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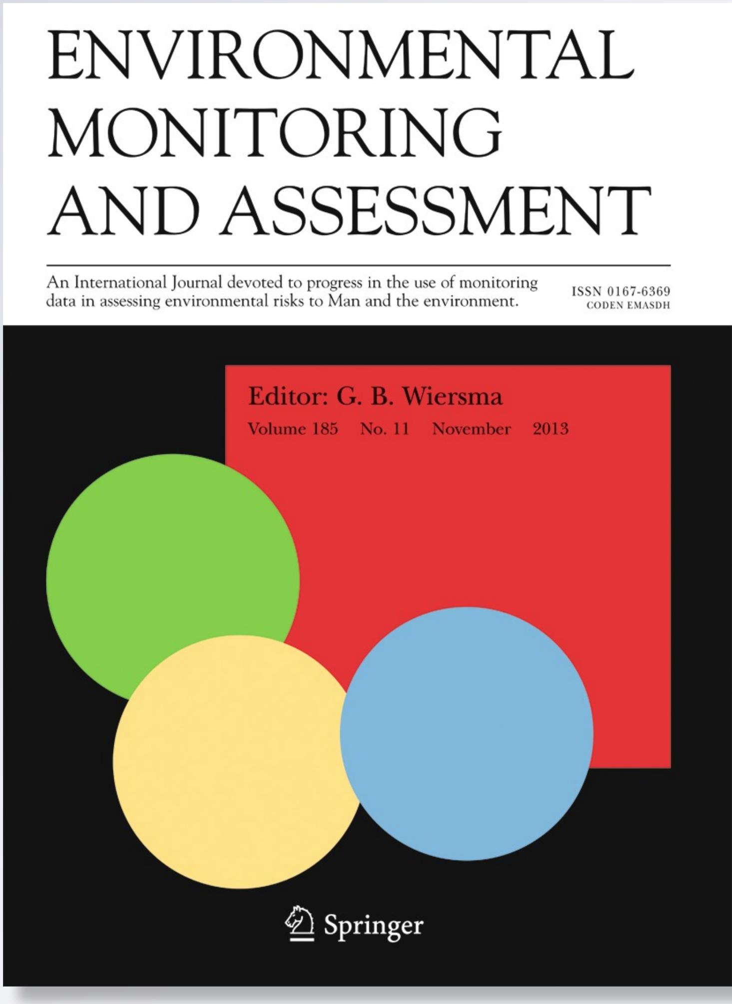
Environmental Monitoring and Assessment
An International Journal Devoted to Progress in the Use of Monitoring Data in Assessing Environmental Risks to Man and the Environment

ISSN 0167-6369
Volume 185
Number 11

Environ Monit Assess (2013)
185:9161-9168
DOI 10.1007/s10661-013-3243-y



Springer

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Received: 3 October 2012 / Accepted: 26 April 2013 / Published online: 17 May 2013

Abstract The lower portion of the Reconquista River is highly polluted. However, little is known about the state of the high and middle basins. The aims of this work were to assess the water quality on the high and middle Reconquista River basins and to determinate if the presence of a reservoir in the river has a positive effect on the water quality. We conducted a seasonal study between August 2009 and November 2010 at the mouth of La Choza, Durazno, and La Horqueta streams at the Roggero reservoir—which receives the water from the former streams—at the origin of the Reconquista River and 17 km downstream from the reservoir. We measured 25 physical and chemical parameters, including six heavy metal concentrations, and performed a multivariate statistical analysis to summarize the information and allow the interpretation of the whole data set. We found that the Durazno and La Horqueta streams had better water quality than La Choza, and the presence of the reservoir contributed to the improvement of the water quality, allowing oxygenation of the water body and processing of organic matter and ammonia. The water quality of the Reconquista River at its origin is good and similar to the reservoir, but a few kilometers downstream, the water quality declines as a consequence of the presence of industries and human settlements. Therefore, the Roggero reservoir produces a significant improvement of water quality of the river, but the discharge of contaminants downstream quickly reverses this effect.

