 31.5 mg L<sup>-1</sup>, respectively).

**Table 1** Chemical composition of pore water and column water in both arm of Lake Caviahue  
DIN: Dissolved inorganic nitrogen = NNH<sub>4</sub><sup>+</sup> + NNO<sub>3</sub><sup>-</sup>. (\*): from Pedrozo et al. (2008)

		Pore water		Column water (*)	
		North arm	South arm	North arm	South arm
SRP	mg L <sup>-1</sup>	1.1	0.9	0.21	0.24
DIN	mg L <sup>-1</sup>	9.8	6.1	0.15	0.08
Ca	mg L <sup>-1</sup>	27.6	31.5	21.0	18.4
SO <sub>4</sub> <sup>2-</sup>	mg L <sup>-1</sup>	458.0	522.0	281.0	2.80
Al	mg L <sup>-1</sup>	40.2	60.3	21.4	–
Fe	mg L <sup>-1</sup>	66.3	92.9	22.8	22.1

The amount of phosphorus in the pore water is generally a very small proportion (less than 1%) of TP content of the sediment (Boström et al., 1982). However, the phosphorus concentration in the pore water has been reported as considerably higher (5-20 times) than levels in the water column (Håkanson and Jansson, 1983). Our results show that nutrient concentrations in pore water were between 5 (SRP) and 100 times (DIN) higher than in the water column (Table 1). This sharp concentration gradient between the sediment-water interface has been seen to favor the diffusion of phosphorus from the sediment to the water column (Syers et al., 1973; Boström et al., 1982; Håkanson and Jansson, 1983).

The importance of texture lies in its inherent role as a means of description (e.g. fine sand, well-sorted silt, poorly-sorted mud) (Last, 2001). Knowledge of the texture of a lacustrine deposit is important because of its influence on other key properties of the sediment. On the other hand, the size distribution is important because smaller particles have greater specific surface area for pollutant adsorption (Lee-Hyung et al., 2003). Our results show that the clay fraction represented 5% of the total. The silt and fine sand fractions predominated in all groups, representing between 10 and 20% of the total. In this sense, the sediments of both arms are classified as sandy-loam soils. According to Golterman (2004) and Wang et al. (2006), the maximum P adsorption and the efficiency of this process, decrease with increasing particle size. Thus, the finest fractions have a greater capacity to adsorb contaminants. The textures of the core sediment in both arms of the lake (dominated mainly by medium to coarse texture fractions = 20 to 250 µm), indicate that the retention capacity of nutrients, especially P, should be low.

The element ratio in sediments (Table 2), was Si >> Al > S > Na > Fe > P > Ca > K > Mg in the BN and slightly different in the BS: Si >> Al > S > Fe > Na > P > Ca > K > Mg. In both arms, the SiO<sub>2</sub> (73.0%) was predominant in all layers whereas

aluminum oxides ranged between 11.4% (BN) and 12.0% (BS). The SO<sub>3</sub>, in both cores, accounted for 3.4% and 6.1% of total oxides. On the other hand, the relationship of the elements collected in sediment traps (Table 2), was slightly different than that found in sediments cores (Si>> Al> Fe> Na> S> Ca> Mg> P> K). The SiO<sub>2</sub> was predominant in all samples collected (58%), while SO<sub>3</sub> accounted for 2.5% of total oxides. The highest concentration of SiO<sub>2</sub> was recorded in the trap located at 65 m (67%), while the highest concentrations of Al<sub>2</sub>O<sub>3</sub> were recorded in the traps at 10 m (20%) and 55 m (19%). On the other hand, the highest percentages of contents of Fe<sub>2</sub>O<sub>3</sub> and SO<sub>3</sub> were recorded in traps located at 20 m (Fe<sub>2</sub>O<sub>3</sub> = 14% and SO<sub>3</sub> = 3%) and 55 m (Fe<sub>2</sub>O<sub>3</sub> = 16.5% and SO<sub>3</sub> = 4%). The highest percentage of P<sub>2</sub>O<sub>5</sub> content was found in the trap located at 55 m depth (3.6%).

The predominant rock type in the Cavihue area is andesitic lava and pyroclastic and is related to the dynamics of Andean volcanism (Pesce, 1989). However, Le Maitre (1976), analyzed the average composition of andesitic rocks (2600 analysis), which is shown in Table 2. The results obtained from the analyses carried out in this investigation in both the sediment corer and the material collected with sediment traps show a very good correlation ( $R^2 = 0.98$ ) with the composition of andesitic rocks.

