The Role of Sediments and Phosphorus in the Evaluation of Water Resources Quality in Patagonia

Pedro Temporetti, Guadalupe Beamud, José León, Leandro Rotondo, Mayra Cuevas, and Fernando Pedrozo

Abstract Among the processes of anthropogenic contamination of aquatic environments, eutrophication is one of the most studied. Phosphorus is a key nutrient in eutrophication and, in many cases, the limiting nutrient in various water bodies. Furthermore, sediments from an aquatic environment can be considered as an "environmental information bank". They play an important role in the nutrient cycle in lakes since nutrients are transported to the bottom by sedimentation and can return to the water column by various mechanisms which are sometimes extremely complex. The aim of this chapter is to summarize 30 years of research carried out by the Water Quality Group (INIBIOMA, CONICET-UNComahue) on sediments from several lake environments in Argentinian Patagonia and their role in aquatic resource assessment. A total of 11 water bodies in the region were analyzed, considering different physical and chemical parameters, always applying the same methodology (in field and laboratory). The results show that (1) pH is one of the main parameters that influence the P exchange between sediments and the water column; (2) texture, chemical composition, and mineralogy are essential to understand sediment genesis and transport mechanisms; (3) three gradients determine the distribution of the studied environments: (a) North–South geographic gradient, (b) pH gradient and (c) trophic gradient; (4) the use of sediment bioassays with native algae is a particularly useful tool for rapidly evaluating the anthropic impact on water bodies; and (5) sediment studies allow obtaining information on, for example, contaminated and uncontaminated areas and distribution patterns of contaminants, and should be included in monitoring programs.

Keywords Sediments · Phosphorus · Water resources · Patagonia

P. Temporetti (✉) · G. Beamud · L. Rotondo · M. Cuevas · F. Pedrozo
Instituto de Investigaciones en Biodiversidad y Medioambiente, Centro Regional Universitario Bariloche-UNComahue, CCT-Patagonia Norte, CONICET, San Carlos de Bariloche, Argentina
e-mail: temporettipf@comahue-conicet.gob.ar

J. León
Centro de la Región Semiárida, Instituto Nacional del Agua. Villa Carlos Paz, Córdoba, Argentina

1 Introduction

For more than 80 years, since the first works by Einsele (1936, 1938) and Mortimer (1941, 1942), lake sediments have been considered in limnology studies. The growing interest in sediment studies has clearly been triggered by the problems caused by anthropogenic contamination of water bodies.

In aquatic systems, sediments are made of organic and inorganic substances, including particulate material washed from the basin (allochthonous material), as well as material originated from the same water body (autochthonous material). In this sense, sediment composition is highly influenced and controlled by the composition of the rocks from which they derive either by erosion and/or weathering processes, and the type of basin (Golterman 2004). These processes are affected by many factors, such as climate, relief, biota, time, and anthropic factors like land-use conditions.

Sediments from an aquatic environment can be considered as an "environmental information bank" (Håkanson and Jansson 1983) because they provide much information regarding, for example, which areas are contaminated, as well as the dispersion patterns of different polluting substances, supplying relevant data at different levels (e.g. local and regional). Eutrophication is one of the most studied processes of contamination in aquatic environments (Wetzel 2001; Golterman 2004). It is defined as the excess of nutrients (mainly phosphorus (P) and nitrogen (N)), and organic matter that causes an increase in biological production (Sinke 1992; Wetzel 2001). The effects of this process on water bodies are numerous, among which are worth highlighting the decrease in water column transparency and dissolved oxygen concentration, the appearance of toxic algal species and, in very severe cases, fish mortality (Smith et al. 2006b).

Phosphorus is a key nutrient in eutrophication processes, and frequently the limiting nutrient in various water bodies (Elser et al. 2007; Zhongyao et al. 2020). Moreover, water column nutrient concentration is the main parameter considered for the trophic classification of water bodies (OECD 1982; Horne and Goldman 1994; Wetzel 2001; Schindler et al. 2008). The trophic state of aquatic environments is determined using physical (e.g. transparency) and chemical parameters [e.g. total phosphorus concentration (PT), soluble reactive phosphorus (PRS), and chlorophyll a (Chl-a)] (OECD 1982; Horne and Goldman 1994; Cunha et al. 2013). However, these parameters usually present seasonal fluctuations, hindering the trophic classification of water bodies (Maasen et al. 2005).

Several studies have related the P concentration in surface sediments with its concentration in the water column (Lee-Hyung et al. 2003; Smith et al. 2006a; McDaniel et al. 2009), supported by the concept that trophic state can be substantially influenced by P release from sediments (Carey and Rydin 2011). In this sense, sediments play an important role in the nutrient cycle in lakes since nutrients are transported to the bottom by sedimentation and can be returned into the water column by various (physical, chemical and biological) mechanisms, sometimes extremely

complex (Forsberg 1989). Håkanson and Jansson (1983) proposed that this recircula-tion can be very important when the involved elements are essential nutrients such as P and N, a phenomenon known as *internal load* in the specialized literature (Ryding and Forsberg 1976; Larsen et al. 1981; Boström et al. 1982; Golterman et al. 1983; Håkanson and Jansson 1983; Søndergaard et al. 2003; Jeppesen et al. 2005). This load represents a problem in the lake restoration process, even when the pollutant source has been eliminated (Boström et al. 1982; Carpenter 2005). Consequently, the knowledge of the sediment state and function is essential to predict the effects of different nutrient loads released to the environment and is necessary to plan the restoration of impacted water bodies.

Argentinian Patagonia comprises the southern portion of the Province of Mendoza, parts of the provinces of La Pampa and Buenos Aires, and the provinces of Chubut, Neuquén, Río Negro, Santa Cruz, Tierra del Fuego, Argentinian Antarc-tica, and Southern Atlantic Islands. This region is the largest in Argentina, with an area of 930,638 km^2. It can be divided into two sub-regions (Matteucci 2012b): (a) **Patagonian Andes**, with poorly developed soils, derived mainly from volcanic ash, and rich in allophones. This sub-region contains the largest and deepest glacial lakes of South America (over 300 lakes of different sizes), many of which are the sources of the longest Patagonian rivers that feed large reservoirs located on the Patago-nian plateau (Quirós and Drago 1999). The vast majority of these water bodies are chemically poor (low ions and nutrients concentration) and, in general, dominated by silica (Pedrozo et al. 1993). (b) **Patagonian steppe**, with typically alkaline soils with high salt content, negative water balances and evaporation dominance. It is a complex landscape, mainly characterized by a basaltic plateau and tectonically uplifted pebble fans (Iriondo 1989). The allochthonous-exoreic rivers originating in the Andes can cross this arid region and feed large artificial lakes. Furthermore, some large depressions in Patagonia contain permanent natural and artificial lakes, while others have temporary waters with evaporitic deposits in central areas (Quirós and Drago 1999).

The first studies on lake sediments in the Patagonian region date back to 1990, when phosphorus retention in sediments from different lentic water bodies in the Nahuel Huapi National Park and in the Patagonian plateau was studied in response to the anthropic influence (Temporetti 1990). Since then, the number of studies on lake sediments in this region has increased considerably, addressing different aspects of the effect of anthropic activities on the aquatic environments (Temporetti 1998; Temporetti and Pedrozo 2000; Diaz et al. 2001, 2015; Temporetti et al. 2013, 2014a, b, 2019; Ribeiro Guevara et al. 2003, 2005a, b, 2009, 2010; Cabrera et al. 2016, 2020; León et al. 2017; Juncos et al. 2017; Williams et al. 2017).

The aim of this chapter is to summarize 30 years of research carried out by the Water Quality Group (INIBIOMA, CONICET-UNComahue) on sediments from lake environments in the Patagonian region and their role in aquatic resource assessment.