Keywords Reconquista River basin · Water quality · Depuration · Reservoir

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Introduction

The Reconquista River basin is one of the most polluted in Argentina. Poor water quality has been reported as well as the presence of several contaminants (Topalián et al. 1999a, b; Rovedatti et al. 2001;

Topalián and Castañé 2003). The main course of the river is 82 km long, and the whole basin extends 1,574 km^2 over 20 districts that contain over 4.5 million people (INDEC 2011). This represents the third most densely populated area in the country. Thus, the middle-low and low basins of the river are affected by sewage disposal as well as discharges from industries that are not equipped with proper effluent treatment facilities (Salibián 2006). In addition, during the recent years, farming has extended over 72,000 ha in the headers. This increases the anthropic impact with effect that has not been evaluated properly.

The Roggero reservoir is located between the limit of the upper and middle basins of the Reconquista River. This reservoir was built between 1967 and 1972, in the confluence area of the La Choza, Durazno, and La Horqueta streams. The reservoir, also known as San Francisco Lake, is the origin of the main stream of the Reconquista River. The reservoir, with a surface of 460 ha at 17.5 m high, covers Moreno, General Rodríguez, Marcos Paz, and Merlo districts. The mean depth is 1.8 m, with a maximum of 9 m.

It is well known that reservoirs can improve water quality because the relatively slow water flow (compared with rivers and streams) allows the sedimentation of suspended material and the occurrence of processes such as denitrification and phosphorus diminution (Garnier et al. 1999; Harrison et al. 2009). Although the reservoir was built to reduce overflow due to flooding, its presence could be considered as a depuration system of the transported material and, therefore, of the water quality. This has special importance since, as described, the water from the La Choza stream enters the reservoir transporting sewage water among other contaminants (Basílico 2012).

Therefore, Roggero reservoir is expected to carry out a depuration process, causing an improvement in the water quality. However, this expected improvement of the water quality could be limited because of contaminants entering the reservoir or handicapped due to the reservoir management or the action of perturbation factors such as wind (Marcé et al. 2007). The importance of the reservoir as a purification system should be carefully assessed to allow the maintenance of the ecological quality of the whole aquatic system.

In spite of the fact that several studies have been carried out in the middle-low and low basins, the information about headwaters is scarce and fragmented. In fact, in the last years, only the La Choza and Durazno streams have been studied (Vilches et al. 2011; Basílico 2012), and there is no information about the La Horqueta stream or the reservoir water quality. The aims of this study are to assess the spatial variability of water quality in the high-middle basin of the Reconquista River and to analyze the dam effect in the water quality.

Methods

Sampling sites

The Reconquista River is a major tributary of the Luján River near its end at the Río de La Plata. It is situated at the north of Buenos Aires City, in a region with mean annual temperature between 13 and 17 °C and rainfall distributed throughout the year (range 600–1,200 mm). Thus, according with Köpper–Geiger climate classification, the sampling sites are placed in a region with temperate climate without dry season and hot summer (Peel et al. 2007).

The study ran from August 2009 to November 2010 with seasonal frequency and took place in the mouth of the streams of La Choza (Ch), Durazno (D), and La Horqueta (H), within the reservoir (Rv), at the beginning of the Reconquista River (R1) and 17 km downstream from R1 (R2) (Fig. 1). The La Choza, Durazno, and La Horqueta streams and the reservoir belong to the high basin, whereas the sites sampled in the Reconquista River are placed in the middle basin. The flow of the streams of La Choza, Durazno, and La Horqueta are in the same order of magnitude, although the La Choza stream is the largest and the La Horqueta stream the smallest.

