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# The Trophic State of Patagonian Argentinean Lakes and its Relationship with Depth Distribution in Sediment Phosphorus

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**ABSTRACT:** The parameters used to determine the trophic state of a water body are: total phosphorus (TP), transparency (Secchi disk depth) and chlorophyll ***a***. However, these parameters show strong seasonal fluctuations which may hinder the estimation of trophic state. Some authors have proposed that sediments be used as an additional tool to evaluate the trophic state of a water body. The aim of this study was to determine the depth distribution of sediment TP in relation with the lake trophic state. Nine sediment corers from water bodies located in Patagonian Region (Argentina) were studied. The nutrient concentrations in pore water and in sediments were analyzed. The results obtained showed that there is a relationship between the depth distribution of sediment TP and the trophic state for all studied environments. Two exceptions were noted to this general pattern (Lakes Caviahue and Lácar). Our findings indicate that both pore water and sediments could be considered as the best parameters to estimate the tropic state of a water body compared to the water column.

**Key words:** Sediments, Trophic evaluation, Lakes and reservoirs, Pore water, Total phosphorus

## INTRODUCTION

Eutrophication of a water body is defined as the process of adding excess inorganic nutrients (phosphorus (P), nitrogen (N)) and organic matter leading to an increase in the biological production (Sinke 1992). This process, which has created significant environmental problems, has been extensively studied (Wetzel 2001; Golterman 2004). Phosphorus is a key nutrient in eutrophication processes and, in many cases, the limiting nutrient in various water bodies (Wetzel 2001; Schindler *et al.,* 2008). Furthermore, water-column nutrient concentrations are the main parameter used to classify water bodies into trophic states (OECD 1981; Horne and Goldman 1994; Wetzel 2001; Schindler *et al.,* 2008). The main sources of P input to a water body comprise external (precipitation, runoff, industrial and wastewater effluents) and internal (bottom sediments) sources (Horne and Goldman 1994; Wetzel 2001; Kaiseli *et al.,* 2002; Golterman 2004). The latter source may often determine the eutrophication process even when external sources have been reduced (Carpenter 2005). In this regard, sediments play an essential role in the processes of transformation and accumulation of P in aquatic systems (Kowalczewska-Madura *et al.,* 2007). Boström *et al.* (1988) observed that in the surface sediment layer there is an interaction at the sediment-water interface, which can increase the P flux from the sediment to the water column when conditions are favorable for the desorption of this nutrient. Under aerobic conditions, the P concentration at the interface is generally lower compared with the P concentration in the surface sediment layer (Van der Molen *et al.,* 1988), and P is retained in the surface layer. This situation is reversed when the redox potential decreases and the P flux from the sediment to the water column increases. According to Gao *et al.* (2005), the P concentration in sediments depends on several factors such as trophic state, sediment composition, sedimentation rates and physicochemical conditions thereof.

The parameters used to determine the trophic state of a water body are: total phosphorus (TP), transparency (Secchi disk depth) and chlorophyll ***a***. However, these parameters show strong seasonal fluctuations that may hinder the estimation of trophic state (Maassen *et al.,* 2005). Several studies have linked the TP concentration in the surface sediment

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layer to the water column (Håkanson 2003; Carpenter 2005), supported by the concept that trophic state can be substantially influenced by the release of P from the sediments (Carey and Rydin 2011). Maassen *et al.* (2005) showed that pore water can influence the water body trophic state because of the presence of usually high concentrations of soluble reactive phosphorus (SRP), alkalinity and ammonium. Moreover, there are other parameters that affect the trophic state of an aquatic environment which are linked to the sediment, such as the ratios of iron (Fe) to P (Fe:P) and aluminium (Al) to P(Al:P), and sediment P fractions. These authors propose that sediments can be used as an additional tool to evaluate the water body trophic state. Although they did not find a direct relationship between the sediment TP and the water column TP, they suggest that the surface sediment layer TP represents the P of the settled particles from the water column and not the P of diagenetic processes occurring in the sediment (Golterman 2001). Carey and Rydin (2011) suggest that, to determine the relationship between the sediment P and the water column, it is necessary to compare the TP concentration in the surface sediment layer with a reference concentration, or the TP concentration at which diagenetic processes in the sediment are stabilized. These authors call "stabilization point" (SP) to the depth at which the sediment TP becomes constant. SP is dependent on sedimentation rates, which are determined by external and internal loading, resuspension and internal focusing of sediments (Søndergaard *et al.,* 1993; 1996; Weyhenmeyer *et al.,* 1997). Above the SP values, the mobile P is released into the water column while below the SP, the P remains trapped (Håkanson 2003). In this regard, the release of P to the water column in oligotrophic lakes is significantly less than that in eutrophic lakes (Nurnberg *et al.,* 1986). Carey and Rydin (2011) analyzed a database of 94 lakes (oligotrophic, mesotrophic and eutrophic) in North America and Europe. They hypothesize that TP depth patterns in lake sediments can vary significantly between oligotrophic and eutrophic environments, which may explain the trophic state of aquatic environments.

The aim of this study was to determine the depth distribution of sediment TP in Patagonian Argentinean lakes in relation with their trophic state.

## MATERIALS & METHODS

The water bodies considered in this study are distributed between 35° and 50° S and 40° and 72° W (Fig. 1). Most of them (8 lakes) are located in the Patagonian region, and only one reservoir at the south of Mendoza province (site 1). The Patagonian region can be divided into two sub-regions: Patagonian Andes and Patagonian Steppe (De Aparicio and Difrieri 1985). The soils in this region, derived primarily from volcanic ash, are poorly developed and rich in allophones. In contrast, the Patagonian steppe soils are typically alkaline with high salt content, negative water balance and dominant salinization. Water bodies in the Patagonian Andes are of glacial origin, chemically poor and, in general, dominated by silica (Pedrozo *et al.,* 1993). According to Quirós and Drago (1985), the Patagonian lakes have been classified as warm monomictic, with a stratification period during the summer. The climate in the Andean-Patagonian region is continental, classified as humid cold temperate in the mountain Andes to arid in the steppe region (Speck *et al.,* 1982). Periods of rain occur primarily between late winter and early spring. Due to the loss of moisture from the prevailing western winds, a strong west-east gradient in annual rainfall is found, ranging from 2700 mm/year at the Argentine-Chilean border (altitude 1020 m) to 500 mm/year in the Patagonian steppe (800 m) within a distance of only 50 km to the east. The average annual temperature varies between 20 °C at high altitudes (above 2000 m) and 8.0 °C in protected valleys, and between 7.5 and 12.5 °C in the Patagonian steppe. Table 1 shows the physical and chemical parameters, trophic classification and history, of the 9 environments studied (8 lakes and 1 reservoir). The surfaces ranged from 0.6 to 1892.0 $km^2$, while the maximum depths ranged from 5 to 550 m. The selected environments are located in a pH gradient from 2.50 (Lake Caviahue) to 9.21 (Lake Cardiel). According to the TP concentration in the water column, the environments are classified as oligotrophic (TP <10 µgP/L), mesotrophic (TP between 10 and < 30 µgP/L) and eutrophic (TP > 30 µgP/L) (Table 1). The sediment cores were extracted between 2006 and 2008 using a Uwitec-type corer with a diameter of 6 cm at depths ranging from 5 m to 20 m with the exception of Lake Caviahue (90 m) (Table 1). Each core was cut into layers of 2 cm thickness from the surface and up to 14 cm depth. Immediately after cutting them, the pH and redox potential (ORP) were measured in each layer using an Orion 920 A specific electrode with automatic temperature compensation.