1.1 Study Area

The studied water bodies are located between 33° and 50° S and 68° and 72° W (Fig. 1). According to Quirós and Drago (1999), the aquatic environments of this region have been classified as warm monomictic, with a stratification period during summer. The climate in the Patagonian region is continental, classified as humid cold temperate in the mountains to arid in the steppe (Speck et al. 1982; Matteucci 2012a). Rain periods occur mainly between late winter and early spring. Due to moisture loss from the prevailing western winds, a strong annual west–east precipitation gradient is observed, ranging from 2700 mm y^{-1} on the Argentina/Chile border (altitude 1020 m a.s.l.) to 500 mm y^{-1} in the Patagonian steppe (800 m a.s.l.) in a distance of only 100 km. The annual average temperature varies between 8.0 °C at high altitudes (above 2000 m a.s.l.) and 20.0 °C in protected valleys, and between 7.5 and 12.5 °C in the Patagonian steppe. The studied environments are seven lakes, five reservoirs and two shallow lakes. Table 1 shows the geographic coordinates, morphometric data, physical and chemical parameters, and the trophic classification of the 14 environments. These environments include two very marked gradients: (a) **pH**, ranging from 2.5 in Lake Caviahue, a naturally acidic environment, to 9.2 in
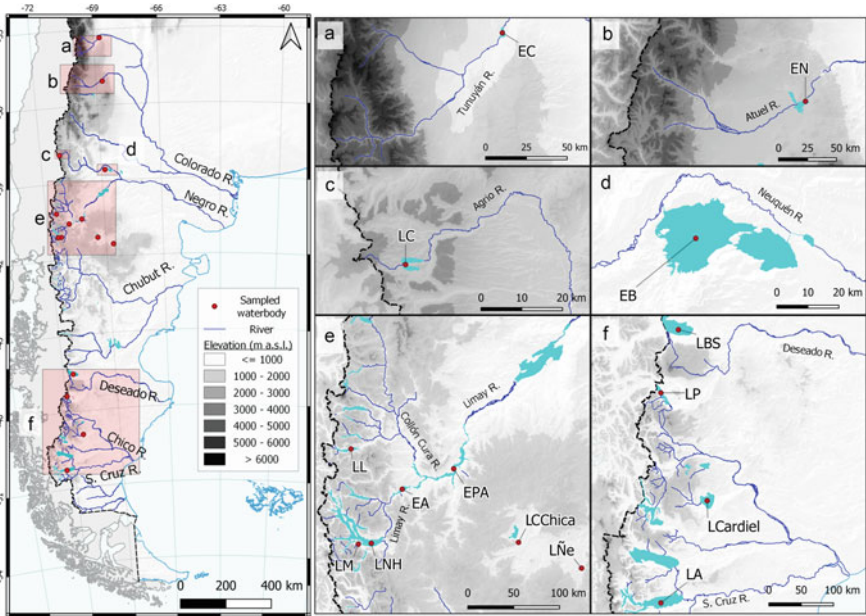

Fig. 1 Study area: **EC** = Reservoir El Carrizal; **EN** = Reservoir El Nihuil; **LC** = Lake Caviahue; **EB** = Reservoir Los Barreales; **LL** = Lake Lacar; **EA** = Reservoir Alicura; **EPA** = Reservoir Piedra del Aguila; **LM** = Lake Moreno; **LCChica** = Lagoon Cari-Laufquen Chica; **LÑe** = Lagoon Ñe-Luan; **LNH** = Lake Nahuel Huapi; **LBS** = Lake Buenos Aires; **LP** = Lake Pueyrredón; **LCardiel** = Lake Cardiel; **LA** = Lake Argentino

Table 1 Geographic position, morphometric data, physical and chemical parameters, trophic classification, and Eutrophication History for the 15 analyzed lakes. In brackets the acronyms for each water body. Water EC: Electric conductivity of water

	Geographic location	Altitude (m a.s.l.)	Area (km²)	Maximum depth (m)	Secchi disk (m)	Water pH	Water EC (µS cm⁻¹)	Trophic classification	Eutrophication history
Reservoir El Carrizal [1] (EC)	33° 17′ 55.0″ S	786	31	40	1.4	8.1	1265	Mesotrophic	Man made reservoir for irrigation and hydropower generation
	68° 43′ 20.0″ W								Sparsely vegetated basin. Population: 10,000 inhabitants
Reservoir El Nihui [1] (EN)	35° 04′ 21.0″ S	1251	75	17	> 3	8.3	1283	Mesotrophic	Man made reservoir for hydropower generation. Sparsely vegetated basin
	68° 41′ 13.7″ W								Small urban settlements. Agricultural use of the land
Lake Caviahue[2] (LC)	37° 52′ 17.0″ S	1650	922	90	3.6	2.5	1259	Eutrophic	Naturally acidic lake of volcanic origin. Sparsely vegetated basin
	71° 00′ 53.0″ W								Stable population of 1000 inhabitants, which increases in tourist seasons

(continued)

Table 1 (continued)

	Geographic location	Altitude (ma.s.l.)	Area (km²)	Maximum depth (m)	Secchi disk (m)	Water pH	Water EC (µS cm⁻¹)	Trophic classification	Eutrophication history
Reservoir Los Barreales[3] (EB)	38° 33′ 03.0″ S	422	407	120	3.3	8.0	265	Mesotrophic	Reservoir of anthropic origin flood attenuation, located in Vaca Muerta
	68° 49′ 21.0″ O								Basin, one of the five producing oil fields in Argentina. Sparsely vegetated basin
Lake Lácar[4] (LL)	40° 09′ 37.8″ S	625	49	279	25	7.7	60	Oligotrophic	Deep glacial lake. Wooded basin. City of 25,000 inhabitants. Tourist destination
	71° 21′ 47.3″ W								Discharge of effluents with different degrees of treatment
Reservoir Alicura[5] (EA)	40° 35′ 09.0″ S	705	65	115	6.9	7.4	36.0	Oligotrophic	Reservoir of anthropic origin. The main uses of this environment are:

(continued)

Table 1 (continued)

	Geographic location	Altitude (ma.s.l.)	Area (km²)	Maximum depth (m)	Secchi disk (m)	Water pH	Water EC (µS cm⁻¹)	Trophic classification	Eutrophication history
	70° 45′ 09.0″ W								Power generation and intensive trout farming (1132 Tn y⁻¹)
Reservoir Piedra del	40° 11′ 25.0″ S	592	285	120	6.4	7.0	50.0	Oligotrophic	Reservoir of anthropic origin. The main uses of this environment are:
Aguila[5] (EPA)	69° 59′ 30.0″ W								Production of electrical energy and intensive trout aquaculture (42 Tn y⁻¹)
Lake Moreno[6] (LM)	41° 04′ 33.0″ S	778	164	100	12.5	7.0	35.9	Oligotrophic	Deep glacial lake. Basin forested. Little village of 800 inhabitants. Tourist destination
	71° 30′ 22.0″ W								Without effluent treatment. Fish farming center (50 Tn y⁻¹)

(continued)

Table 1 (continued)

	Geographic location	Altitude (m.a.s.l.)	Area (km²)	Maximum depth (m)	Secchi disk (m)	Water pH	Water EC (µS cm⁻¹)	Trophic classification	Eutrophication history
Lagoon Cari-Laufquen	41° 13′ 04.6″ S	150	5	5	0.3	8.4	440	Eutrophic	Shallow lagoon of wind origin. Sparsely vegetated basin
Chica (LCChica)	69° 25′ 54.3″ W								No nearby urban settlements. Livestock-related land use
Lagoon Ñe-Luan (LÑe)	41° 30′ 15.9″ S	1000	0.6	15	0.7	8.2	324	Eutrophic	Shallow lagoon of wind origin. Sparsely vegetated Basin
	68° 37′ 32.3″ W								No nearby urban settlements. Livestock-related land use
Lake Nahuel Huapi[7] (LNH)	41° 05′ 25.0″ S	764	529	438	20	7.3	34	Oligotrophic	Deep glacial lake. 3 cities on its coasts:

(continued)

Table 1 (continued)

	Geographic location	Altitude (ma.s.l.)	Area (km^2)	Maximum depth (m)	Secchi disk (m)	Water pH	Water EC (µS cm^{-1})	Trophic classification	Eutrophication history
	71° 20′ 08.0″ W								SC de Bariloche (130,000 inhabitants.), Villa la Angostura (15,000 inhabitants.) and Dina Huapi (6000 inhabitants). The main activity is tourism
Lake Buenos Aires[8] (LBS)	46° 18′ 14.0″ S	200	1892	550	3.3	7.8	77	Oligotrophic	Deep glacial lake. Very wide and partially wooded basin
	71° 42′ 57.1″ W								No significant human activity. Livestock-related land use
Lake Pueyrredón[8] (LP)	47° 26′ 20.2″ S	112	320	280	8.0	8.3	174	Oligotrophic	Deep glacial lake. Very wide and partially wooded basin

(continued)

Table 1 (continued)

	Geographic location	Altitude (m a.s.l.)	Area (km²)	Maximum depth (m)	Secchi disk (m)	Water pH	Water EC (μS cm⁻¹)	Trophic classification	Eutrophication history
	71° 55′ 18.4″ W								No significant human activity. Livestock-related land use
Lake Cardiel[8] (LCardiel)	48° 48′ 38.6″ S	300	460	491	1.3	9.2	4512	Eutrophic	Shallow lake of wind origin. Sparsely vegetated basin
	71° 11′ 57.9″ W								No urban settlements. Livestock-related land use
Lake Argentino[8] (LA)	50° 07′ 40.1″ S	187	1466	500	2.0	7.5	40	Oligotrophic	Deep glacial lake. Very wide and partially wooded basin
	72° 06′ 51.9″ W								City of 20,000 inhabitants. Important tourist center. Livestock-related land use

Data from: (1) León et al. (2017), (2) Pedrozo et al. (2001), (3) Rotondo et al. (2020), (4) Temporetti et al. (2009), (5) Othaz Brida (2021), (6) Queimaliños et al. (2012), (7) Alonso et al. (2006), (8) Alemanni (2006) and (9) Pedrozo et al. (2006)

Lake Cardiel, an alkaline environment; and (b) **altitude**, ranging from 1650 m a.s.l. (Lake Caviahue) up to 112 m a.s.l. (Lake Pueyrredón).

1.2 Methodology

Sediment cores were collected between 1990 and 2019, at least once at each sampling site using a 6 cm diameter Uwitec-type extractor or an Ekman-Birge dredger in most cases. All samples were extracted at depths ranging from 5 to 20 m except for Lake Caviahue (90 m). The first 10 cm of the sediment column were considered in the analysis of all samples. In situ, pH and redox potential (Eh) were measured with specific and temperature-adjusted electrodes. The storage and conservation of the samples were carried out in accordance with APHA (1999). In the laboratory, samples were oven-dried at 60 °C, homogenized in a ceramic mortar, and sieved through a 500 µm mesh (Newark, ASTM Nº 36 USA Standard Series Sieves) to remove the least reactive coarse fraction. All performed analyses followed standardized analytical recommendations: (a) **Texture**: sieving method (2.00, 1.00 and 0.25 mm USA Standard Series Sieves) and densimeter (0.05 to 0.002 mm and < 0.002 mm) according to Forsythe (1985). (b) **Nutrients**: TP (Total Phosphorus): 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) and Total Nitrogen (TN) and Total Carbon (TC) by automatic Thermo-Flash 1112 analyzer. (c) **Elemental composition**: by SEM–EDX microanalysis (Philips 515-EDAX Genesis 2000) (Last 2001b; Saarinen and Petterson 2001). (d) **Mineralogy:** by X-ray diffraction (PANalycal Empyrean Diffractometer). (e) **Phosphorus fractionation**: following the recommendations by Hieltjes and Lijklema (1980), discriminating the labile fraction (P-Labile) (extracted with 1 M NH_4Cl), 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-OM) (calculated as the difference between the sediment TP and the sum of the previous mentioned fractions). (f) **Phosphorous fixing isotherms**: Batch experiments were performed by measuring dissolved P in a mixture of dried sediment and a set of increasing P concentration solutions (0.0, 1.7, 2.7, 3.7, 4.5, 5.5, 8.5, 10.0 mg P L^{-1} prepared from a 1000 mg L^{-1} PO_4^{3-} Merck Certipur® solution). Sediment aliquots (*ca.* 0.2 g) were put in centrifuge tubes (50 mL), filled with PO_4^{3-} solution (10 mL), and placed in the dark at room temperature (20 °C) for 48 h with periodic mixing (2 h in orbital shaker). The supernatant was filtered (through a 0.45 µm pore size) and analyzed for P (Murphy and Riley 1962). The maximum P adsorption capacity of the sediment (Pmax, mg g^{-1}) was estimated using the linearized Langmuir equation (Langmuir 1997):

$$1/Pads = 1/(KL \cdot Pmax) \, Pdis + (1/Pmax)$$

where Pads (mg g^{-1}) is the net P adsorbed to sediment estimated by mass difference of dissolved P between initial and final solutions after 48 h, KL (mg L^{-1}) is a constant related to the binding energy of P to the sediment, and Pdis (mg L^{-1}) is the P concentration remaining in solution after 48 h (Sposito 2008). Furthermore, the phosphorus retention coefficient (PRC) by sediments for each site was calculated as a percentage of the Pmax difference, estimated from the Langmuir equation, and the TP in sediments.