Although the principal activity in the headwaters is agriculture and farming, the La Choza stream also receives raw sewage from a country club, from a rural zone, and from a small industrial park, all located upstream from the sampling site. On the other hand, the Reconquista River is highly affected by anthropic activity whose impact increases in intensity from upstream to downstream.

Physical and chemical parameters

We analyzed the variables dissolved oxygen (DO), electrical conductivity (EC), pH, and temperature in

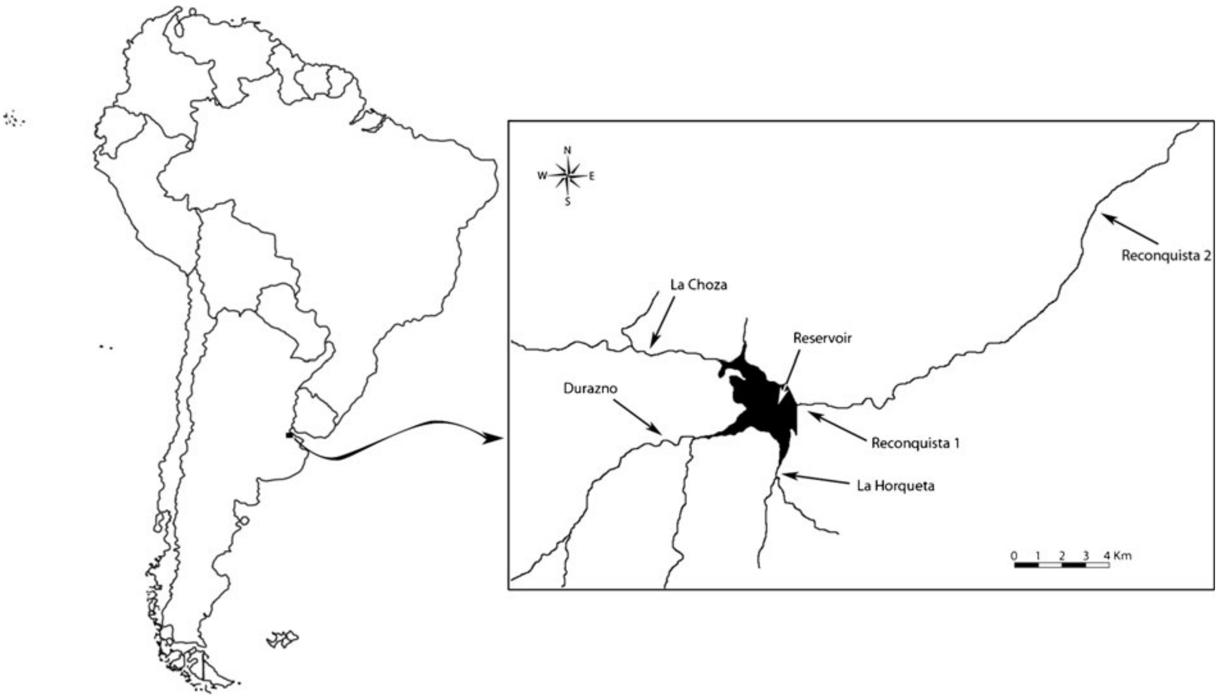

Fig. 1 Sampling sites in the Reconquista River basin, in the northwest of Buenos Aires province, Argentina

the field with Hach portable instruments. We also took water samples which were placed in acid-washed bottles, transported to the laboratory on ice packs, and stored at 4 °C in dark conditions. A portion of the sample was filtered through filters Whatman GF/F to carry out the chemical analyses. The remaining sample was used within 24 h in order to carry out the 5 days of biological oxygen demand (BOD_5) by dilution method and chemical oxygen demand (COD) by a photometrical method using potassium dichromate to oxidize organic substances. The chemical analysis of each sample was performed in triplicate. In Table 1, we summarized the parameters measured and the methodology used. All the analyses were performed according the recommendations of the APHA (2005).