Pore water was removed from each layer of sediment by centrifugation at 4000 rpm for 15 minutes. The supernatant was removed and filtered through membrane filters of 0.45 µm pore. Each fraction obtained was integrated into a single sample for each of the cores collected, kept in the dark and refrigerated, and taken to the laboratory. Similarly, each sediment sample was also transferred to the laboratory where they were dried at 60 °C, homogenized in ceramic mortar and sieved through a 500 µm sieve (Newark, ASTM N 36 USA Standard Series Sieves) to remove less reactive fractions. Pore water samples were analyzed for soluble

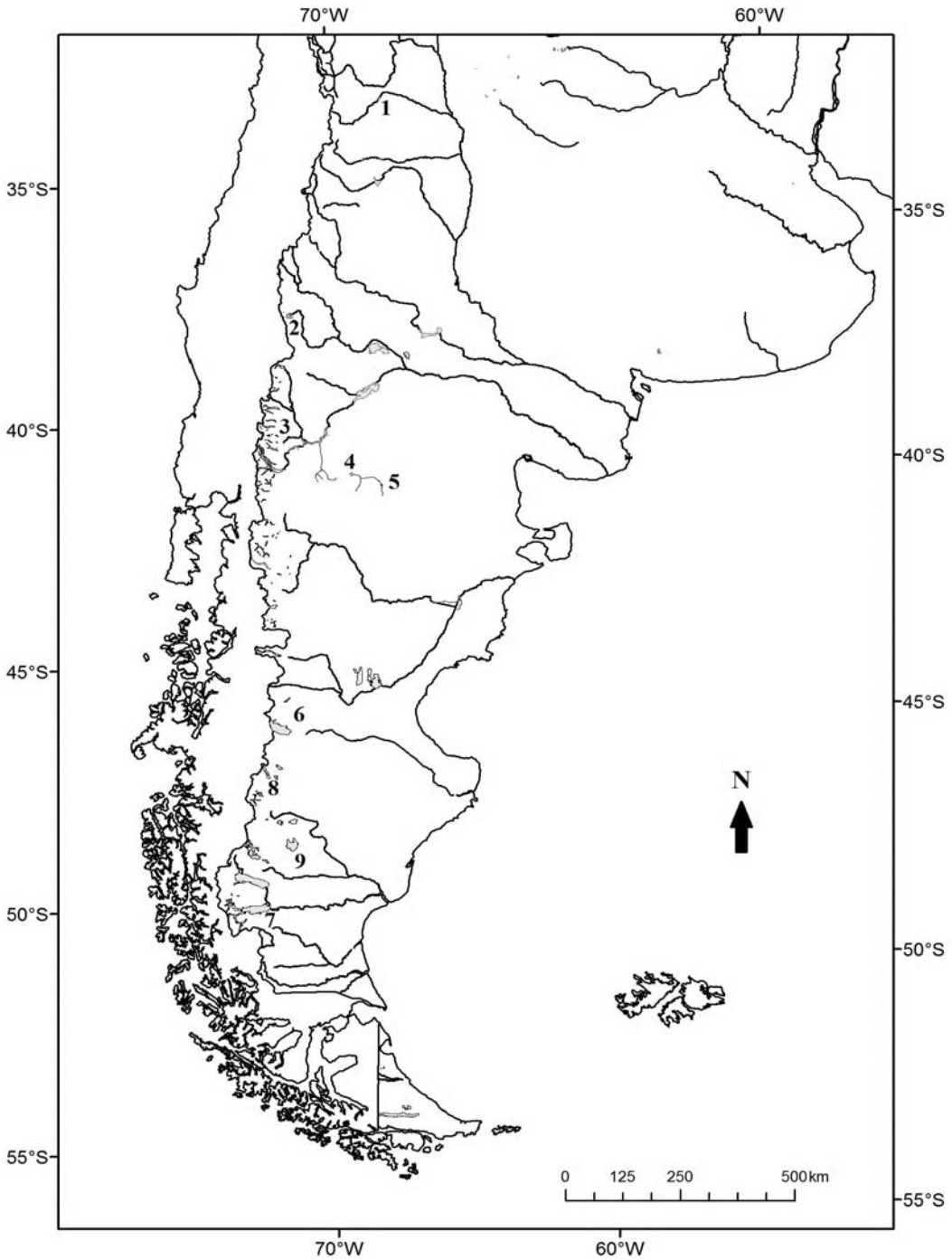


**Fig. 1. Location of sampling sites**

reactive phosphorus (SRP) and ammonium (N-$NH_4^+$), in compliance with APHA (1995). Dried sediment samples were analyzed for the following parameters: **a)** Total phosphorus (TP): a sediment fraction was digested with $SO_4H_2$ and 30% hydrogen peroxide ($H_2O_2$) (Carter 1993). After digestion, the dissolved P was determined by the Murphy and Riley method (1962). **b)** Chemical characterization of sediments: silica (Si), Al, Fe, sodium (Na), potassium (K), magnesium (Mg), calcium (Ca), titanium (Ti), (expressed as oxides of each element) was determined by the SEM-EDAX method (Last, 2001; Saarinen and Petterson, 2001). The Fe and Al concentrations were estimated from the concentrations of the respective oxides. **c)** Different P

**Table 1. Geographic position, morphometric date, physic and chemical parameters, and trophic classification for the 9 lakes analyzed. Zmax: Maximum depth of water bodies, SD: Secchi Disk; Water EC: Electric conductivity of water, Water TP: Total Phosphorus concentration in water, Water SRP: Soluble phosphorus reactive concentration in water, Chlo-a: Chlrophyll a concentration. (Dates from: 1) Baffico *et al.*, 2007; 2) Pedrozo *et al.*, 2001; 2010; 3) Temporetti *et al.*, 2009; 4) Macchi *et al.*, 2001; 5) Pedrozo 2006).**

| | Geographic location | Altitud (m.a.s.l) | Area $Km^2$ | Zmax (m) | Sediment core extraction depth (m) | SD (m)* | pH | Water EC (µS/cm) | Water TP (µg/L) | Water SRP (µg/L) | Chlo-a ($mg/m^3$) | Trophic state | Eutrophication history |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Pueyrredón[5] | 47º 26' 20.2'' S 71º 55' 18.4'' W | 112 | 320.0 | 280 | 10 | 8.0 | 8.30 | 174 | 2 | 0.45 | 0.42 | Oligotrophic | Deep glacial lake. Very wide and partially wooded basin. No significant human activity. Land used for livestock. |
| Argentino[5] | 50º 07' 40.1'' S 72º 06' 51.9'' W | 187 | 1466.0 | 500 | 20 | 2.0 | 7.53 | 40 | 3 | 0.52 | 0.28 | Oligotrophic | Deep glacial lake. Very wide and partially wooded basin. City of 20,000 inhabitants on one of its banks. Important tourist centre. Livestock use of the land |
| Buenos Aires[5] | 46º 18' 14.0'' S 71º 42' 57.1'' W | 200 | 1892.0 | 550 | 15 | 3.3 | 7.82 | 77 | 9 | 2.00 | 0.44 | Oligotrophic | Deep glacial lake. Very wide and partially wooded basin. No significant human activity. Land used for livestock. |
| Lácar[3] | 40º 09' 37.8'' S 71º 21' 47.3'' W | 625 | 49.0 | 279 | 10 | 19.0 | 7.75 | 60 | 9 | 1.10 | 1.89 | Oligotrophic | Deep glacial lake. Forested basin. City of 25,000 inhabitants. Important tourist centre. Overturning of effluents with different degrees of treatment on the main watershed. |
| Nihuil[1] | 35º 04' 21.0'' S 68º 41' 13.7'' W | 1251 | 72.0 | 17 | 6 | 0.7 | 8.29 | 1032 | 23 | 2.00 | 3.74 | Mesotrophic | Reservoir of anthropic origin for power generation. Sparsely vegetated basin. Small urban settlements. Land used for agriculture. |
| Cari-Laufquen Chica[4] | 41º 13' 04.6'' S 69º25' 54.3'' W | 150 | 5.0 | 5 | 5 | 0.3 | 8.40 | 440 | 191 | 46.40 | 6.50 | Eutrophic | Wind-formed shallow lake. Sparsely vegetated basin. No nearby urban settlements. Land used for livestock. |
| Ñe-Luan[4] | 41º 30' 15.9'' S 68º 37' 32.3'' W | 1000 | 0.6 | 15 | 9 | 0.7 | 8.20 | 324 | 200 | 26.30 | 5.60 | Eutrophic | Wind-formed shallow lake. Sparsely vegetated basin. No nearby urban settlements. Land used for livestock. |
| Cardiel[5] | 48º 48' 38.6'' S 71º 11' 57.9'' W | 300 | 460.0 | 49 | 10 | 1.3 | 9.21 | 4512 | 360 | 342.70 | 0.71 | Eutrophic | Wind-formed shallow lake. Sparsely vegetated basin. No urban settlements. Land used for livestock. |
| Caviahue[2] | 37º 52' 17.0'' S 71º 00' 53.0'' W | 1650 | 9.2 | 90 | 90 | 3.6 | 2.50 | 1259 | 370 | 230.00 | 0.35 | Eutrophic | Natural acidic lake of volcanic and glacial origin. Sparsely vegetated basin. Stable population of 1000 inhabitants that increases during tourist seasons. |

fractions were determined according to the fractionation scheme proposed by Hieltjes and Lijklema (1980), discriminating the labile fraction (P-Labile) (extracted with 1 M $ClNH_4$), the fraction bound to Al/Fe oxy-hydroxides (P-Al/Fe) (extracted with 0.1 M NaOH), the fraction bound to calcium compounds (P-Ca) (extracted with 0.5 M HCl) and the organic fraction (P-MO) (calculated as the difference between the sediment TP and the sum of the previous/mentioned fractions).