2 Effect of pH in P Adsorption Dynamics in Sediments

The factors that influence P exchange between sediments and the water column can be physical (temperature, wind action, etc.), chemical (pH, dissolved oxygen, nitrates, sulfates, etc.) and biological (bioturbation, bacterial activity, etc.) (Boström et al. 1982; Golterman 2004). In any of the compartments of the waterbody (water, sediment, water–sediment interface, interstitial water), pH is one of the factors that affect P release, and it has been one of the most studied (Jin et al. 2006; Wang et al. 2005; Wu et al. 2014). An increase in pH can release P bound to Fe and Al complexes due to site-specific competition between hydroxyl ions and P bound to these metal (hydro)oxides (Anderson 1974; Kim et al. 2003; Li et al. 2016). In this sense, pH is an important parameter in controlling P availability in sediments. The pH in lake sediments often varies because of specific microbial processes or changes in environmental conditions (Wang et al. 2005). Most of the studies to demonstrate the relationship between pH and P release/retention in lake sediments were carried out in laboratory tests, where a pH gradient is simulated by adding solutions of hydrochloric acid or sodium hydroxide. However, there are very few studies on the adsorption of phosphate by sediments with different pH values in natural systems (Ding et al. 2016). In a recent contribution, Temporetti et al. (2019) evaluated the pH effect on P dynamics (release/adsorption) in sediments in a river system with a natural pH gradient (from 1.5 to 6.7): the Agrio River, Neuquén province. The authors observed that, while TP concentration in water decreased with increasing pH, an inverse relationship occurred in sediments. On the other hand, the results also indicated that the phosphorus retention capacity was greater at low pH and decreased with increasing pH (Fig. 2), affecting the retention capacity of sediments from the upper part of the river, where the pH was more acidic. This P retention capacity varied according to the time of year, possibly due to several factors such as variations in river water level, temperature gradient, oxide precipitation (mainly as Fe and Al oxyhydroxides), the presence of algae and bacteria that consume dissolved nutrients and the formation of complexes with organic matter in sediments. Although the results of the different fractions of P in sediments showed the existence of an alternation in P control in relation to the variation in pH (Fe/Al at pH < 5.5 and Ca at pH > 5.7). According to Golterman (2004), increase in pH causes a change towards the co-precipitation of CaCO$_3$-P and a decrease in Fe(OOH)-P, while the decrease in pH produces the opposite effect. It was demonstrated that sediment P control of all
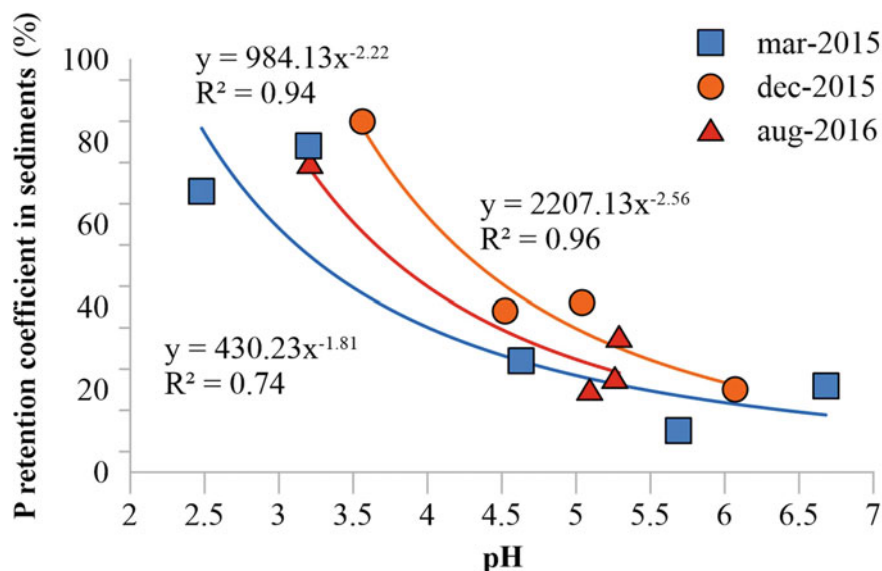
Fig. 2 Variation of phosphorus retention coefficient (PRC) with the pH gradient in sediments of Agrio River. Modified from Temporetti et al. (2019)

the system was regulated by Fe/Al oxyhydroxides and, to a lesser extent, by organic matter (OM) and not by Ca, as it occurs in alkaline pH sediments.

3 Texture, Chemical Characterization and Mineralogy

According to Lewis (1984), the three basic descriptors of sediments are texture, structure, and composition. The first involves the general physical appearance of sediments or rocks (Last 2001a) Besides, texture can provide information about sediments such as origin, transport mechanisms and environmental conditions within the basin. Knowing the textures of lake sediments is necessary because it enables us to understand their capacity to fix pollutants, among other things. Sediment structure enables us to comprehend their chemical properties and the behavior of the chemical substances inside them (Boyle 2001) by describing the elemental composition and understanding the interactions between different parts of the environment. Finally, like texture and structures, sediment mineralogical analysis is essential to adequately describe the material (Lewis 1984), in order to comprehend the genesis of sediments in a lake basin, to decipher transport mechanisms, and to infer limnological, hydrological and climate conditions (Last 2001b). According to Last (2001b), from a mineral origin perspective, there are three different types of minerals in most water bodies: (a) **Allochthonous or detrital minerals**, those which are introduced into the environment through surface currents, erosion from the coast, sheet

flooding, mass movement, or wind activity; (b) **Autochthonous minerals**, which are those inorganic components that originate within the water column, either by inorganic or biologically induced chemical precipitation; and (c) **Autigenic minerals**, those which originate from the diagenetic alteration of the sediment that is already deposited (secondary minerals) or by chemical reactions within the interstitial water of the sediment (primary or secondary minerals). According to Xiao et al. (2013), minerals are often important as very effective absorbents of environmental pollutants. Consequently, in order to better understand the interaction of phosphorus with sediments, it is necessary to study the characteristics of phosphorus adsorption by the sediment mineral matrix.

The sediments of the studied Patagonian environments were dominated (average = 69%) by a sand fraction (2 > sand > 0.05 mm), the reservoirs located at the south of Mendoza (El Carrizal and El Nihuil) and the lagoons of the Patagonian plateau (Carrilafquen Chica and Ñe-Luan) being the environments with the lowest percentages. The silt fraction (0.05 > silt > 0.002 mm) was 24.5% on average for all the environments, turning out to be the main fraction in the environments mentioned above. The clay fraction (< 0.002 mm) represented 19.3% on average in the sediments from El Carrizal and El Nihuil, and 13.2% on average in those from Carrilafquen Chica and Ñe-Luan lagoons, while it was present in a very low proportion (1.0% on average) in sediments from the rest of the environments. Following the textural classification established by the USDA (United States Department of Agriculture 1999), the sediments of the studied environments can be classified as: (a) Loam-Silt Loam, at southern Mendoza and the Patagonian Plateau and (b) Sand-Loamy Sand, at the Andean Patagonian region and southern Patagonia (Fig. 3a). The multivariate Principal Component Analysis (PCA) was used to display a graphical ordination of textural data, in order to highlight similarities or differences between the water bodies, and to verify an environmental gradient (Fig. 3b). The PCA showed that
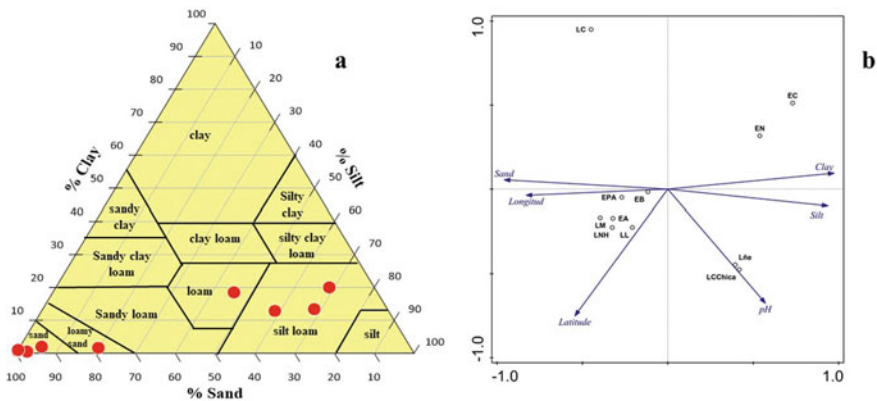

Fig. 3 **a** Textural classification triangle of the sediments from the studied environments. **b** PCA of textural variables performed on sediment samples from the studied environments. Both axes explain 98% of the total variance of the data

the more alkaline environments presented a higher percentage of silt and clay than the acid and neutral pH environments, which correlated significantly ($p < 0.05$). Both axes explained 85% of the total variance of the data. The sands presented a negative correlation ($r = -0.62$) while the silts and clays presented a positive correlation ($r = 0.67$ and $r = 0.72$, respectively). According to Wang et al. (2005), the finer textures have greater pollutant adsorption capacity and suspension potential. Therefore, the sediment with a higher proportion of clay and silty textures could be more contaminated. On the other hand, Wang et al. (2020) studied the adsorption of two pollutants in the sediments of a river in China, evaluating the effect of particle size, humic acids, pH and temperature. The authors found a significant interaction between particle size and pH, observing that the adsorption capacity of pollutants increased with the interaction between these two variables, arguing that pH can change the configuration of the deposited particles favoring adsorption. In this sense, an increase of pH would cause an increase in negative charges on the surface of the sediment.