Statistical analyses

We used Statistica 6.0® software for statistical analysis. The variables which did not conform to the assumption of normality were log transformed. We tested the normality using the Kolmogorov–Smirnov test. Those variables which could not be adjusted to a normal distribution were excluded from the analysis. We carried out a multivariate factor analysis using the principal components extraction method with Varimax rotation and included every physical and chemical variable except those associated to avoid redundancy.

In addition, we performed ANOVA tests for comparisons among sites for normal and homoscedastic data sets. When either those assumptions were not met, we performed nonparametric Mann–Whitney test (Zar 1999).

Results

The Roggero reservoir receives water from three streams which have different levels of pollution (Table 2). The La Horqueta and Durazno streams showed the best water quality with highly dissolved oxygen concentration and low values of BOD_5, COD, and nutrient concentration. Although similar, Durazno had higher levels of electrical conductivity than La Horqueta (ANOVA $p<0.01$) mainly due to chloride content. The La Choza stream showed poor water quality with low concentration of dissolved oxygen, high concentration of phosphorus and ammonia, and high levels of BOD_5. Reservoir and Reconquista 1 sites had similar values in most parameters, but

Table 1 Summary of the parameters measured on water samples of each measuring point, and methodology used. All the measures were performed according the APHA (2005)

Parameter	Methodology
pH, temperature, electrical conductivity, dissolved oxygen	Hach portable instruments, HQ 40d multi
Soluble reactive phosphorus (SRP)	Ascorbic acid method
Ammonia	Phenate method
Nitrates	Cadmium reduction method
Nitrites	Colorimetric method
Chlorides	Ag^+ titration (Mohr method)
Total hardness	EDTA titration
Alkalinity	Sulfuric acid titration
5-Day biological oxygen demand	5-Day BOD test
Chemical oxygen demand	Closed reflux, colorimetric method
Heavy metals: As, Cd, Cr, Cu, Pb, Zn	Atomic absorption spectrometry
Suspended particulate organic (SPOM) and inorganic (SPIM) matter	Gravimetric method
Dissolved solids (DS)	Evaporation at 108 °C
Chlorophyll-*a* and phaeopigments	Spectrophotometrically according Aminot (1983)

Reconquista 2 site presented lower values of dissolved oxygen, and the highest BOD_5, nutrients, and heavy metal concentrations. Thus, in the river, there was an increase of nitrate and a diminution of ammonia concentration that was promoted by the reservoir presence. However, this process is reversed downstream where we found a sharp increase in ammonia concentration. There was also a diminution of the suspended particulate organic/inorganic matter ratio in the reservoir in relation to the entries (Fig. 2, Mann–Whitney $p<0.005$) which suggests that the reservoir is successful in processing organic particulate matter.

Figure 3 shows a comparison for variables related with organic matter and eutrophication. A correlation analysis reveals an association among BOD_5, PRS, ammonia and nitrite concentration ($p<0.001$).

We carried out a factorial analysis using the four factors that explained 68 % of total variance. The first factor was associated with dissolved salts (chloride, electrical conductivity, soluble solids, hardness, and arsenic); the second one was associated with BOD_5, SRP, ammonium, and nitrites; the third factor was related to the organic and inorganic suspended materials; and the fourth factor was linked with chlorophyll-*a* (Fig. 4). Thus, the first axis was associated with geological characteristics, the second with eutrophication, the third with optical properties of the water, and the fourth with biological parameters. The last ones are less important in the explanation of variance, whereas those factors linked with salt concentration and eutrophication are highly significant, explaining up to 45 % of the variance.

We drew a scatterplot considering the factor scores of every site including the first and the second factors (Fig. 5). The sites of the La Horqueta stream are at the bottom of the graph, representing higher water quality, whereas the Reconquista 2 stream sites, which have the highest contamination level, are at the top. The Durazno stream, characterized by its high salinity, is on the right. On the left of the graph is one sample from each stream that came from the summer of 2010 when a high flow condition took place a few days before the sampling date, decreasing the normal concentrations of most of the parameters, in particular those associated with the dissolved salts.