**Table 2** Chemical composition (%) of sediment core, sediment traps and andesitic rock  
(1) Average for all strata; (2) Average for all traps and (3) From Le Maitre (1976)

	Sediment BN <sup>1</sup>	Sediment BS <sup>1</sup>	Sediment traps <sup>2</sup>	Andesitic rock <sup>3</sup>
SiO <sub>2</sub>	73.3	73.5	57.8	58.7
Al <sub>2</sub> O <sub>3</sub>	1.5	12.2	17.7	17.2
Fe <sub>2</sub> O <sub>3</sub>	2.4	2.5	10.8	3.3
SO <sub>3</sub>	6.1	3.5	2.5	0
MgO	0.7	0.8	1.9	3.4
CaO	1.1	1.7	2.3	6.9
Na <sub>2</sub> O	2.6	2.1	2.7	3.5
K <sub>2</sub> O	0.9	1.3	1.1	1.6
P <sub>2</sub> O <sub>5</sub>	1.3	1.8	1.6	0.2

The diversity of minerals in sediments is mainly controlled by the significant influence of the geology of the basin and soil composition (Last, 2001). In our investigation, mineralogical analysis of core sediments and material collected with sediment traps showed that the predominant minerals are: Andesite ((Na, Ca) (Si, Al) 4O<sub>8</sub>), Albite (Na (Si<sub>3</sub>Al) O<sub>8</sub>), Anorthite (Na (Al<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>) and Cristobalite (SiO<sub>2</sub>). These results indicate that the lake sediments are volcanic material supplied mainly by the Rio Agrio and reflect volcanic features of the basin.

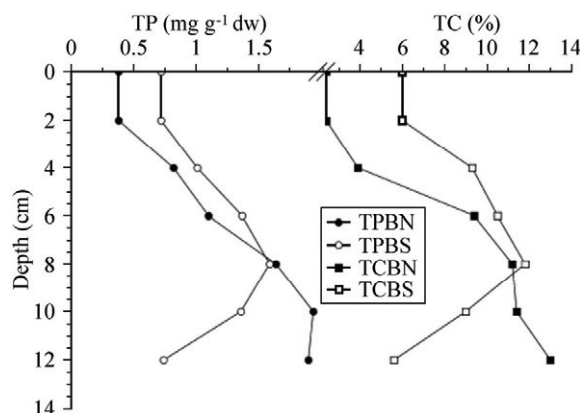
This contribution is also observed in the sedimentation rate calculated for the Lake Cavihue. The average sedimentation rate was of  $2.5 \times 10^{-2}$  mg m<sup>-2</sup> day<sup>-1</sup>. An increase in the rate of sedimentation was observed from the trap located at 10 m depth ( $1.5 \times 10^{-2}$  mg m<sup>-2</sup> day<sup>-1</sup>) to the deepest one at 65 m depth ( $3.8 \times 10^{-2}$  mg m<sup>-2</sup> day<sup>-1</sup>). The calculated sedimentation rates for Lake Cavihue were very high compared with those of other water bodies in the Andino-Patagonian Lake District (e.g., Lake Mascaradi,  $1.6 \times 10^{-4}$  to  $1.3\text{--}2.0 \times 10^{-6}$  mg m<sup>-2</sup> day<sup>-1</sup>, Villarroza et al., 2002) and some lakes with similar characteristics in other regions ( $2.3 \times 10^{-5}$  mg m<sup>-2</sup> day<sup>-1</sup>, Mawson et al., 1983, and  $2.2 \times 10^{-5}$  mg m<sup>-2</sup> day<sup>-1</sup>, Gasiorowsky, 2008).

TP concentrations found in the first 2 cm of sediment and associated organic matter (Fig. 2) can be explained by the deposition of living plankton due to drag mediated by volcanic ash from the eruption of the Copahue volcano which occurred in July 2000 (Pedrozo et al., 2008). This eruption resulted in an increase of suspended matter (mainly ashes) in the lake, with a decrease in water transparency and total phytoplankton biomass from 2.5 mg L<sup>-1</sup> (April 2000) to 0.3 mg L<sup>-1</sup> (February 2001), (Pedrozo et al., 2008). This mortality of phytoplankton involved the release of P and C at sediment. The increase in particulate matter and its subsequent deposition was observed (Pedrozo et al., 2010) in the surface layer of sediment cores taken in February 2001. The TP concentration in the core collected on the BN in February 2000 was 0.4 mg g<sup>-1</sup> dw, while in the same place, in February 2001, it was 0.7 mg g<sup>-1</sup> dw. On the other hand, the TP content in volcanic ash was low (0.09 to 0.13 mg g<sup>-1</sup> dw).

The profiles of TP and TC in core sediments are shown in Fig. 2. The concentration of TP for the BN ranged between 0.4 mg g<sup>-1</sup> dw (in the top tier) and 1.8 mg g<sup>-1</sup> dw (in the deeper layer) with a maximum of 1.9 mg g<sup>-1</sup> dw at 10 cm depth. On the other hand, for the BS, TP concentration was similar in the upper (0.7 mg g<sup>-1</sup> dw) and in the deeper layer (0.8 mg g<sup>-1</sup> dw), with a maximum of 1.6 mg g<sup>-1</sup> dw at 8 cm deep. The concentration of TC (Fig. 2) ranged from 2.4% on the surface and 13.0% at 12 cm depth in the BN and between 6.0% and 5.6% for the surface layer and deep layer respectively, in the BS. The maximum values of TC in the BN were recorded at 12 cm depth (13.0%) while maximum value in the BS was recorded at 8 cm depth (12.0%).