To evaluate the association between the chemical variables determined in sediment cores at different depths, a Principal Component Analysis (PCA) was performed. This analysis, as every multivariate descriptive technique, is an exploratory study used to describe behavior structures in observations (Lebart *et al.,* 1995). The matrix of observations consisted of 10 columns representing the variables measured in sediments: pH, PT, $SiO_2$, $Al_2O_2$, $Fe_2O_3$, MgO, CaO, $Na_2O$, $K_2O$ and $TiO_2$ and 9 rows representing lakes and reservoir studied: Caviahue, Argentino, Buenos Aires, Pueyrredón, Nihuil, Lácar, Cardiel, Cari-Laufquen Chica and Ñe-Luan. This analysis was repeated for the following layers of the core: 0-2 cm, 2-4 cm and 8-10 cm. All variables were active in the PCA. Values of sediment TP with depth in each core were fitted to different regression models in order to determine the distribution pattern and estimate the most appropriate fitting model which describes the relationship between sediment TP and core depth. We used the criterion proposed by Carey and Rydin (2011) where the data are fitted to two different models: *a)* linear model ($\mathbf{Y} = \boldsymbol{\beta_0} + \boldsymbol{\beta_1}*\mathbf{Z}$) and *b)* exponential model ($\mathbf{Y} = \mathbf{c}*\mathbf{e}^{\beta 1*Z}$) where: **Y** is the sediment TP, **Z** is the depth of the cores, $\boldsymbol{\beta_0}$ is the intercept, $\boldsymbol{\beta_1}$ is the slope and **c** is a constant value. The linear model was used in oligotrophic lakes and the exponential model in eutrophic ones (considering linear increase, exponential increase, linear decrease and exponential decrease).

Moreover, the values of the different P fractions (P-labile P-Fe/Al, P-Ca and P-MO) in depth in each sediment core were fitted to different regression models to evidentiate a distribution pattern in data. As for the sediment TP, the following models were used: *a)* linear model ($\mathbf{Y} = \boldsymbol{\beta_0} + \boldsymbol{\beta_1}*\mathbf{Z}$) and *b)* exponential model ($\mathbf{Y} = \mathbf{c}*\mathbf{e}^{\beta 1*Z}$), where: **Y** is the P associated with the different fractions, **Z** is the depth of the core, $\boldsymbol{\beta_0}$ is the intercept, $\boldsymbol{\beta_1}$ is the slope and **c** is a constant value. The linear model was used for oligotrophic lakes and exponential model for eutrophic (considering linear increase, exponential increase, linear decrease and exponential decrease). To assess whether the pattern of sediment TP can predict the water column TP concentration, a polynomial regression model that included a quadratic term for linear slope (Carey and Rydin 2011) was used. To this purpose, TP data of the water column and sediments that were previously fitted to an exponential model were transformed ($\log_e$). Then processed data were fitted to a linear model, where TP was the dependent variable and core depth was the independent variable. All the linear slopes obtained in the fittings were used to estimate the water TP according to the following model: $\mathbf{Y} = \boldsymbol{\beta_0} + \boldsymbol{\beta_1}*\mathbf{Z} + \boldsymbol{\beta_2}*\mathbf{Z}^2$, where: **Y** represents the water column TP, **Z** is the core depth, $\mathbf{Z}^2$ is the quadratic term of the core depth, $\boldsymbol{\beta_0}$ is the intercept, and $\boldsymbol{\beta_1}$ and $\boldsymbol{\beta_2}$ are the parameters (slopes) of the model. To evaluate the existence of a relationship between the TP in the first two centimeters of sediment core and the TP in the water column ($\log_e$ transformed data) a simple linear regression analysis was performed. The regression model used was the following: $\mathbf{Y} = \boldsymbol{\beta_0} + \boldsymbol{\beta_1}*\mathbf{Z}$, where: **Y** represents the water TP values, **Z** is the core depth, $\boldsymbol{\beta_0}$ is the intercept, and $\boldsymbol{\beta_1}$ is the slope of the model. The principal component analysis, linear and exponential settings and regression analyzes were performed using Infostat statistical package (Di Rienzo *et al.,* 2011).

## RESULTS & DISCUSSION

The TP average concentrations for all cores and layers ranged from 693 µgP/g d.w. (Lake Argentino) and 1121 µgP/g d.w. (Reservoir Nihuil) (Table 2). Overall, we found a pattern in the TP depth distribution of the cores that was related to trophic state (Fig. 2). The oligotrophic environments showed an increase in TP concentration in the sediment profiles with depth, and fitted to a linear model with positive slopes ($\boldsymbol{\beta_1}$ = 43.56, $R^2$ = 0.94) (Fig. 2). On the other hand, the eutrophic environments showed a decrease in TP concentration with depth and, when fitted to an exponential model, exhibited negative slopes ($\boldsymbol{\beta_1}$ = -0.01, $R^2$ = 0.43) (Fig. 2). Reservoir Nihuil ($TP_{water}$ = 23 µgP/L, mesotrophic) was the only environment where TP concentration with depth along the core did not follow a linear model ($\boldsymbol{\beta_1}$ = -9.38, $R^2$ = 0.18) nor an exponential one ($\boldsymbol{\beta_1}$ = -0.001, $R^2$ = 0.16) (Table 3). These results show that there is a relationship between the depth distribution of sediment TP and the trophic state of the studied freshwater ecosystems. Same results were obtained by Carey and Rydin (2001). However, two exceptions were noted to this general pattern: **a)** Lake Caviahue, which showed a sediment TP distribution pattern typical of oligotrophic environments, although according to the water column TP concentration, it should be classified as eutrophic. This distribution pattern had been observed before by Temporetti *et al.* (2013). This lake, also of glacial origin, is characterized by low transparency (2.8 to 3.6 m Secchi disk), low pH (2.0-3.0) and high electrical conductivity

(1.0 mS/cm) (Diaz *et al*., 2007), and is the only natural lake which is extremely acidic in South America because it receives the influence of volcanic acidity. The high concentrations of $Fe_2^+$ in the water column causing the SRP (Table 1) to remain in solution representing from 90 to 95% of TP (Pedrozo *et al.,* 2008). **b)** Lake Lácar is considered an oligotrophic lake (Table 1); however, its sediments behave like those in a typical eutrophic environment. This glacial lake is located within the Lanin National Park, and on the east margin of the lake the densely populated city of San Martin de los Andes is settled. The city is located at the drainage point of its main tributary on which all effluents are discharged and, after several levels of sewage treatment, are carried into the Lake Lácar (Werner 2007).