Discussion

We found that streams that flow into the reservoir have different water quality. The La Choza stream had the poorest quality due to extremely low oxygen concentration, and high concentrations of phosphorus and ammonia. Similar findings have been reported by Basílico (2012) who studied the inputs of contaminants at the La Choza stream. Although the Durazno stream had higher water quality than La Choza, it showed higher chloride concentration and, therefore, higher values of electrical conductivity than this stream. This characteristic was also reported by Arreghini (2005)

Table 2 Mean values and standard deviation (inside parentheses) of different variables and sampling sites, measured between August 2009 and November 2010 (number of samples per site=6)

Streams	Durazno	La Choza	La Horqueta	Reservoir	Reconquista 1	Reconquista 2
Temperature (°C)	19.6 (7.05)	19.57 (6.64)	19.25 (6.08)	19.92 (5.57)	20.65 (6.16)	20.55 (5.38)
pH	8.33 (0.52)	8.00 (0.63)	8.45 (0.55)	7.78 (0.97)	8.24 (0.75)	7.35 (0.68)
EC (μS/cm)	1430 (557)	1108 (476)	836 (391)	617 (327)	698 (256)	862 (335)
DO (mg/L)	7.33 (4.00)	1.05 (1.03)	6.50 (3.47)	5.18 (2.51)	6.72 (1.57)	3.28 (2.71)
DO saturation (%)	76.37 (37.42)	10.71 (9.83)	67.00 (32.87)	55.24 (25.33)	73.50 (12.50)	35.09 (26.06)
Alkalinity (mg $CaCO_3$/L)	556.7 (232.7)	594.8 (55.4)	615.4 (190.3)	343.9 (59.1)	491.6 (282.2)	630.1 (171.5)
Hardness (mg $CaCO_3$/L)	110.5 (70.7)	110.8 (40.6)	102.0 (30.8)	77.5 (30.1)	74.3 (17.5)	114.8 (28.3)
Chloride (mg/L)	112.02 (55.03)	46.53 (22.75)	15.68 (9.18)	31.46 (16.99)	33.50 (14.93)	51.66 (17.84)
Nitrites (mg N-NO_2^-/L)	0.04 (0.04)	0.06 (0.07)	0.01 (0.01)	0.02 (0.01)	0.02 (0.01)	0.25 (0.12)
Nitrates (mg N-NO_3^-/L)	0.59 (0.62)	0.28 (0.41)	0.09 (0.08)	0.74 (0.59)	0.76 (0.52)	0.81 (0.63)
Ammonia (mg N-NH_4^+/L)	0.53 (0.25)	2.78 (2.93)	0.02 (0.02)	0.08 (0.06)	0.07 (0.06)	5.94 (4.94)
SRP (mg P-PO_4^{-3}/L)	0.34 (0.13)	1.00 (0.50)	0.25 (0.15)	0.47 (0.12)	0.47 (0.11)	1.42 (0.56)
BOD5 (mg O_2/L)	5.04 (2.78)	10.02 (3.51)	6.02 (2.68)	6.57 (2.42)	6.68 (1.05)	22.05 (12.24)
COD (mg O_2/L)	36.86 (29.97)	41.43 (22.50)	40.83 (17.81)	60.31 (15.20)	58.62 (21.37)	76.48 (43.47)
Chlorophyll-*a* (μg/L)	13.70 (17.52)	39.33 (76.00)	25.42 (31.09)	28.25 (27.77)	32.16 (31.66)	26.33 (21.26)
Phaeopigments (μg/L)	3.41 (1.42)	1.11 (0.98)	12.33 (15.69)	41.65 (56.86)	18.47 (11.82)	13.33 (7.92)
SPM (mg/L)	20.15 (13.12)	19.78 (6.41)	71.46 (65.98)	133.04 (83.33)	112.76 (73.59)	76.07 (50.07)
SPOM (mg/L)	5.06 (2.68)	7.98 (3.83)	10.91 (8.83)	19.15 (11.78)	16.18 (10.71)	17.86 (9.72)
SPIM (mg/L)	15.05 (10.75)	11.86 (5.39)	51.71 (55.94)	114.41 (72.60)	96.43 (62.91)	58.56 (46.12)
DS (mg/L)	586.91 (527.22)	449.46 (398.87)	388.29 (313.12)	243.96 (286.68)	364.91 (260.40)	453.60 (303.32)
As (μg/L)	38.80 (25.52)	27.20 (16.13)	18.40 (8.26)	17.20 (8.14)	20.20 (10.06)	20.20 (6.02)
Cd (μg/L)	0.70 (0.27)	1.25 (1.37)	1.00 (0.61)	0.80 (0.27)	1.00 (0.61)	1.80 (2.36)
Cr (μg/L)	2.17 (0.41)	2.00 (0.00)	2.17 (0.41)	3.00 (2.00)	2.00 (0.00)	11.17 (13.29)
Cu (μg/L)	4.33 (3.01)	3.20 (1.64)	5.67 (1.51)	6.33 (3.44)	4.67 (2.34)	5.67 (1.97)
Pb (μg/L)	3.00 (1.90)	3.17 (2.40)	3.33 (1.86)	3.67 (2.34)	2.67 (1.86)	4.17 (3.31)
Zn (μg/L)	33.33 (30.20)	38.33 (45.86)	28.00 (22.57)	29.50 (39.87)	16.00 (6.16)	39.00 (17.37)