The chemical composition of the sediments of all the studied environments (Table 2) was dominated by silicon oxides (SiO_2) with an average content of 61.4% (73.3–55.3%) followed by aluminum oxides (Al_2O_3) with concentrations ranging between 11.5% in Lake Caviahue and 22.5% in Lake Lácar. Overall, the mineralogy was dominated by quartz (SiO_2), a stable mineral and a main component of clays. In general, from the performed PCA (Fig. 4), we can identify a first gradient (axis 1) given by pH and SiO_2 that clearly separates Lake Caviahue from the rest of the

Table 2 Average pH values in water and chemical composition of sediments of the analyzed water bodies. The acronyms for each water body are defined in Table 1

|	Water	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2
	pH	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)
EC	8.1	58.9	17.9	4.8	9.5	3.3	2.9	2.2	0.6
EN	8.3	59.0	17.9	4.9	9.9	3.0	2.6	2.1	0.5
LC	2.5	73.3	11.5	2.4	1.1	0.7	2.6	0.9	1.3
EB	8.0	55.3	18.4	8.9	5.3	2.9	2.8	3.2	1.2
LL	7.7	57.0	22.5	9.0	3.7	2.5	3.4	1.1	0.8
EA	7.4	–	–	–	–	–	–	–	–
EPA	7.0	–	–	–	–	–	–	–	–
LM	7.0	63.5	15.1	10.3	2.9	1.6	2.0	1.7	0.7
LCChica	8.4	56.6	17.4	7.0	7.4	4.0	1.4	1.4	0.8
LÑe	8.2	62.3	20.7	7.5	3.2	3.1	0.7	1.4	0.8
LNH	7.3	–	–	–	–	–	–	–	–
LBS	7.8	62.6	19.7	6.3	2.2	2.4	3.2	2.3	0.8
LP	8.3	60.0	20.9	6.6	0.6	1.2	1.5	3.9	0.7
LCardiel	9.2	65.4	17.3	5.7	2.7	3.3	3.2	1.7	0.8
LA	7.5	62.6	19.7	6.3	2.2	2.4	3.2	2.3	0.8
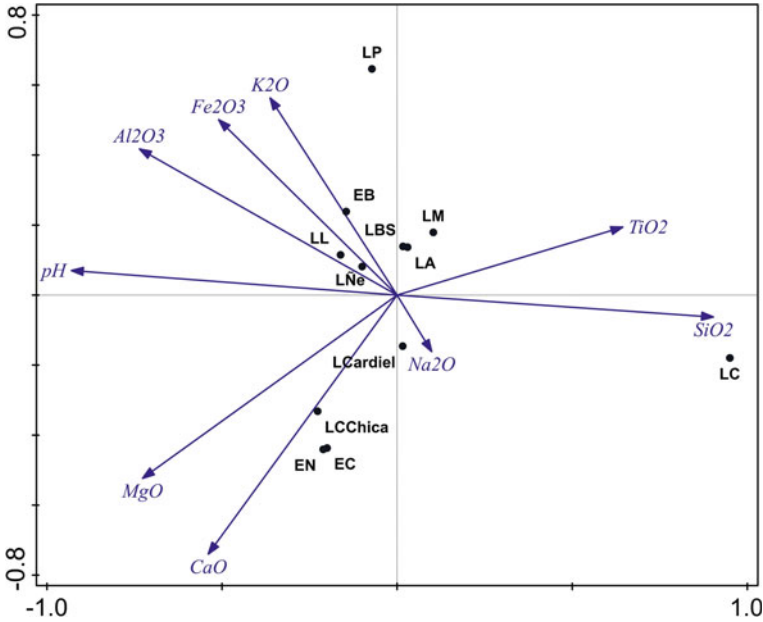
Fig. 4 PCA of chemical variables performed on sediment samples from the studied environments. Both axes explain 61.06% of the total variance of the data. The acronyms for each water body are defined in Table 1

studied environments, while a second gradient (axis 2) was linked to pH with the oxides of Fe, Al, Ca, K and Mg. Both axes explained 61.1% of the total variance of the data.

Certain distinctive peculiarities could be observed in some of the studied environments:

(a) The environments of Southern Mendoza (El Carrizal and El Nihuil reservoirs) were characterized by the presence of CaO as the third most important component of sediments with an average concentration of 9.7%. In this sense, León et al. (2017) found that the chemical composition of sediments from these two environments was characterized by calcium enrichment compared to the chemical composition of the Earth's continental crust and suspended material transported by rivers of South America, North America, Africa, Asia, and Europe. This was in accordance with the basin lithology, which is characterized by deposits rich in gypsum and calcite (Sruoga et al. 2005; Ramos et al. 2010), suggesting an endogenous formation of calcium minerals (León and Pedrozo 2015).

(b) For the rest of the water bodies located in the North–South geographic gradient, iron oxides (Fe_2O_3) were the third most important component of the sediments with an average concentration of 7.0% (between 5.7 and 10.3%).

(c)   For the acidic environment Lake Caviahue, Temporetti et al. (2013) found
      that SO_3 was important in the chemical composition of lake sediments, with
      concentrations varying between 3.4 and 6.1%.

Regarding the mineralogical composition, the analysis of Lake Caviahue sediments showed that the predominant minerals were andesite $((Na, Ca)(Si,Al)_4O_8)$, albite $(Na(Si_3Al)O_8)$, anorthite $(Na(Al_2Si_2O_8))$ and cristobalite (SiO_2), indicating the volcanic origin of this sediments (Temporetti et al. 2013). According to Pesce (1989), the predominant rocks in this area are andesitic and pyroclastic lavas related to the dynamics of Andean volcanism. Furthermore, Murad and Rojík (2003) showed the relationship of pH with the mineralogy by studying the effect on drainage water of abandoned mines in the Czech Republic. These authors found a direct relationship between pH variation and mineral precipitation. In this sense, Temporetti et al. (2019) studied the Agrio River sediments in a natural pH gradient ranging from 1.7 to 6.7 from the river headwaters to 50 km downstream. They found a greater mineral diversity in this gradient. In sites where the pH varied between 2.8 and 4.9, the minerals associated with Fe such as magnetite, pigeonite, and iron and calcium silicates were predominant. On the other hand, minerals associated with aluminum compounds, such as anorthite and Al and Na silicates, predominated in sites from Agrio River where the pH varied between 5.4 and 6.7, although, in this case, pH would not control the crystallization of these minerals. These results were reflected in the formation of coatings found along this gradient (Fig. 5) and coincided with those reported by Parker et al. (2008), who observed orange coatings of hydrated ferric oxide $(Fe_2O_3.xH_2O; HFO)$ and others of white hydrated aluminum oxide $(Al_2H_2O_4; HAO)$ on rocks along the pH gradient of the Agrio River.
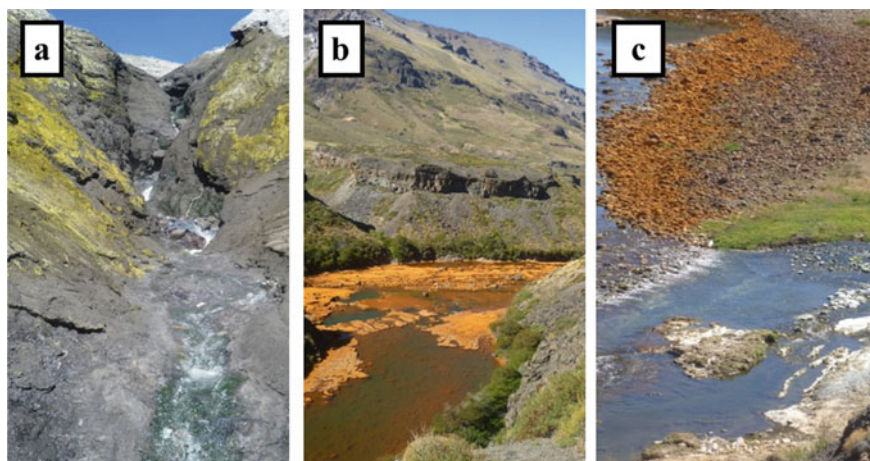