The element composition was dominated, firstly, by $SiO_2$, then by $Al_2O_3$, and finally by $Fe_2O_3$, except in Reservoir Nihuil and Lake Caviahue, where CaO and $Na_2O$, were dominant respectively (Table 2). In Fig. 3 are shown the principal component analysis (PCA) results of the following layers analyzed in sediments: 0-2 cm, 2-4 cm and 8-10 cm. In all three cases, the patterns of association between individuals (lakes) and variables were similar. For this reason the graphics only show the variables and individuals for the last layer (8-10 cm). For the PCA corresponding to 0-2 cm depth, factor 1 explained 39.7% of the total variance, which increased to 66.0% when adding the second factor. The most important variables that contributed to the formation of the factors were: $SiO_2$, MgO, $Al_2O_3$ and $K_2O$. The individuals (lakes/reservoir) were divided according to their trophic state along factor 2, and according to pH through factor 1. Regarding the PCA of the layer 2-4 cm made, factor 1 explained 43.5% of the total variance, while it increased to 68.3% when adding the second factor. The most important variables that contributed to the formation of the factors were: $SiO_2$, TP, $Al_2O_3$ and $TiO_2$. As in the uppermost layer, individuals were divided according to their trophic state, throughout factor 2 and according to pH, through factor 1. We described different associations: one of them between variables, and the other one between variables and individuals, for both layers mentioned above (0-2 and 2-4 cm). Considering the relationships between variables in the first two dimensions graph, it was observed that the pH is positively related to $Fe_2O_3$ and CaO and the TP, and negatively to $SiO_2$. Eutrophic lakes (lakes Ñe-Luan, Cardiel, Cari-Laufquen and Lácar) had higher contents of TP, $Fe_2O_3$ and CaO, high pH and low $SiO_2$. Moreover, the oligotrophic environments (lakes Pueyrredón and Argentino) showed high $Al_2O_3$content. In this case, Lake Buenos Aires was not well represented in the analysis. On the other hand, Lake Caviahue was separated from the rest of the environments in the graph and was characterized by high concentrations of $SiO_2$ and low TP, $Fe_2O_3$ and pH. Reservoir Nihuil, presented high values of TP and low $Al_2O_3$. In the PCA of the 8-10 cm layer (Fig. 3), factor 1 explained 41.7% of the total variance, increasing to 68.1% by adding the second factor. As in the most superficial layers, individuals were separated

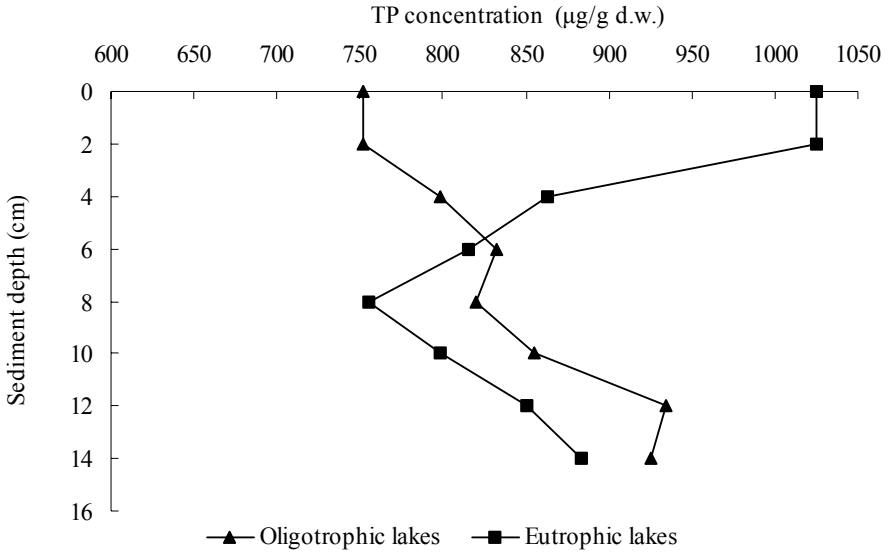


**Fig. 2. Average TP concentrations observed in the cores analyzed. Oligotrophic (Water column TP <10 µgP/L) and Eutrophic (Water column TPe" 30 µgP/L). Lake Caviahue and Reservoir Nihuil were excluded \ (see explanation in the text)**

**Table 2. mean values (maximum and minimum values in parentheses), for all stratum, of pH, TP concentration and chemical composition of water body sediments**

| | pH | TP | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | CaO | MgO | $Na_2O$ | $K_2O$ | $TiO_2$ |
|---|---|---|---|---|---|---|---|---|---|---|
| | | (µgP/g d.w.) | (%) | (%) | (%) | (%) | (%) | (%) | (%) | (%) |
| L. Pueyrredón | 7.1 | 735 | 60.0 | 20.9 | 6.6 | 0.6 | 1.2 | 1.5 | 3.9 | 0.7 |
| | (7.0-7.4) | (623-868) | (57.7-67.3) | (19.5-25.0) | (5.2-9.4) | (0.5-0.6) | (1.0-1.9) | (0.7-3.2) | (3.2-5.0) | (0.4-1.1) |
| L. Argentino | 6.7 | 693 | 62.6 | 19.7 | 6.3 | 2.2 | 2.4 | 3.2 | 2.3 | 0.8 |
| | (6.4-6.9) | (653-741) | (55.2-62.5) | (22.1-23.2) | (5.1-8.7) | (0.8-2.0) | (2.2-2.9) | (1.0-2.1) | (2.9-3.6) | (0.4-1.1) |
| L. Buenos Aires | 6.8 | 1073 | 62.6 | 19.7 | 6.3 | 2.2 | 2.4 | 3.2 | 2.3 | 0.8 |
| | (6.5-7.1) | (907-1255) | (60.4-65.8) | (17.5-21.2) | (4.3-11.7) | (0.9-5.5) | (1.9-3.0) | (1.7-6.0) | (1.7-3.3) | (0.5-1.5) |
| L. Lácar | 6.3 | 1031 | 57.0 | 22.5 | 9.0 | 3.7 | 2.5 | 3.4 | 1.1 | 0.8 |
| | (6.4-6.5) | (982-1091) | (55.6-58.1) | (21.2-23.1) | (8.3-10.1) | (3.0-3.9) | (2.2-2.6) | (2.9-4.0) | (0.9-1.2) | (0.7-1.1) |
| R. Nihuil | 7.0 | 1121 | 58.0 | 19.8 | 5.6 | 7.7 | 3.4 | 2.6 | 2.2 | 0.6 |
| | (6.8-7.1) | (997-1275) | (57.6-58.4) | (19.0-20.4) | (5.5-5.8) | (7.1-8.2) | (3.4-3.5) | (2.4-2.9) | (2.2-2.3) | (0.5-0.6) |
| L. Cari-Laufquen Chica | 7.7 | 953 | 56.6 | 17.4 | 7.0 | 7.4 | 4.0 | 1.4 | 1.4 | 0.8 |
| | (7.5-7.8) | (805-1096) | (64.2-66.9) | (16.4-18.0) | (4.8-6.1) | (2.3-3.3) | (2.7-3.8) | (2.7-3.9) | (1.5-1.8) | (0.7-1.0) |
| L. Ñe-Luan | 7.6 | 964 | 62.3 | 20.7 | 7.5 | 3.2 | 3.1 | 0.7 | 1.4 | 0.8 |
| | (7.4-7.8) | (808-1134) | (55.5-65.8) | (18.5-24.7) | (4.5-13.6) | (2.0-5.0) | (2.4-3.5) | (0.4-1.0) | (1.0-1.7) | (0.6-1.2) |
| L. Cardiel | 8.6 | 714 | 65.4 | 17.3 | 5.7 | 2.7 | 3.3 | 3.2 | 1.7 | 0.8 |
| | (8.4-9.0) | (563-846) | (64.2-67.0) | (16.4-18.0) | (4.8-7.0) | (2.3-3.3) | (2.7-3.8) | (2.7-3.9) | (1.5-1.8) | (0.7-1.0) |
| L. Caviahue | 2.9 | 1064 | 73.3 | 11.5 | 2.4 | 1.1 | 0.7 | 2.6 | 0.9 | 1.3 |
| | (2.6-2.9) | (378-1943) | (70.6-76.3) | (9.2-12.3) | (1.6-3.0) | (0.7-1.4) | (0.2-2.1) | (1.8-4.0) | (0.7-1.1) | (1.1-1.5) |