EC electrical conductivity; *DO* dissolved oxygen; *SRP* soluble reactive phosphorus; BOD_5 5-day biological oxygen demand; *COD* chemical oxygen demand; *SPM*, *SPOM*, and *SPIM* suspended particulate total, organic and inorganic matter, respectively; *DS* dissolved solids; *As* arsenic; *Cd* cadmium; *Cr* chromium; *Cu* cupper; *Pb* lead; *Zn* zinc

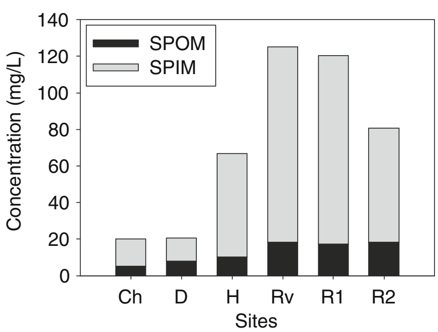

Fig. 2 Average values of the suspended particulate inorganic matter and suspended particulate organic matter for the complete sampling period

and may be related to local soil types. The La Horqueta stream showed low concentration of inorganic phosphorus and nitrogen but high occurrence of inorganic suspended materials. Unfortunately, there is no previous information about this stream. There were no industrial or urban installations upstream of the sampling point which would explain this finding, and we observed only cattle farming and scarce agricultural practices.

The mixture of the water that comes from the three different entries runs into the reservoir. This leads to an improvement of water quality due to the increase of dissolved oxygen. Once in the reservoir, a transformation of substances takes place (i.e., decrease in ammonia and increase in nitrate by oxidation), and as a result, there is a