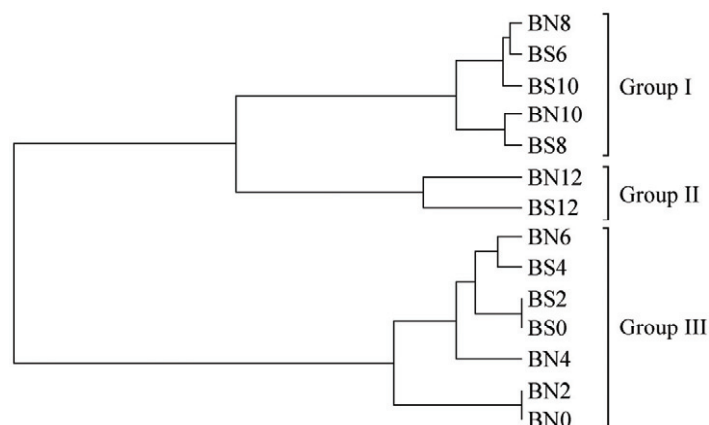
An increase of TP and TC from 0 to 10 cm depth of both arms was observed. Cayelan and Rydin (2011) propose that the distribution of P concentration with depth of sediment is related to the trophic state of the environment. They argue that the increase of P in sediment depth is characteristic of oligotrophic environments and can be explained by: a) the formation of P minerals associated with Al in the deeper layers, which can create P forms of low solubility product,

resulting in a flow of P to the oldest layers of sediment and b) an associated increase in P bond to oxyhydroxides of Al, which correlated well with the increase of the total Al concentration. The increase of Al at depth could be due to a decrease of the contribution of Al from the watershed or an increased load of organic material. The Al is associated permanently with P, increasing the P concentration at depth.



**Fig. 2** TP and TC Profiles of in the sediment cores (taken in 2008) of both arms

In this sense, we conducted a Principal Component Analysis (PCA) performed on the symmetric correlation matrix and an analysis of hierarchical classification. We used the following variables: TP, TC, P-Fe/Al, P-labile-P Organic, P-Ca,  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  as active variables and pH and Eh as illustrative variables. In all cases, the variables were continuous. Individuals were represented by all layers in the sediment. The results are shown in Fig. 3. The first two axes explain 81% of the variability of the data. Three groups were identified: Group I: represented by the layers from 0 cm to 6 cm in both arms and characterized by relatively low values of TP, TC, P-Fe/Al, P-Org. and P-labile. Group II: comprised of the deeper layers of both arms (12 cm), characterized by high percentages of  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  and Group III consisting of the intermediate layers (6 to 10 cm), characterized by high values of PT and P-Fe/Al. These results support the idea that Caviahue lake sediments represent sediment characteristic of oligotrophic environments.



**Fig. 3** Dendrogram illustrating similarity of the sediment compositions at different layers in both Arms

Table 3 shows the nutrient concentrations measured in the sedimentable material. A slight decrease in the concentration of TP from the trap located at 10 m ( $4.2 \text{ mg g}^{-1} \text{ dw}$ ) to that at 65 m ( $3.4 \text{ mg g}^{-1} \text{ dw}$ ), although not statistically significant, was observed. By contrast, an enrichment of TN was observed from the trap located more superficially ( $68.0 \text{ mg g}^{-1} \text{ dw}$ ) to the deepest ( $87.0 \text{ mg g}^{-1} \text{ dw}$ ), with a maximum of  $104.0 \text{ mg g}^{-1} \text{ dw}$  in the trap located at 20 m depth. With regard to TC, the concentrations in the four traps were similar, with an average of  $7.2 \text{ mg g}^{-1} \text{ dw}$ .

The sediment material collected at shallower depths such as at 10 m, has a higher content of TP which reflects the composition provided by the Rio Agrio Superior. Pedrozo and Diaz (2011) found a low N:P ( $= 0.1:1$ ) in the Upper Rio Agrio. However, the pellet collected in the sediments trap is influenced by the deposition of material due to growth of plankton native origin (especially at greater depths) which increases the N:P molar ratio (avg 36-57:1) (Table 3). Baffico (2005) determined the composition of microalgae in a core collected in 2003 in the North Arm, where six species of planktonic diatoms (PD) and 16 epilithic diatom species (ED) were recorded preserved in sediments, and estimated a rate PD:ED. This ratio was used by Batterbee (1986) as indicator of changes in productivity. Baffico (2005) suggested that the changes observed in this relationship could be associated with the P increases due to the mineralization of dead