**Table 3. TP concentration in the water column ($TP_{water}$); best sediment TP model fit; the linear slope of the function of sediment total phosphorus with depth (linear slope); model equation and model $R^2$ for the 9 lakes analyzed. * = *p< 0.05*, n.s. = *p> 0.05***

| | $TP_{water}$ µgP/L | Model | Linear Slope ($\beta_1$) | Best fit equation | $R^2$ |
|---|---|---|---|---|---|
| L. Pueyrredón | 2 | Linear | 13.63 | Y = 13.63*Z+639.2 | 0.63* |
| L. Argentino | 3 | Linear | 5.81 | Y = 5.807*Z+6.525 | 0.73* |
| L. Buenos Aires | 9 | Linear | 21.4 | Y = 21.4*Z+9.227 | 0.78* |
| L. Lácar | 9 | Exponential | -10.81 | $Y = 1085*e^{-0.01Z}$ | 0.69* |
| R. Nihuil | 23 | Exponential | -0.001 | $Y = 1178*e^{-0.001Z}$ | n.s. |
| R. Nihuil | | Lineal | -9.38 | Y = -9,386*Z + 1186 | n.s. |
| L. Cari-Laufquen Chica | 191 | Exponential | -14.71 | $Y = 1053*e^{-0.01Z}$ | 0.49* |
| L. Ñe-luan | 200 | Exponential | -10.38 | $Y = 1025*e^{-0.01Z}$ | 0.15 |
| L. Cardiel | 341 | Exponential | -12.87 | $Y = 797.8*e^{-0.01Z}$ | 0.35* |
| L. Caviahue | 370 | Linear | 133.3 | Y = 133.3*Z+130.5 | 0.92* |

according to their trophic state along to factor 2, and according to pH through factor 1 (Fig. 3A). The variables (Fig. 3B) that contributed to the formation of the factors were: pH, TP, $Al_2O_3$ and $TiO_2$. By analyzing the relationships between variables (Fig. 3B), we found that the pH is positively related with $Fe_2O_3$ and negatively with $SiO_2$, TP and MgO. Eutrophic lakes (lakes Cardiel, Cari-Laufquen and Lácar) showed higher $Fe_2O_3$ content, high pH and low $SiO_2$, TP and MgO (Fig. 6). In this analysis, Lake Ñe-Luan (also eutrophic) was not well represented in the plane. On the other hand, oligotrophic environments (lakes Pueyrredón, Argentino and Buenos Aires) showed high $Al_2O_3$ content and low CaO content (Fig. 3). Lake Caviahue was separated from the rest of the environments in the plan and was characterized by high concentrations of $SiO_2$, TP, MgO and low $Fe_2O_3$ and pH. Reservoir Nihuil showed high values of CaO and lower $Al_2O_3$ (Fig. 3).

Table 4 shows the results from the P fractioning made to cores and grouped in relation with trophic classification (now defined considering the P distribution pattern in sediment). In oligotrophic environments (lakes Buenos Aires, Pueyrredón, Argentino and Caviahue), the main fraction was bound to organic matter (P-MO), followed by the fraction bound to compounds of Ca (P-Ca). P fraction bound to Al and Fe oxy-hydroxides (P-Al/Fe) was the third fraction in importance, whereas the P-labile fraction was very low. By contrast, in eutrophic environments (lakes Cardiel, Cari-Laufquen, Ñe-Luan, Lácar and Reservoir Nihuil), the main P fraction was associated with Ca compounds, followed by the fraction linked to organic matter. As noted for the oligotrophic environments, the P fraction bound to Al and Fe oxy-hydroxides was the third fraction in importance while labile fraction was low. We observed a distribution pattern of P-labile fraction with depth in the cores analyzed and the trophic state thereof. The oligotrophic environments showed increased labile P concentration with depth (Table 5) and were fitted to a linear model, exhibiting a positive slope ($\beta_1 = 0.804$, $R^2 = 0.92$). On the other hand, the eutrophic environments showed a decrease in the P-labile concentration with depth (Table 5), conforming to an exponential model and showing negative slopes ($\beta_1 = -0.08$; $R^2 = 0.59$). Similarly, we observed the same pattern of depth distribution of the P fraction associated to Al and Fe oxy-hydroxides (P-Al/Fe) and the environment trophic state (Table 5): fitting oligotrophic environments to a linear model ($\beta_1 = 9.38$, $R^2 = 0.50$, $p > 0.05$) and eutrophic environments to an exponential model ($\beta_1 = -0.04$, $R^2 = 0.85$). The other two fractions (P-Ca and P-MO) did not fit any model used. While the P extraction method used in our work cannot differentiate between the P bound to Al from the P fraction bound to Fe, the results of the chemical composition of sediment indicate that the Al content (estimated from those Al oxides) was between 4.7 and 5.4 times higher than Fe content in all environments and all layers. Furthermore, the results of the P fractioning in the sediments of each environment studied indicate that oligotrophic lakes showed, on average, higher concentrations of P-Fe/Al fraction (111 µgP/g d.w.) than those in the eutrophic environments (81.3 µgP/g d.w.). Also, considering the associations observed in the multivariate analyzes, we can see that oligotrophic lakes were characterized by higher concentrations of $Al_2O_3$ (21%) than those in eutrophic lakes (17%). Likewise, we found a positive linear relationship between the P-Al/Fe concentrations with depth in sediments in oligotrophic environments

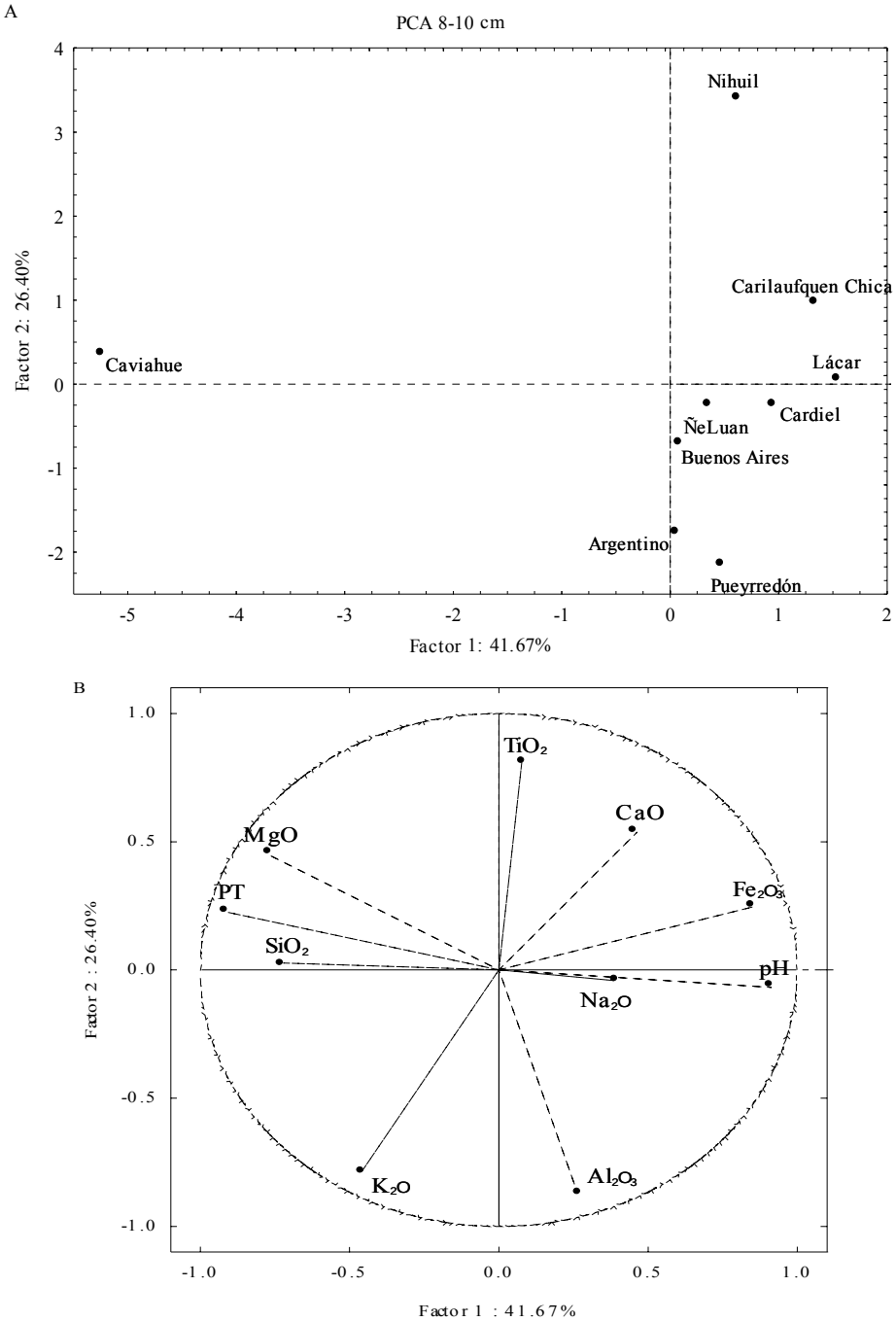


**Fig. 3. Two-dimensional plot of the PCA analysis (8-10 cm) showing the distribution of A: the 9 different water bodies sampled. B: the physical and chemical variables recorded in the water bodies**