Fig. 5 Photographs of the rocks coatings taken at three different sites of Agrio River. **a** Sulfur coatings in the river headwater (water pH = 1.77); **b** iron coating downstream Agrio River Cascade (water pH = 4.11), and **c** aluminum coating in the confluence of Agrio (water pH = 5.30) and Ñorquín (water pH = 7.00) rivers

Moreover, for El Carrizal and El Nihuil reservoirs, León et al. (2017) observed that sediment mineralogy reflected the richness of calcium in the system, and the most abundant identified minerals (14%) were calcium carbonates and phosphates. Furthermore, these authors found that the amount of P-containing minerals was relatively high, mainly Ca phosphates and hydrated Al and Fe phosphates (11% and 3%, respectively).

4 Phosphorus and Its Fractions

In most of the aquatic environments of the Patagonian region, the main contamination problem is linked to eutrophication. It is an environmental issue of great global concern. In this sense, it is necessary to know not only the total amount of nutrients in the sediment, mainly P, but also the main sediment phases to which this nutrient is associated. Data on phosphorus fractionation enables the evaluation of the bioavailable fraction, which can contribute to the trophic state of the system (Pardo et al. 2003). On the other hand, in aquatic systems, the highest amount of P associated with sediments can be found linked to Fe/Al(OOH) or $CaCO_3$ (Golterman 2004). In addition, a considerable amount of phosphate is present as organic P, most of which is in the solid phase and a little portion in solution like inorganic P.

The analysis of TP concentration and its fractions in sediments of the studied water bodies can be carried out by considering three approaches: (a) **North–South geographic gradient**: TP concentration decreases southwards (Fig. 6a). From the data analysis, a negative (r = -0.56) and significant ($p < 0.05$) correlation was found between the latitude and TP concentration in sediments. This is probably related to the fact that the studied environments located south of 42º S have a very low anthropogenic pressure. (b) **pH gradient**: when analyzing P fractions, we observed that in environments with acidic and neutral pH, P control was associated with P bound to Fe/Al oxyhydroxides (Fig. 6b). However, this control begins to reverse when pH exceeds 7.0. As pH increases, P control is associated with bonding to Ca compounds (Fig. 6c). Although correlation analysis only showed a negative (r = −0.95) and significant ($p < 0.05$) correlation between the environments and the P bound to Fe/Al oxyhydroxides, the PCA indicated the existence of a gradient linked to the pH in the studied environments. Similar results were observed by Temporetti et al. (2019) when they analyzed the sediments of The Agrio River which shows a natural pH gradient. (c) **Trophic gradient**: when analyzing the content of P-labile (Fig. 6d), which is the one that is released more quickly into the water column (internal load) and is readily available for algal growth, it is observed that oligotrophic water bodies present lower P-labile concentrations than mesotrophic and eutrophic water bodies. In this case, the effect of the geographic gradient is less noticeable for the oligotrophic water bodies than for the mesotrophic and eutrophic studied water bodies. The performed PCA showed this gradient, and a negative (r = -0.83) and significant ($p < 0.05$) correlation was found between the studied water bodies and their meso-eutrophic condition.

Fig. 6 a Variation of TP concentration in sediment samples from the studied environments. **b** Variation of P concentrations bound to iron and aluminum oxyhydroxides (P-Fe/Al) and calcium compounds (P-Ca) in sediments from acidic and neutral studied environments. **c** Variation of P concentrations bound to iron and aluminum oxyhydroxides (P-Fe/Al) and calcium compounds (P-Ca) in sediments from alkaline studied environments. **d** Variation of the P-labile concentration in relation to the trophic state of the studied environments. The acronyms for each water body are defined in Table 1
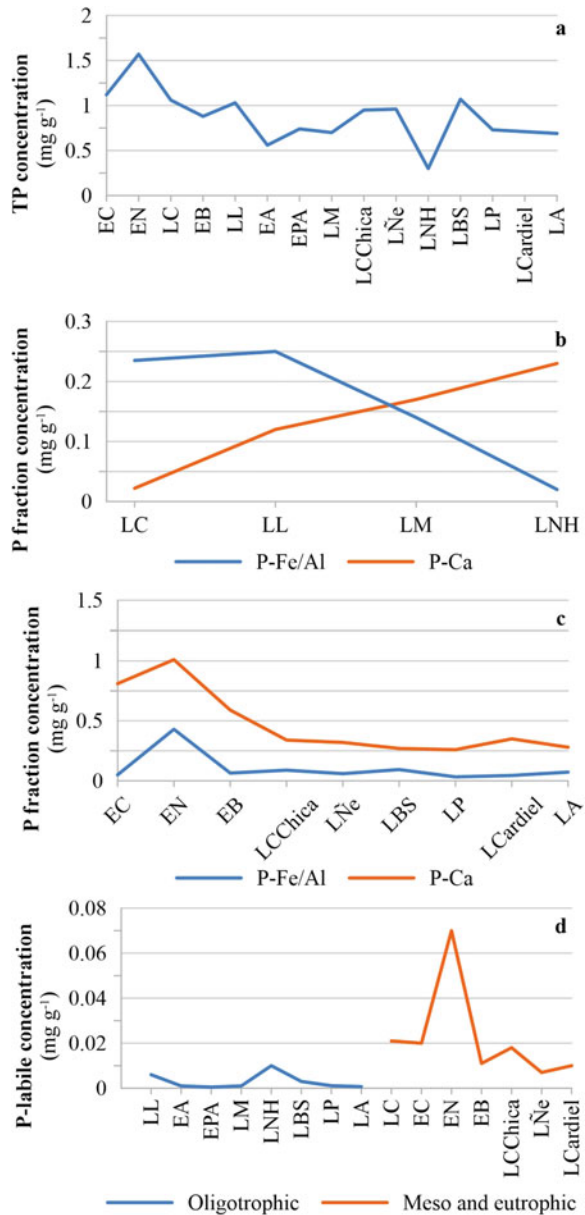
In an aquatic environment, P distribution in the sediment profile may indicate that the potentially mobile P may be represented by the difference between TP concentration in sediment surface and TP concentration at the stabilization depth (Carey and Rydin 2011). This potentially mobile P will eventually be released into the water column (Boström et al. 1982; Rydin 2000) and is mainly associated with iron and organic matter (Rydin 2000). According to Carey and Rydin (2011), the depth pattern of TP distribution in lake sediments can vary significantly between oligotrophic and eutrophic systems, which may explain the differences between low and high levels of nutrients in environments of different trophic states. Temporetti et al. (2014b) evaluated this hypothesis in the sediments of eight Patagonian environments such as lakes, lagoons and reservoirs. The results showed that oligotrophic lakes tend to accumulate P, whereas eutrophic lakes tend to release this nutrient into the water column. On the other hand, they observed that certain parameters of interstitial water and sediments were significantly correlated with the trophic state of the studied environments; in particular: (a) soluble reactive phosphorus (SRP) concentration in pore water, (b) P-labile fraction concentration, (c) TP depth distribution pattern, and (d) metal/P ratio (MPS). In the study mentioned above, only reservoir El Nihuil was classified as mesotrophic, presenting a homogeneous sediment TP distribution pattern that was intermediate between oligotrophic and eutrophic environments. In this case, sediments could be enriched with phosphorus, but they would be close to saturation, showing a homogeneous pattern of TP depth distribution. On the other hand, these authors observed that oligotrophic environments had a positive linear slope while eutrophic environments had a negative linear slope. However, some exceptions to these patterns were detected: (a) Lake Lácar, an oligotrophic environment which should have shown a positive linear slope but actually presented a negative linear slope; and (b) Lake Caviahue, an eutrophic environment (according to P concentration in water) presented a positive linear slope characteristic of oligotrophic environments. Finally, Temporetti et al. (2014b) concluded that, to define the trophic state of aquatic environments both, sediments, and interstitial water, could be considered more comprehensive parameters than the typical water column parameters. By considering the sediment TP distribution pattern, it is possible to determine if P fixation or sediment release into the water column is occurring.