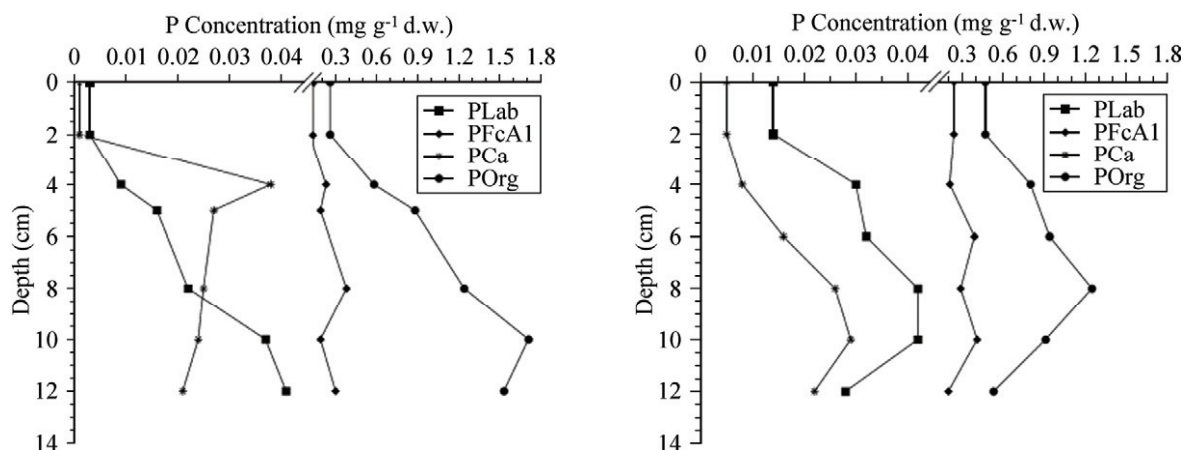


plankton after the eruption of July 2000. Pedrozo et al. (2008) reached a similar conclusion from the phytoplankton biomass loss in the water column. These authors found a net sink of 12 times after the eruption in terms of algae biomass. This nutrient enrichment in the sediments, especially P, may also be associated with a high rate of microbial activity found by Wendt-Potthoff and Koschorrek, (2002). After death, most of the plankton biomass is then reflected in the composition of pore water of sediments. In this, the concentration of SRP and inorganic N ( $\text{N-NH}_4^+$  was more than 90 % of DIN) in pore water was several times higher than those given by Pedrozo et al. (2008) for the water column (Table 1). This can be interpreted as mineralization processes which occur releasing nutrients that are maintained in solution in the pore water. It is remarkable that ammonium is 100 times more concentrated than in the water column. While the origin of dissolved P and N has some explanation from the volcano sources, as dissolved and/or linked to suspended solids (Pedrozo et al., 2008), the concentration of N as ammonium could only be explained by an autochthonous origin from plankton after death.

**Table 3** Molar concentrations of nutrient and molar ratios measured in the material collected with sediment traps

	Trap 10m	Trap 20m	Trap 55m	Trap 65m
TP	0.14	0.13	0.13	0.11
TN	4.86	7.43	5.86	6.21
TC	0.58	0.67	0.58	0.58
TN:TP	36	56	45	57
TC:TP	4	5	5	5

The fractionation of P in sediments of both arms is shown in Fig. 4 (a and b). The main fraction of P was linked to organic matter for both arms. In the BN (Fig. 4a), this fraction ranged between  $0.3 \text{ mg g}^{-1} \text{ dw}$  in the top and  $1.5 \text{ mg g}^{-1} \text{ dw}$  in deeper strata with a maximum at 10 cm depth of  $1.7 \text{ mg g}^{-1} \text{ dw}$ . For the BS (Fig. 4b), the maximum concentration of P bound to organic matter was  $1.2 \text{ mg g}^{-1} \text{ dw}$  (at 8 cm layer), varying between  $0.5 \text{ mg g}^{-1} \text{ dw}$  and  $0.6 \text{ mg g}^{-1} \text{ dw}$  in the upper and deep layers, respectively. A good correlation was obtained for both arms, between the TP and TC ( $r^2 = 0.95$  for the BN and  $r^2 = 0.96$  for the BS). The fraction of P bound to oxihydroxides of Fe and Al ranged from  $0.1 \text{ mg g}^{-1} \text{ dw}$  (in the top layer) and  $0.3 \text{ mg g}^{-1} \text{ dw}$  (in the layer of 12 cm depth) for the BN and between  $0.2 \text{ mg g}^{-1} \text{ dw}$  (in the surface layer) and  $0.1 \text{ mg g}^{-1} \text{ dw}$  (at 12 cm depth) for the BS. Maximum concentration of this fraction was recorded at 8 cm depth in the BN ( $0.4 \text{ mg g}^{-1} \text{ dw}$ ) and 10 cm deep in the BS ( $0.4 \text{ mg g}^{-1} \text{ dw}$ ). The P-labil fraction and the P-Ca fraction represented a low percentage of the TP. The P-labil fraction represented, on average, only 1.4% of TP ( $0.02 \text{ mg g}^{-1} \text{ dw}$ ) in the BN and 2.7% of TP ( $0.03 \text{ mg g}^{-1} \text{ dw}$ ) in the BS, while the P fraction bound to Ca compounds represented, on average, 1.7% ( $0.02 \text{ mg g}^{-1} \text{ dw}$ ) and 1.5% ( $0.01 \text{ mg g}^{-1} \text{ dw}$ ) for the BN and BS, respectively.



**Fig. 4** Phosphorus fractions profiles in: north arm (A) and south arm (B)

These results indicate that organic matter is the main factor controlling P retention in sediments of this environment. This organic matter would, mainly, be of autochthonous origin produced by the sedimentation of dead phytoplankton and a lower proportion of fine-grained mineral material. These results are corroborated by the concentrations of N and C that were found in the material collected by the sediment traps (Table 3), which showed an enrichment of these nutrients between the traps located on the surface (10 m) and on the bottom (65 m).