($R^2$ = 0.50). By contrast, we obtained a significant negative exponential relationship ($R^2$ = -0.85) in eutrophic lakes. Both in oligotrophic and in eutrophic environments, the most important fraction was the P-organic matter one (Table 4). Wilson *et al.* (2010) suggest that probably in all lakes, regardless of their trophic state, organic P is mineralized in the sediment. Sorption capacity of this organic fraction controls the degree in which the dissolved P is released into the water. For the lakes studied, no relationship was found between the P-Labile fraction and the P-organic matter fraction for oligotrophic environments. In the eutrophic lakes a clearly significant relationship ($R^2$ = 0.90) was obtained between the two P fractions.

**Table 4. Average concentrations (minimum and maximum values in parentheses) of different P fractions analyzed in terms of the depth of the cores extracted. The environments were grouped according to their trophic state explained by the concentration of water column TP (see Materials and methods)**

| | Strata | P-Lábil | P-Fe/Al | P-Ca | P-MO |
|---|---|---|---|---|---|
| | (cm) | (µgP/g d.w.) | (µgP/g d.w.) | (µgP/g d.w.) | (µgP/g d.w.) |
| Oligotrophic | 0-2 | 2.4 (0.9-4.1) | 78.8 (32.2-113.7) | 98.4 (1.3-226.4) | 478.9 (261.2-806.5) |
| | 2-4 | 3.3 (0.6-9.4) | 112.8 (26.4-230.1) | 171.1 (38.4-332.2) | 612.0 (420.4-773.2) |
| | 4-6 | 5.0 (0.6-16.5) | 97.4 (29.4-189.8) | 182.0 (27.2-346.1) | 621.6 (469.0-882.9) |
| | 6-8 | 6.4 (0.8-21.9) | 142.6 (32.8-383.7) | 233.1 (24.9-379.1) | 651.4 (321.1-1236.9) |
| | 8-10 | 10.1 (0.7-36.8) | 98.4 (35.0-190.9) | 248.9 (23.7-373.3) | 777.7 (305.7-1713.6) |
| | 10-12 | 10.2 (0.7-40.1) | 134.0 (37.8-303.9) | 256.2 (21.2-408.9) | 774.5 (307.7-1535.9) |
| Eutrophic | 0-2 | 21.1 (17.2-29.0) | 105.9 (62.7-205.1) | 441.3 (308.4-732.1) | 514.0 (399.7-698.5) |
| | 2-4 | 11.7 (2.7-21.7) | 86.6 (50.0-162.0) | 423.5 (307.1-642.1) | 392.1 (294.4-503.3) |
| | 4-6 | 7.1 (2.7-13.1) | 79.3 (36.2-188.0) | 433.2 (314.1-651.0) | 374.9 (250.5-519.9) |
| | 6-8 | 7.2 (2.6-16.6) | 79.4 (32.6-193.0) | 426.3 (285.1-642.9) | 350.4 (240.5-439.5) |
| | 8-10 | 7.8 (2.5-20.2) | 77.4 (33.0-170.0) | 445.3 (322.0-718.5) | 381.2 (279.9-551.3) |
| | 10-12 | 8.8 (4.0-19.1) | 53.7 (34.1-78.2) | 444.4 (313.1-759.1) | 416.0 (278.5-561.0) |

**Table 5. Best fit model between depth and phosphorus labile fraction (P-labile), and the fraction of phosphorus bound to iron and aluminum oxy-hydroxides (P-Fe/Al). * = *p< 0.05*, n.s. = *p> 0.05***

| | | Model | Best fit equation | $R^2$ |
|---|---|---|---|---|
| Oligotrophic | Z vs P-labile | Lineal | $y = 0.804*\mathbf{Z}+0.994$ | 0.92* |
| | Z vs P-Fe/Al | Lineal | $y = 9.38*\mathbf{Z}+108.1$ | 0.50 n.s. |
| Eutrophic | Z vs P-labile | Exponencial | $y = 18.73*e^{-0.08\mathbf{Z}}$ | 0.59* |
| | Z vs P-Fe/Al | Exponencial | $y = 108.3*e^{-0.04\mathbf{Z}}$ | 0.85* |

**Table 6. SRP and N-$NH_4^+$ concentration in pore water**

| | SRP | N-$NH_4^+$ |
|---|---|---|
| | (µgP/L) | (µgN/L) |
| L. Pueyrredón | 23 | 94 |
| L. Argentino | 25 | 87 |
| L. Buenos Aires | 35 | 72 |
| L. Lácar | 80 | 231 |
| R. Nihuil | 288 | 46 |
| L. Cari-Laufquen Chica | 782 | 36 |
| L. Ñe-Luan | 305 | 94 |
| L. Cardiel | 1034 | 116 |
| L. Caviahue | 1100 | 9600 |

According to Carey and Rydin (2011), the depth distribution of TP in the sediments of oligotrophic and eutrophic lakes is determined by the Al content in the sediments. These authors hypothesize that the most important difference between oligotrophic and eutrophic environments could be the lack of sufficient P-binding agents, such as Al, in the latter. In this sense, these authors found that oligotrophic lake sediments have concentrations of phosphorus bound to Al (P-Al) higher than eutrophic lake sediments. This may be related to the increased TP concentration with depth in the sediment in oligotrophic environments.