5   Phosphorus Fixation/Release Capacity

Sediment TP content in aquatic environments depends on factors such as physicochemical conditions, chemical and textural composition, sedimentation rates, and diagenetic processes (Anshumali and Ramanathan 2007; Li et al. 2007). The balance between P fraction associated with sediments and that dissolved in the water column is determined by redox conditions (Boström et al. 1982; Sinke 1992; Katsev et al. 2006), adsorption processes, solubility in the mineral phase and mineralization of OM (Kaiserli et al. 2002), among other parameters.

According to Li et al. (2007), particulate OM sedimentation, anaerobic bacteria activity and dissolved oxygen decrease at the sediment surface produce reduced compounds that cause a decrease in redox potential. In turn, this decrease triggers the release of electrons that can be transferred to the oxidizing components (e.g. iron, aluminum and manganese oxides). These reduced compounds dissolved in the water column can decrease P adsorption capacity. Besides, the products of the reduction reactions [e.g. organic anions, ammonium (N-NH$_4^+$) and elemental sulfur (S)] compete with P for adsorption sites in sediments, generating phosphorus release into the water column (Koski-Vähälä et al. 2001). In sediments, P sorption mechanisms are generally studied through empirical models that describe the characteristics of these processes, such as Freundlich and Langmuir isotherms (Langmuir 1997; Limousin et al. 2007). Isotherm tests have been widely used to estimate P adsorption in soils (Tunesi et al. 1999), in river sediments (Lin et al. 2009), lake and reservoir sediments (Wang et al. 2009), and in purified solid media (Freeman and Rowell 1981; Yagi and Fukushi 2012; Perassi and Borgnino 2014; Abdala et al. 2015).

León et al. (2017) studied two reservoirs with naturally high sulfate waters in Southern Mendoza (El Nihuil and El Carrizal) to assess the effect of this anion concentration on geochemical processes acting upon P bonding and speciation in sediments. These authors observed that only El Carrizal sediments adjusted to a typical Langmuir isotherm, while El Nihuil sediments adjusted to a steeper slope that changed from positive to negative. These authors concluded that this last pattern was established as a result of initial adsorption at low concentrations of dissolved P and co-precipitation of P bound to carbonates at higher concentrations of P. The percentage of dissolved P after the test carried out with El Nihuil sediments reservoir was low (18%) compared to that of El Carrizal sediments (69%), which suggests that the co-precipitation of P in the first reservoir may be occurring at higher rates than in the second reservoir.

Furthermore, P fixation isotherms were used to determine the sorption capacity of natural sediments and those affected by intensive salmonid farming in Lake Moreno and reservoir Alicura (Temporetti et al. 1991; Temporetti 1998). The results of P uptake kinetics by natural sediments from both environments confirmed that the dominant processes were regulated by equilibrium reactions and that is the reason why they could be described by the Freundlich and Langmuir isotherms. These sediments are receiving part of the phosphorus entering the basin. Phosphorus fixing capacity was lower in Moreno sediments than in Alicura sediments; this could be due to the fact that the dominant texture in Lake Moreno was sand, while the silty fraction predominated in reservoir Alicura. The predominance of the Ca as a control mechanism for P precipitation over the organic matter-iron mechanism agrees with the results obtained by Shulka et al. (1971), who observed that calcareous sediments retained more phosphorus than non-calcareous sediments. On the other hand, Temporetti (1998) observed in the reservoir Alicura, that the sediments in the area affected by fish farming, compared with sites located upstream and downstream of it, had a high P content that exceeded its fixation capacity, releasing P into the water column (Fig. 7). Othaz Brida (2021) used P sorption experiments to estimate P adsorption capacity in sediments from three reservoirs in Patagonia. In two of them
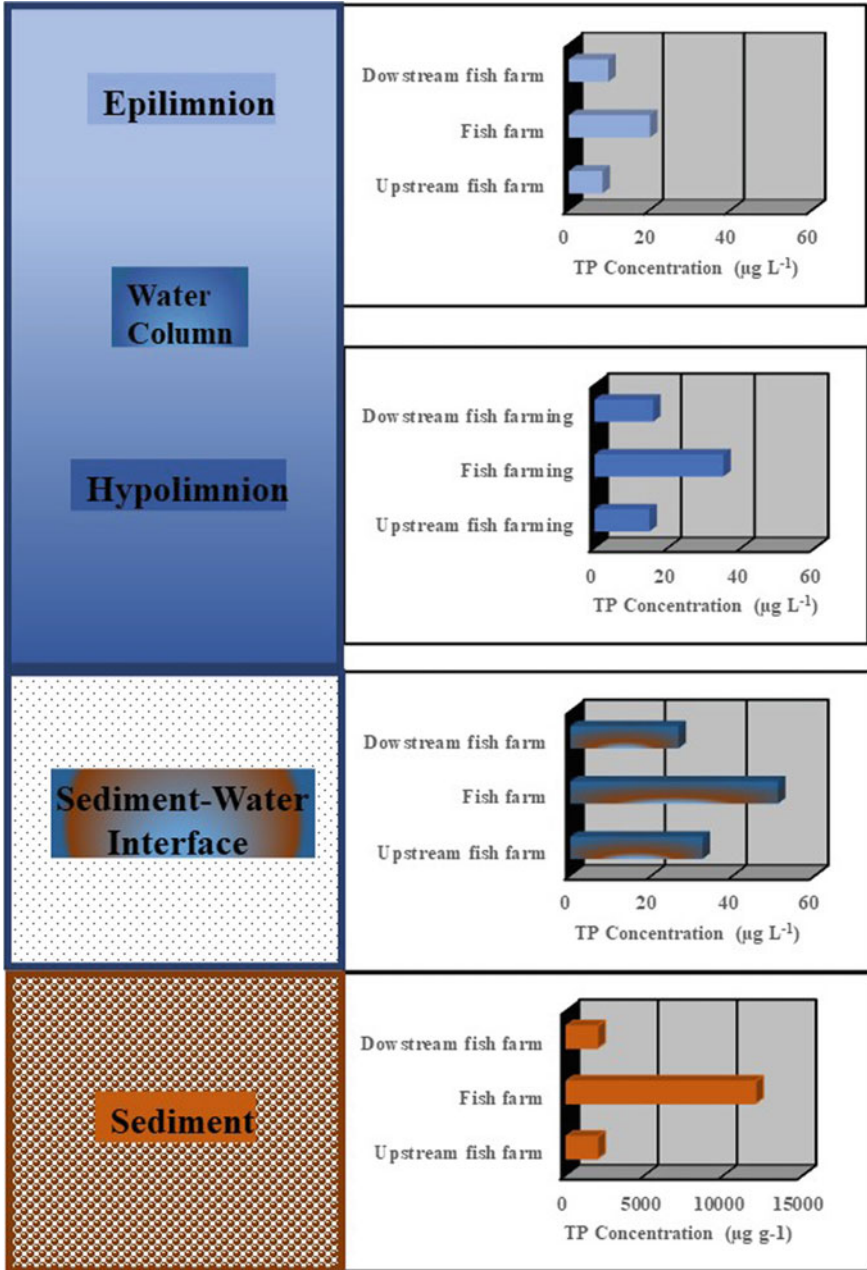
Fig. 7 Decreasing pattern of TP concentration from sediments to epilimnion at three stations in Reservoir Alicura: upstream of fish farm, fish farm and downstream fish farm