The phosphorus adsorption to organic matter is very strong and is probably a result of the union of P with  $\text{Fe}^{3+}$  chelated compounds with humic complexes (Boström et al., 1982). In addition, Satoh et al. (2006) argues that ferric ion is expected to co-precipitate with dissolved substances and negatively charged colloids, such as organic matter. This process is pH dependent and has its optimum pH of 4.8-5.0. On the other hand, according to Friese et al. (1998), under conditions of extreme pH and high concentrations of metals, such as those seen in Lake Cavihue (Gammons et al.,

2005; Pedrozo et al., 2008), it is expected that the degradation of organic matter can be inhibited. The pH in Caviahue sediments increases with depth (Fig. 5). In the BN, the pH ranged from 2.67 in the surface layer and 3.19 at 12 cm depth, while in the BS, the pH ranged between 2.53 and 2.76 on the surface to 12 cm deep. On the other hand, the anoxic condition can increase the P that could be attributed to the redissolution of ferric-phosphate salts, because low redox conditions promotes a reduction of the  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  and consequently, the P is released from ferric salts.

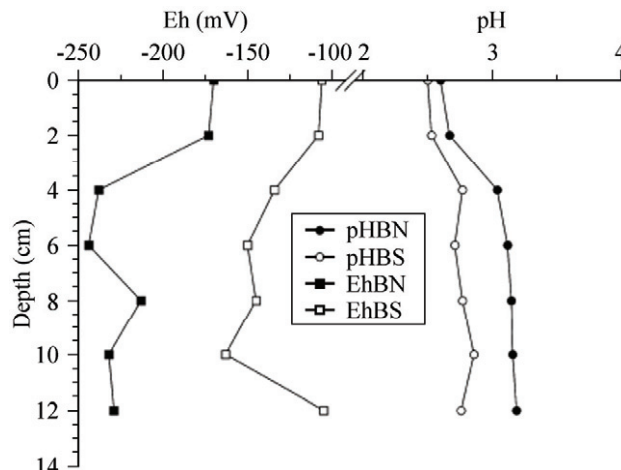


Fig. 5 Variation of pH and Eh in cores of the two arms of the lake Caviahue

Our experience in anoxic conditions ( $0.9 \text{ mgO}_2 \text{ L}^{-1}$ ) showed no change in pH (3.0) or EC ( $1,100 \text{ mS cm}^{-1}$ ) compared with those under high conditions of oxygen ( $7.1 \text{ mgO}_2 \text{ L}^{-1}$ ). pH and EC were on average similar to those observed in the water column of Lake Caviahue.

The experiences in anoxic conditions in comparison to aerobic ones showed a continuous release of dissolved P (78 %) (Fig. 6) and an increase (25 %) in the concentration of TFe ( $23 \text{ mg L}^{-1}$ ). This may be explained by the presence of  $\text{Fe}^{2+}$ . This situation, only in part, is similar to that expected in neutral environments under the influence of anoxia because only ferrous iron showed an increase linked to the release of P. There were no changes in the concentrations of  $\text{SO}_4^{2-}$  ( $363.3 \text{ mg L}^{-1}$ ) and Si ( $15.2 \text{ mg L}^{-1}$ ). To assess whether simple diffusion may have contributed to a concentration of base, an experiment was designed with sediment and de-ionized water. In all cases, the final concentrations at the equilibrium for TFe, Si and  $\text{SO}_4^{2-}$  were similar to those found in the experiments without anoxia.

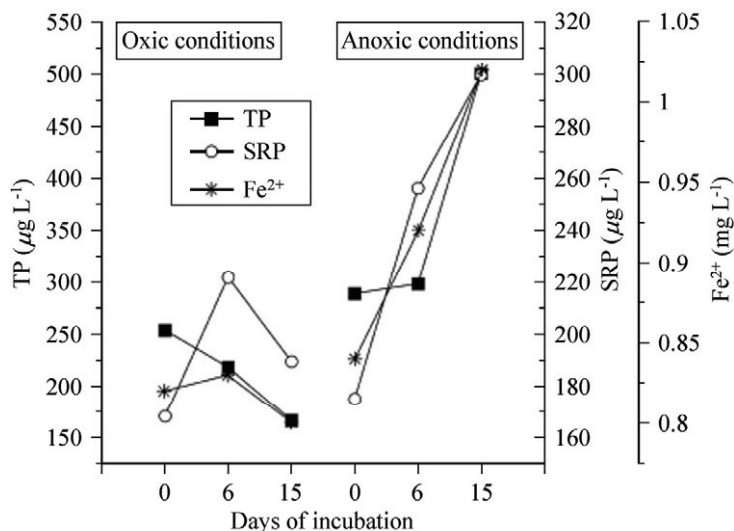


Fig. 6 TP, SRP and  $\text{Fe}^{2+}$  variations in Oxic and Anoxic experiences

Moreover, in the mining lakes, Hupfer et al. (1998) reported that P is bound mainly to the fraction associated with oxides and hydroxides of iron and aluminum, which means that these elements control the P retention in sediments. In Lake Caviahue, the second most important fraction of P was associated with Fe and Al compounds, which, acting in relation to organic matter controlled the adsorption of P in the sediment. This interpretation is related to the relatively high concentrations of iron oxides and aluminum measured in the sediments.