The average pH for all the layers and the nine corers is shown in Table 2. In Lake Caviahue the lowest pH (2.50) was in recorded and, in Lake Cardiel, the highest (9.21). Fig. 4 shows changes in the ORP for all environments studied. In oligotrophic environments, Lake Argentino was the only one that showed high and positive ORP values throughout the core (average = +719 mV, range of variation between +454 and +880 mV). Moreover, Reservoir Nihuil showed lower and negative ORP values (average = -273 mV, variation range between -303 and -236 mV). The traditional model used to explain the processes of phosphorus liberation from sediment describes anaerobic P release, followed by chemical reduction of $Fe_3^+$ bound to the sediment when the redox potential is below +200 mV. This causes the dissolution of $Fe_2^+$ and the associated P (Mortimer 1971; Wetzel 2001; Golterman 2004). However, Gätcher and Müller (2003) demonstrated that the P releasing from sediment may also occur during aerobic processes. The results of our study showed that the redox potentials in sediments measured in oligotrophic environments, with the exception of Lake Argentino, were below +200 mV (Fig. 4) some values resulted even negative (-22 to - 125 mV). According to the traditional model, in this condition P should be released from sediment to water column. The results of our study indicate that oligotrophic lake sediment shows an increase in the P concentration depending on the depth. Kopáček *et al.* (2005) suggest an alternative explanation for Mortimer´s traditional model (1971). These authors found that the sediments that have not ability to release P (such as in oligotrophic lakes) have enough $Al(OH)_3$ to provide additional absorption capacity to retain the P released from $Fe(OH)_3$ under low ORP conditions. In pore water, the SRP concentrations increased with the trophic state in the environments studied (Table 6). The maximum SRP concentration in pore water in oligotrophic environments was recorded at Lake Lácar with 80 µgP/L, while the highest concentration in eutrophic environments corresponded to Lake Caviahue with 1100 µgP/L. The $N\text{-}NH_4^+$ concentrations did not show a clear pattern in relation to the increasing environment trophic state, as it was observed in SRP concentrations. However, as in the case of the dissolved P fraction, the highest concentration of this nutrient for oligotrophic environments was recorded at Lake Lácar (231 µgN/L) and for eutrophic environments in Lake Caviahue (9600 µgN/L) (Table 6). It is well known from the literature (Wetzel 2001; Golterman 2004) that the physicochemical conditions of pore water are a barrier to the free exchange of P between sediments and the water column. In general, the P in pore water is found in small proportions (less than 1%) compared to concentrations found in sediments (Golterman 2004). But this concentration in pore water is considerably higher (5-20 times) than the concentrations recorded in the water column (Håkanson and Jansson 1983). Highly reactive chemical species, such as metal oxides, tend to concentrate in pore water, and can be quickly transformed into new compounds. Maassen *et al.* (2005) found a strong relationship between Fe and Al contents in sediments and SRP concentration in pore water. According to these authors, this relationship indicates that both metals have a very high affinity for the P in pore water which strongly affects the release of the nutrient from the sediment into the water column. Fig. 5 shows the strong correlation ($r = 0.99$, $p < 0.05$) obtained from Al:SRP and Fe:SRP in the studied environments. The role played by the Fe and Al in the formation of metal compounds in the sediments that immobilize P is widely cited in the literature (Boström 1988; Golterman 2004). Maasen *et al.* (2005) propose a way to estimate the P-binding capacity in sediments: it could be calculated from the sum of the P content and the contents of Fe, Al, etc., and by defining this ratio as Metal:P (MPS). According to these authors, this ratio can be estimated from the following equation: $MPS = [(C_{Fe}/M_{Fe}) + (C_{Al}/M_{Al})] / (C_P/M_P)$, where: MPS is the ratio of the sum of Metals:P (dimensionless), $C_i$ is the concentration of the respective element (Fe, Al and P) in g/kg d.w., $M_i$ is the molecular weight of the respective element (Fe, Al and P) in g/mol. The results of our study indicate a significant increase in pore water SRP concentration when sediment MPS is lower (approximately) than 150 (Fig. 6). This suggests that, for all eutrophic environments (lakes Lácar, Ñe-Luan, Cari-Laufquen Chica, Cardiel and Reservoir Nihuil), an MPS lower than or equal to 150 means that these sediments have a low capacity to retain P and thus they would be expected to easily release the nutrient into the water column. The only exception is the acidic Lake Caviahue, which showed high pore water SRP concentration and where the MPS was also high (224).

The polynomial regression model which $\log_e TP_{water}$ data was fitted to was: $\log_e TP_{water} = 4.2968 + 0.0095*\mathbf{Z}$

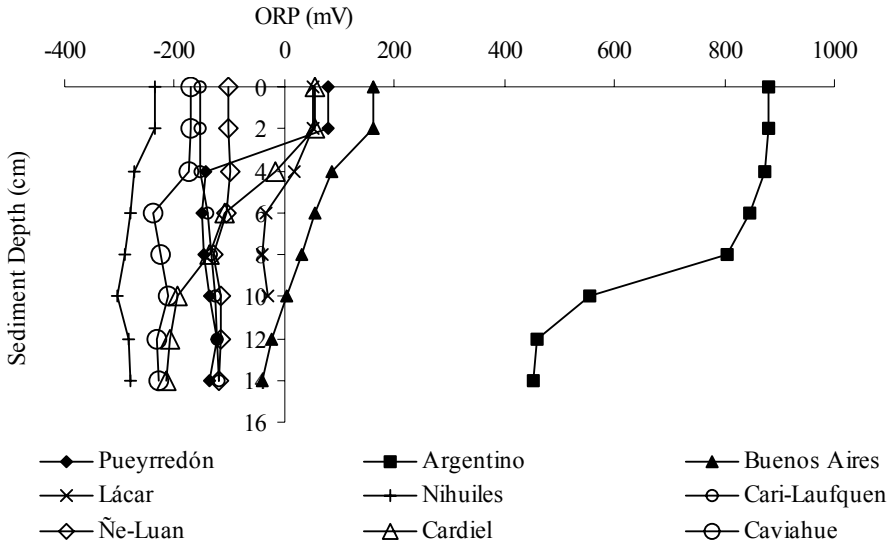


**Fig. 4. Measured ORP profiles in cores of the studied environments. Oligotrophic environments are identified with fill symbols and eutrophic with empty symbols**

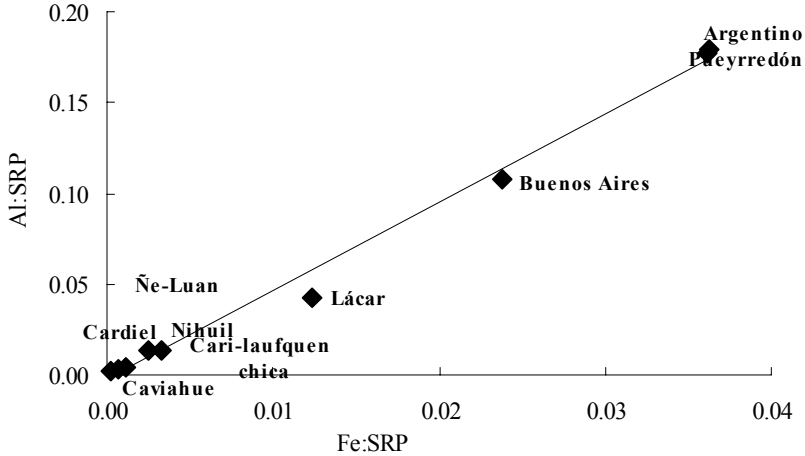


**Fig. 5. Correlation between the ratio of Al (dry weight) to SRP (pore water) and Fe (dry weight) to SRP (pore water) (r = 0.996, *p <0.05*)**

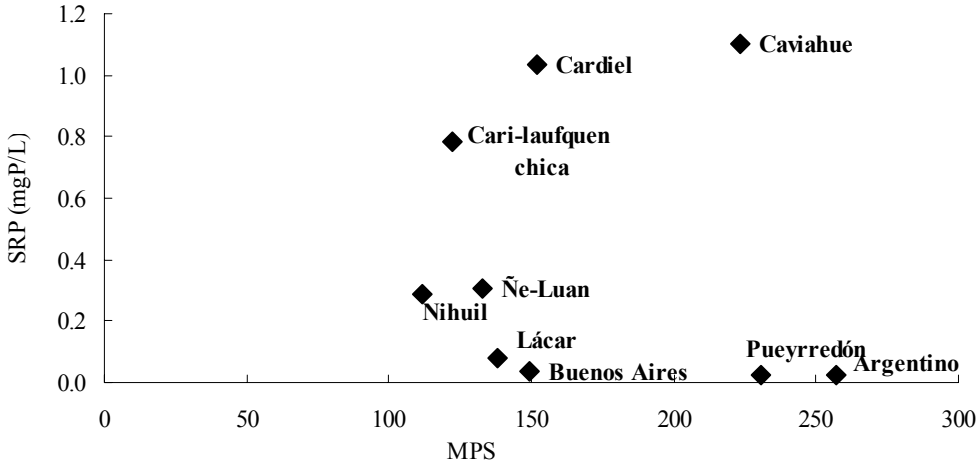


**Fig. 6. Relationship between pore water SRP and MPS molecular ratio in sediments**

- 0.008***Z**². This regression was not significant (F = 2.9, *p> 0.05*, $R^2 = 0.31$) (Fig. 7). Although no relationship was found between the sediment TP in the first layer (0-2 cm) and $\log_e TP_{water}$, we found a positive relationship ($R^2 = 0.89$, *p <0.05*) between the pore water SRP and the water column TP for all environments analyzed (Fig. 8). No relationship was observed between the TP in the first core layer (0-2 cm) and the water column TP. Carey and Rydin (2011) suggest that it is important to analyze the distribution pattern of TP throughout the core rather than only in the surface layer. However, we found a significant linear relationship ($R^2 = 0.89$) between pore water SRP concentrations and water column TP for all water bodies studied (Fig. 8). These results agree with those found by Maassen *et al.* (2005) in four reservoirs in Germany, who observed a direct relationship between the SRP released from the sediments and the TP concentration in the water column.