(Alicura and Piedra del Águila), since the 1990s and promoted by the administrations of Neuquén and Río Negro provinces, salmonid farms have been installed for intensive farming. Currently, its production is concentrated mainly in reservoir Alicura, where seven companies are operating with a total production of 1200 tons y^{-1}, and in Piedra del Águila there are operating three companies with a total production of 100 tons y^{-1}. The results showed that: 1) although the two reservoirs have an adequate P adsorption capacity, Alicura sediments (in the main body of the reservoir) presented a lower P fixation capacity (1026 $\mu g\,g^{-1}$ d.w., 43%) than Piedra del Águila sediments (1268 $\mu g\,g^{-1}$ d.w., 57%). Additionally, evaluations carried out on sediments under Alicura breeding cages showed, in all cases, that sediments are saturated or close to saturation (CFI 2013), highlighting the impact generated by the higher aquaculture production in this reservoir.

Antonuk (2010) and Temporetti et al. (2014a) used P adsorption capacity to determine the saturation degree of sediments affected by sewage discharge into Lake Lácar. These authors evaluated the sediment quality (P contribution) of the eastern bay of the lake, affected by the discharge of residual waters. They compared sites within the bay with a control site located in the center of the lake and away from the bay. For all the evaluated sites, the results of the performed isotherms adjusted for both, Freundlich and Langmuir isotherms. From this last equation, the authors estimated that the maximum P fixation capacity to the sediment was 17% within the bay and 36% for the control site. These percentages indicated that the sediments within the bay are almost saturated, which may cause a release of nutrients from sediments into the water column.

6 Bioassays with Sediments

By definition, a bioindicator is any species or group of species whose function, population, or condition can reveal the qualitative state of the environment (Ospina Álvarez and Peña 2004). In the case of biological indicators, the presence or absence of certain species constitutes a unit of measurement for the qualitative conditions of a water body. Once an aquatic ecosystem is characterized, the presence and quantity of certain species could directly and accurately indicate the concentrations of specific pollutants (Ptacnik et al. 2008). The most widely used techniques to assess the bioavailability of nutrients and the toxicity of contaminated sediments are **phytoplankton** bioassays (Aksmann and Tukaj 2004; Ramadass et al. 2016). Due to short generation times, the use of planktonic algae as indicators is useful given its rapid response to a contamination process. Quantitative variation in phytoplankton communities is the first response to aquatic environmental changes, and an increase or decrease in algae abundance can be observed depending on the type of damage. Furthermore, qualitative changes can also be observed in phytoplankton communities since new species can colonize the environment while others can decrease and occasionally disappear (Ptacnik et al. 2008). Autochthonous phytoplankton populations are widely used

as bioassays to determine nutrient limitation and resource competition (Tilman and Kilham 1976; Goldman 1978; Tilman et al. 1986; Reynolds 1992).

Diaz et al. (2001) used bioassays with native phytoplankton to assess the response of this communities to the addition of nutrients generated by the intensive production of cage trout in reservoir Alicura. Bioassays were carried out by using sediments affected and unaffected by fish farming, with water and phytoplankton from the environment. These authors found that both, algal biomass, and fresh weight, as well as chlorophyll-a content showed the highest concentrations in bioassays with contaminated fish farming sediments, increasing biomass up to 700% compared to bioassays with uncontaminated sediments. On the other hand, they also observed that nutrient concentrations released from the contaminated sediments to the water in the bioassays increased considerably after 15 days of incubation. These authors concluded that the main consequences of aquaculture activities in the reservoir are an increase in nutrient concentrations, algae density, and phytoplankton biomass due to the release of nutrients from the sediments into the water column. Similar results were obtained by Temporetti (1998), who used algal bioassays to evaluate the effect of contaminated sediments by fish farms in Lake Moreno.

Rotondo et al. (2021) worked in reservoir Los Barreales, located in the most important oil basin of Argentinian Patagonia, Vaca Muerta, and they used bioassays to evaluate the response of phytoplankton and the nutrient availability from contaminated sediments with increasing doses of polycyclic aromatic hydrocarbons (PAHs). On the other hand, they determined the use of native algae from this environment as bioindicators of PAH contamination in sediments. These authors carried out four different bioassays that allowed them to evaluate: (a) the effect of sediment contamination on nutrient availability in solution; (b) the effect of sediment contamination on phytoplankton to highlight the presence of one or more indicator species; (c) the response of an algae species as a potential indicator of sediment contamination; and (d) the response of an algae species to water contamination. To carry out these bioassays, they used water, algae, and sediment from the reservoir, and contaminated the sediments with increasing concentrations (0 (basal), 50, 100, 250, 500, and 1000 ppm) of Phenanthrene (Ph), Anthracene (An), Pyrene (Py) or Benzo(a)anthracene (Ba). The main obtained results showed that PAH contamination of sediments from reservoir Los Barreales modified the release of nutrients into the water column, and also affected the growth of the dominant species of phytoplankton *Scenedesmus quadricauda* at concentrations of at least 50 ppm Ba, 250 ppm Ph, and 1000 ppm Py. The results indicated that bioassays with native algae species from the reservoir were useful in detecting the effect of PAH contamination on sediments and constitute the first approach to create a rapid monitoring tool for assessing the effect of oil spills on the hydrocarbon formation of Vaca Muerta.

7 Conclusions

In this chapter, we evaluated different parameters related to the sediments of eleven aquatic environments of Argentinian Patagonia with different characteristics and degrees of anthropic impact. The main conclusions are:

(1) pH is one of the main parameters that influence P exchange between sediments and the water column. It was demonstrated that the P adsorption capacity in sediments decreases with increasing pH.

(2) Parameters such as texture, chemical composition and mineralogy are essential to understand sediment genesis and transport mechanisms, and to infer limnological, hydrological and climatic conditions from past events.

(3) Three gradients determine different degrees of approach to the distribution of the studied environments: (a) **North–South geographic gradient**, with a tendency to decrease the TP concentration in sediments. (b) **pH gradient**, which determined that, in general, sediment P control in environments with acidic and neutral pH is by Fe/Al oxyhydroxides, while in environments with slightly alkaline to alkaline pH, sediment P control is by Ca compounds. (c) **Trophic gradient**, which determined that P more readily available for algal growth (P-labile) is lower in oligotrophic environments than in mesotrophic and eutrophic environments.

(4) The study of different P fractions, as well as P adsorption/release capacities from sediments, was essential to define the control mechanisms of this nutrient in sediments. Furthermore, understanding these mechanisms will make it possible to evaluate their internal load, necessary when assessing the degree of eutrophication of a water body and/or the carrying capacity of water bodies. This information is important to carry out any productive activity in any aquatic environment.

(5) The use of sediment bioassays with native algae is a particularly useful tool for rapidly evaluating the anthropic impact on water bodies, enabling the detection of algal species sensitive to the presence of specific contaminants.

(6) Sediment studies are a tool for obtaining information on, for example, contaminated and uncontaminated areas, and contaminant distribution patterns. In this sense, these studies should be included when defining monitoring programs since, in many cases, sediment parameters are usually more stable than those measured in the water column, which can present daily or seasonal fluctuations.

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