The pH values in the sediments of both arms of Lake Cavihue showed an increase in depth (Fig. 5). Besides that, our results showed a good regression between pH and TP (Fig. 2) ( $R^2 = 0.78$ ,  $p < 0.0001$ ) and between pH and the fraction (Fig. 4) of phosphorus bound to Fe/Al ( $R^2 = 0.56$ ,  $p < 0.0001$ ). According to Golterman (2004), this relationship is to expected, due to the fact that the P-adsorption capacity of Fe (OOH) decreases when the increase in the pH values is in the range 7.1-9.0. However, in the acid sediment conditions of Lake Cavihue, the increase of pH from 2.5 to 3.0 promotes the formation of  $\text{Fe}^{3+}$  which increases the P-adsorption capacity. Similar results were found by Friese et al. (1998) in acid mine lakes (East Germany) also as a result of precipitation of oxides and hydroxides of iron and the consequently adsorption of P associated with them.

On the other hand, Eh values for both arms were low and negative, ranging from -173 mV to -229 mV in BN and -109 mV to -105 mV for the BS, with a lowest value of -238 mV at 4 cm deep (BN) and -163 mV at 10 cm depth (BS) (Fig. 5). According to Li et al. (2007), the presence of  $\text{Fe}^{2+}$  and compounds of S, were unfavorable for the retention of phosphorus in the sediments that were analyzed by them. These authors found that when the redox potential was below -200 mV, a higher concentration of PRS was observed in the pore water (in Cavihue the PRS in the pore water was: 1.1 mg/L in BN and 0.9 mg/L in BS). They explain that the sediments had less capacity to retain P, suggesting that the reduction of organic substances, rather than pairs of oxidation-reduction, such as sulfur/sulfate or  $\text{Fe}^{2+}/\text{Fe}^{3+}$ , dominated to lower redox potential in sediment and that the presence of these compounds or ions significantly decreased the adsorption capacity of sediment P.

The Eh values showed a decline to the depth of the layer measured (Fig. 5) due to the mineralization of organic matter which consumes dissolved oxygen and acidity of the medium. The increase in mineralization also coincides with a higher percentage of P bond to OM. The molar C:P ratios of sediments (168 to 203) in this study were much higher than those of seston (C:P = 4-5:1) collected in the traps, which turned out to be very low compared with those obtained Hoshstadter (2000) for seston in Lake Constance (C:P molar = 180-460). This is because this new material is live planktonic seston which contains material of allochthonous origin, highly rich in volcanic inorganic P transported by the RAS. Hessen (2006) explains that detritus seston typically is richer in C than P, compared with live seston. Moreover, the C:P ratio in the sediments is slightly lower than the average (C:P molar = 270) given by Sterner and Elser (2002) for many lakes in the Northern Hemisphere, probably due to low mineralization in the bottom acid conditions of Lake Cavihue. Surprisingly, values are half the given values ratio (C:P molar = 524) for acid mine lakes (average value calculated from data from Geller et al., 1998). An external supply of P would decrease the C:P ratio in the seston which may also be explained by the entry of P of human origin from the North Arm sewage affluent. In this regard, the C:P molar ratio (168:1) in the North Arm was significantly lower than in the South arm (203:1). The low light transparency (Secchi disk = 2.6 to 3.8 m) in Lake Cavihue and the high P concentration, from natural volcanic origin and human sources, could also be determinant of low C:P ratio as has been observed in a large survey of Norwegian lakes by Hessen (2006). Reynolds (1997) considers that when the C:P molar ratio is less than 133:1, there is no P deficiency as a nutritional requirement for phytoplankton. The low values of C:P and C:N ratios in the seston of Lake Cavihue indicate that P is not limiting the phytoplankton, which is in accordance with previous results of Beamud et al. (2007) and Pedrozo et al. (2008), in which it was observed that the limiting nutrient is nitrogen.

On the other hand, the results of the sediment experiments with differing P concentrations showed that the system did not comply with either of the two equations proposed (Freundlich and Langmuir), instead, in all cases there was a continuous release of P from sediment to the solution (Fig. 7).

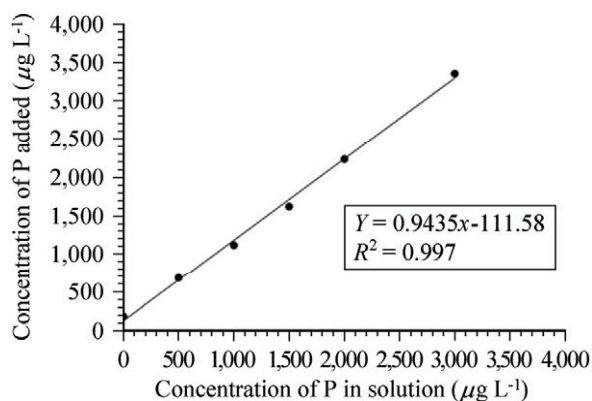


Fig. 7 Incubation of sediments with different concentrations of phosphorus

The pH values in the experiment with the addition of  $\text{CO}_3\text{Ca}$  were similar, and remained within the range of pH originally established (Table 4: B: pH 5.0-6.0 and C: pH 6.8-7.5). The EC was constant throughout the whole experiment ( $977 \mu\text{S cm}^{-1}$  for the control experimental pH = 3.0;  $694 \mu\text{S cm}^{-1}$  for the experimental pH = 6.0 and  $855 \mu\text{S cm}^{-1}$  for the situation experimental pH = 7.5) (Table 4). There was a decrease in DO in the whole experiment from 7.4