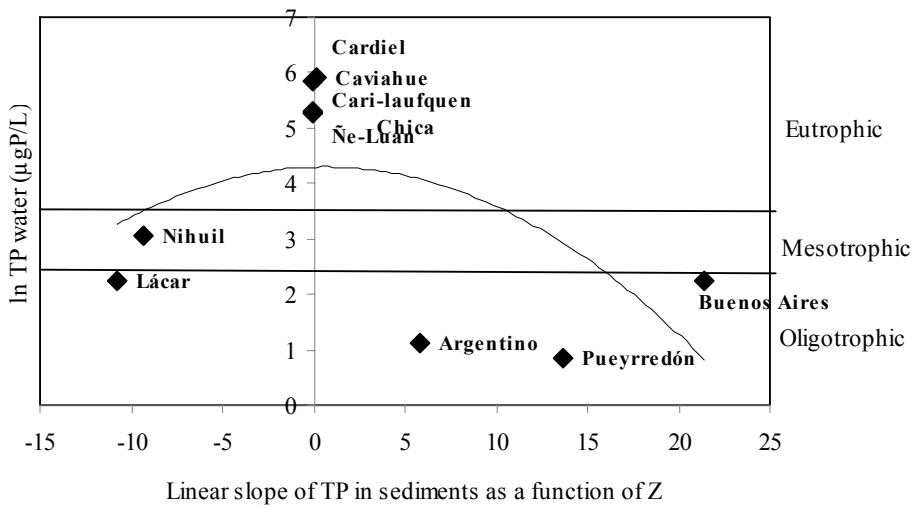


**Fig. 7. The relationship between the linear slope of the function of sediment phosphorus with depth in a sediment P profile and $\log_e$-transformed water column total phosphorus (TP) for each of the 9 water bodies in our study (equation provided in text). The transition between positive and negative linear slopes is denoted by the vertical line in the figure; and the threshold between eutrophic and mesotrophic water column TP concentrations, and mesotrophic and oligotrophic lakes are denoted by horizontal lines (According to Carey and Rydin 2011)**

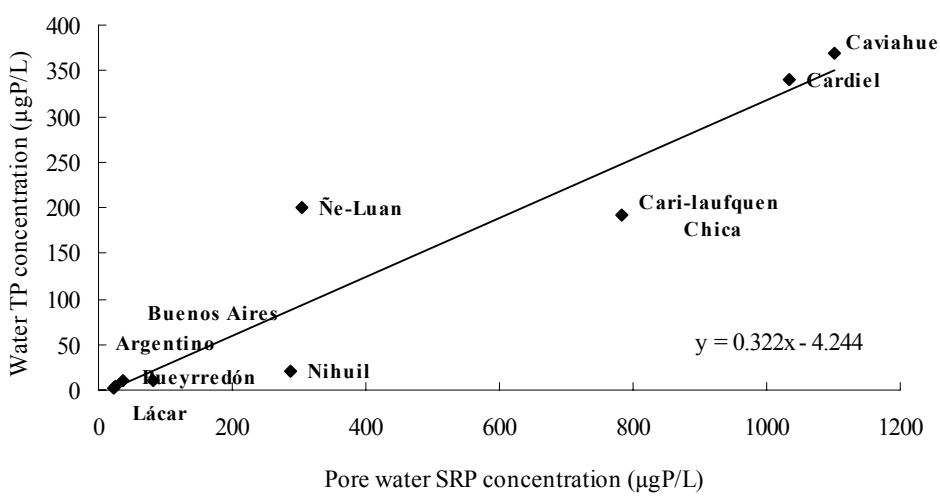


**Fig. 8. Relationship between the concentrations of pore water SRP and water column TP for the studied environments**

**Table 7. A) Trophic classification parameters considering pore water and sediment (1: taken from Maassen *et al.* (2005); 2: this study). B) Trophic classification based on the parameters in Table 7a, for the patagonian environments studied**

| A | Oligotrophic | Mesotrophic | Eutrophic | Eutrophic-Hypertrophic |
|---|---|---|---|---|
| **Pore Water[1]** | | | | |
| SRP (mgP/L) | < 0.10 | 0.10 – 0.25 | 0.25 – 1.00 | 1.00 – 2.50 |
| $N\text{-}NH^{4+}$ (mgN/L) | < 3.00 | 3.00 – 5.00 | 5.00 – 10.00 | 10.00 – 18.00 |
| **Sediments[2]** | | | | |
| MPS ratio | > 150 | > 150 | < 150 | < 150 |

| B | SRP (mg/L) | Trophic state | $N\text{-}NH4^{+}$ (mg/L) | Trophic state | MPS | Trophic state |
|---|---|---|---|---|---|---|
| L. Pueyrredón | 0.02 | Oligotrophic | 0.09 | Oligotrophic | 231 | Oligotrophic |
| L. Argentino | 0.02 | Oligotrophic | 0.09 | Oligotrophic | 257 | Oligotrophic |
| L. Buenos Aires | 0.03 | Oligotrophic | 0.07 | Oligotrophic | 150 | Oligotrophic |
| L. Lácar | 0.08 | Oligotrophic | 0.23 | Oligotrophic | 138 | Eutrophic |
| R. Nihuil | 0.30 | Eutrophic | 0.05 | Oligotrophic | 112 | Eutrophic |
| L. Cari-Laufquen Chica | 0.80 | Eutrophic | 0.04 | Oligotrophic | 122 | Eutrophic |
| L. Ñe-Luan | 0.30 | Eutrophic | 0.09 | Oligotrophic | 133 | Eutrophic |
| L. Cardiel | 1.03 | Eutrophic | 0.11 | Oligotrophic | 152 | Oligotrophic |
| L. Caviahue | 1.10 | Eutrophic-Hypertrophic | 9.60 | Eutrophic | 224 | Oligotrophic |

## CONCLUSIONS

As noted by Carey and Rydin (2011), the results of our work showed that oligotrophic lakes tend to accumulate phosphorus, while eutrophic lakes tend to release this nutrient to the water column. Only one out of the environments analyzed in this study, Reservoir Nihuil, was classified as mesotrophic, presenting a sediment TP distribution pattern which was homogeneous and intermediate between oligotrophic and eutrophic environments. According to the criterion proposed by Carey and Rydin (2011), sediments in mesotrophic environments, as Reservoir Nihuil, could be enriched with phosphorus but would be very close to their saturation, showing a homogeneous depth distribution pattern of TP in the cores. Analyzing the relationship between the linear slope in the sediment P with depth and the TP concentration in the water, it was observed that oligotrophic environments have a linear positive slope while the eutrophic environments have a negative linear slope. The exceptions to this pattern are Lake Lácar which should have shown a positive linear slope and contrarily has a negative linear slope and Lake Caviahue which, as a eutrophic environment, presents a positive linear slope characteristic of oligotrophic environments. The results obtained in our study showed, similarly to those found by Maassen *et al.* (2005) and Carey and Rydin (2011), that certain parameters of the pore water and of sediments were significantly correlated with the trophic state of the studied environments. In particular, 1) the pore water SRP concentration, 2) the concentration of P-labile fraction, 3) the depth distribution pattern of TP and 4) the MPS. By contrast, pore water $N\text{-}NH_4^{+}$ concentrations showed no correlation with the trophic state. To trophically classify the environments studied

in this work using sediment and pore water characteristics, we used the criterion proposed by Maassen *et al.* (2005) but modified (Table 7). According to this classification and considering pore water SRP concentrations, lakes Pueyrredón, Argentino, Buenos Aires and Lácar are oligotrophic while Reservoir Nihuil, Lakes Cardiel, Cari-Laufquen Chica and Ñe-Luan are eutrophic. Lake Caviahue is classified as eutrophic-hypertrophic. However, if we consider the MPS ratio in sediments, the trophic classification of the environments change substantially, especially in Lake Lácar, classified as eutrophic and Lake Caviahue, classified as oligotrophic. This classification was corroborated with depth profiles of TP in cores. From the research conducted, we can conclude that, to define the trophic state of aquatic environments, both pore water and sediments could be considered as better integrator parameters than the typical water column parameters. By considering the distribution pattern of sediment TP, it is possible to determine if what is occurring is P fixation or release from sediments to the water column.

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