mg L<sup>-1</sup> (t = 0) to 4.5 mg L<sup>-1</sup> (t = 13) for the three pH conditions, probably due to bacterial activity (Table 4).

For the control test (Table 4A) in which the pH was kept very low (pH < 3.0), the concentrations of TP were constant throughout the experiments and resembled the natural conditions of the lake. The SRP concentrations were initially affected by the lake water addition which decreased the values. We have no explanation for the sharp initial decline of SRP. At the end of the experiments the remaining acidity from sediments re-solubilized P. The SRP content was similar to those in natural lakes where P dissolved is around 90% of total P. In the case of N-NH<sub>4</sub><sup>+</sup>, the highest concentrations were observed in the pore water sediments rather than in the water column. The addition of lake water re-suspended the sediments and a sudden release of N-NH<sub>4</sub><sup>+</sup> was observed as well as a decrease at the end of the experiments to similar lake concentration. On the other hand, there was a decrease (70%) in the concentration of N-NH<sub>4</sub><sup>+</sup> along the whole experience. Furthermore, there was a decrease (6%) in the concentration of TP in the first 6 days of incubation but this increased by 11% at the end of the experiment (Table 4).

Trials with the addition CaCO<sub>3</sub> to pH 5.0-6.0 (Table 4B) showed a significant decrease (25 to 75%) in the concentrations of SRP and an increase in the concentration of N-NH<sub>4</sub><sup>+</sup> (approximately 5 times) with respect to the control experiment (Table 4A). Similar results were observed in the tests performed adding CaCO<sub>3</sub> to pH 7.0-7.5 (Table 4C) although in this case, the decrease in the concentration of SRP was greater than 50% and increased concentrations of N-NH<sub>4</sub><sup>+</sup> was between 2.3 and 11 times more with respect to the control experiment (Table 4A). Addition of CaCO<sub>3</sub> promotes the precipitation of dissolved P bound to the Ca and the decrease in the DO concentration favors the increase of the concentration of N-NH<sub>4</sub><sup>+</sup>.

**Table 4** Effect of change of pH on concentrations (mean values) of phosphorous (total and soluble reactive), ammonia and sulphate. Incubations of sediments and lake water: A) Control; B) CO<sub>3</sub>Ca addition until pH 5.0-6.0; C) CO<sub>3</sub>Ca addition until pH 7.0-7.5 and D) sewage addition until pH 5.0-6.0)

	pH	EC (μS cm <sup>-1</sup> )	DO (mg L <sup>-1</sup> )	TP (μg L <sup>-1</sup> )	SRP (μg L <sup>-1</sup> )	N – NH <sub>4</sub> <sup>+</sup> (μg L <sup>-1</sup> )	SO <sub>4</sub> <sup>2+</sup> (mg L <sup>-1</sup> )
<b>A</b>							
Day 0	2.96	981.2	7.6	234	70	407	240
Day 6	2.88	978.5	5.4	221	115	367	254
Day 13	2.88	971.5	4.4	246	235	120	269
<b>B</b>							
Day 0	5.64	729.3	7.2	128	51	325	240
Day 6	6.05	682.5	6.5	125	28	–	264
Day 13	6.13	672.0	4.6	165	134	623	269
<b>C</b>							
Day 0	6.82	849.1	7.2	65	19	902	242
Day 6	7.15	825.0	5.0	153	60	960	248
Day 13	7.43	810.5	4.8	–	56	1,320	260
<b>D</b>							
Day 0	4.73	502.5	4.8	825	160	8,639	168
Day 6	5.34	457.3	5.0	343	133	9,585	127
Day 13	3.93	495.0	6.4	358	235	8,168	147

Overall, it was observed that in the control test, the dissolved P represented a significant fraction of TP (50 to 90%, Table 4A). The variation in the percentages of P in the experiments was due to the periodic agitation of the incubations, which provided a greater amount of this nutrient in particulate form. The SRP concentration increased towards the end of the experience but correlated with the decrease in DO, a phenomenon common to all trials. The concentration of N-NH<sub>4</sub><sup>+</sup> also showed a similar pattern, helped by a lower DO.

The addition of sewage water (Table 4D) involved a 20-fold increase in initial concentration of ammonium (8,639 μg L<sup>-1</sup>) and 4 times that of TP (825 μg L<sup>-1</sup>). This condition was expected since both are major components in urban wastewater (TP = 36.9 mg L<sup>-1</sup>, SRP = 7.2 mg L<sup>-1</sup>, N-NH<sub>4</sub><sup>+</sup> = 19.5 mg L<sup>-1</sup>) in Cavihue town. The proportion of dissolved P in relation to the TP on both day 6 and 13 varied between 39 and 65 % (Table 4D). The liquid sewage in the first instance had a dilution effect which reduces the concentration of SRP. The liquid sewage lacks enough buffer capacity to balance the acidity which is released from the sediments, and which ultimately increased the concentration of dissolved P by the end of the experiment.

The sulphate concentrations behaved independently of changes in pH in both experimental conditions (by the addition of CO<sub>3</sub>Ca or liquid sewage). In all scenarios tested, it was observed that SO<sub>4</sub><sup>2-</sup> concentrations were within the range (250 mg L<sup>-1</sup>) of concentrations found in the lake naturally (470 mg L<sup>-1</sup>) (Table 1) except in D experiences where sulfates were diluted to half.

The experiment under pH variation showed a high proportion of dissolved P (50-90%) compared to TP concentration, which indicates that for the pH values examined, the P still remained in solution. This was also observed in the lake and

its main tributary (RAS), (Pedrozo et al., 2008). It shows that the dissolved P fraction is the majority and that the addition of sewage water provides more P in solution with low buffering capacity. From day 13 of incubation in our experiments, the dissolved P had an inverse relationship with pH. On the other hand, the concentration of  $\text{N-NH}_4^+$  remained constant and this can be entirely explained by the simple addition of liquid sewage. The artificial addition of calcite produces the precipitation of calcium-P salts and consequently decreases the EC. Besides, the increase of the pH correlates with the ammonium concentration, as its ionic specie prevails at high pH.

In this sense, the changes in the natural input of nutrients due to derivatives of Copahue volcano fluid, the discharge of sewage, or "leaching" of the basin, to the threshold of neutral pH, maintain a high concentration of SRP and  $\text{N-NH}_4^+$ . On the other hand, Caraco et al. (1989) postulated that in addition to the concentration of dissolved oxygen, the sulfates also have an important influence on the release of phosphorus from the sediments. Of all the variables that were tested, they found that the only significant predictor which showed a correlation, irrespective of oxygen concentrations in the hypolimnion water, was the concentration of sulfates in the water column. This suggests that sulfates can play an important role in the control of fixation and release of phosphorus from the sediments as they compete with this nutrient by the adsorption sites. The effect of inhibiting competition for adsorption sites between sulfates and P could not be established for this range of pH. However, according to Li et al., (2007), high concentrations of  $\text{SO}_4^{2-}$  indicate a large amount of S on the surface of the sediment that may affect the adsorption capacity of P to them. In Lake Caviahue,  $\text{SO}_4^{2-}$  concentrations in the water column and pore water (Table 1) were similar. On the other hand, from our results, we also conclude that the hypothesis of Caraco et al., (1989), is limited to neutral or alkaline pH environment and that both by anoxia or simple diffusion (eg, mechanical agitation), Lake Caviahue can show an internal load of P.

#### 4 Conclusions

The lake sedimentation rates in Lake Caviahue were higher than recorded in other environments of Patagonia and other parts of the world, and sedimentary deposits reflected the volcanic nature of the basin. The enrichment of organic matter in both sediments and in the material collected by sediment traps was mainly autochthonous in origin, produced by the sedimentation of dead phytoplankton and to a lesser extent by detrital mineral material of fine grain. The low values of C:P and C:N ratios in the seston of Lake Caviahue indicate that P is not limiting for the phytoplankton. Laboratory experiments showed that changes in the natural input of nutrients (due to volcanic fluid, the discharge of sewage, or "leaching" of the basin) maintain a high concentration of SRP and  $\text{N-NH}_4^+$  at least to the threshold of neutral pH. These results suggest the hypothesis that P and iron co-precipitate with increasing pH. The factor that controlled the retention of phosphorus in lake sediments in both arms was the availability of organic matter, iron and aluminum, which were found in very high concentrations due to low pH in sediments. This type of control mechanisms observed in this environment is different to that reported by Hupfer et al., (1998) for mining lakes, in which the only explanation for P control is by Al/Fe oxy-hydroxides. We concluded that the Fe or Fe chelated to organic matter could control P fixation/release. On the other hand, the P control in Lake Caviahue has some similarities with those mechanism observed in sediments of other Patagonian lakes with near neutral pH, where the Ca is very low and Fe and OM are the main control of P (Temporetti 1991, 1998). It was shown that under low pH conditions, as in Lake Caviahue, the phenomenon of internal loading should occur, similar to that found in sediments affected by human activities. On the other hand, the increase of P and OM concentrations observed in the sediments of both arms is typical of the sediments of oligotrophic environments. According to the concentrations of phosphorus in solution, the lake could be classified as mesotrophic. The condition of extreme acidity in the water column, maintains high dissolved phosphorus concentrations. However, according to the distribution of this nutrient in sediments, the lake trophic status should be oligotrophic. The slightly higher pH of the sediments, with high concentration of organic matter, Fe and Al ensure that the P, in the deeper layers, is retained and there is no release into the water column. In this sense, our results indicate that sediments in this environment are the best descriptor of the trophic state of the lake.

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