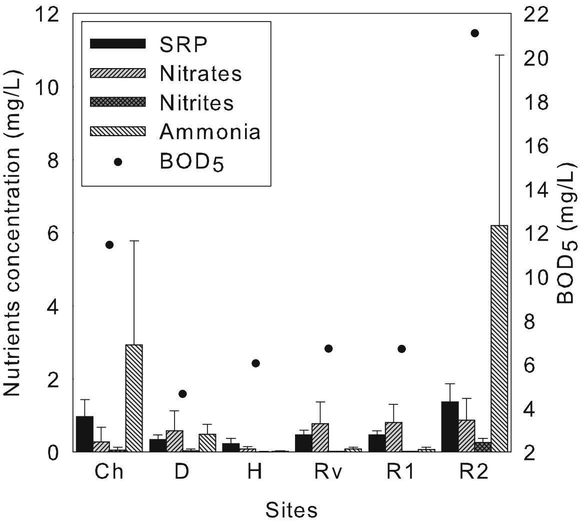

Fig. 3 Average values and standard deviation of soluble reactive phosphorus, ammonia, nitrates and nitrites, and 5 days of biological oxygen demand

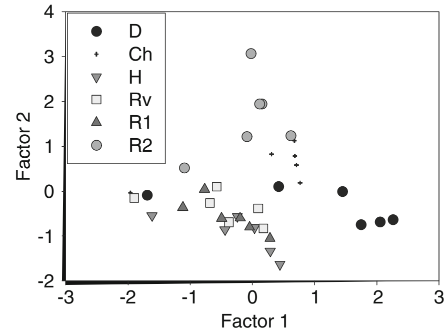

Fig. 5 Scatterplot of the scores for the sampling sites based on the factor analysis results. *D*, Durazno stream; *Ch*, La Choza stream; *H*, La Horqueta stream; *Rv*, inside the Reservoir; *R1*, Reconquista River after the dam; *R2*, Reconquista River, 17 km downstream

decrease in the risk of conversion from ionized ammonia to the highly toxic nonionized ammonia (Canadian Council of Ministers of the Environment 2010). This has special importance because concentrations up to 0.5 mg of N-NH_3 have been reported in the La Choza stream, where the highest contaminant concentrations

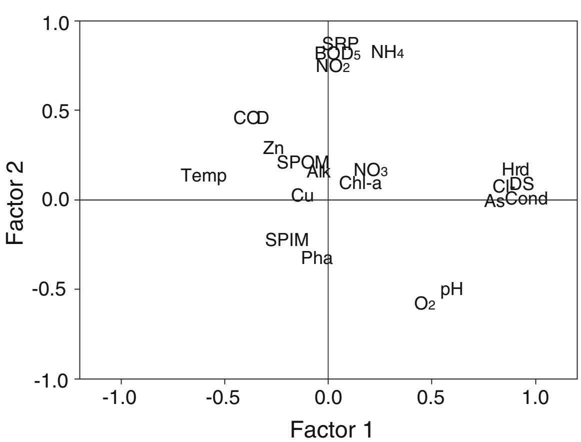

Fig. 4 Results of the factor analysis (principal component extraction; Varimax rotation) based on the physical and chemical variables, nutrients, and heavy metal concentration. *SPOM/SPIM*, suspended particulate organic and inorganic matter; *DS*, dissolved solids; *NO_3*, nitrates; *Temp*, temperature; *Cond*, conductivity; *O_2*, oxygen; *Alk*, alkalinity; *Hrd*, total hardness; *BOD_5*, 5-day biological oxygen demand; *COD*, chemical oxygen demand; *Cl-*, chlorides; *As*, arsenic; *Cu*, cupper; *SRP*, soluble reactive phosphorus; *NH_4*, ammonia; *NO_2*, nitrites; *Chl-a*, chlorophyll-*a*; *Pha*, phaeopigments; *Zn*, zinc

and the lowest levels of dissolved oxygen of all the headwaters were found. When water enters to the reservoir, there is a decrease in velocity, and as a consequence, there is an expected reduction in suspended particulate matter content. However, an increase of the suspended particulate matter was found in our study that is opposite to the expected trend. It has been demonstrated that wind and convective processes can lead to mixing of the water column (MacIntyre et al. 2002), causing the resuspension of particulate material like clay and silt. In addition, the shallowness of the reservoir facilitates the occurrence of these processes as relatively little energy is required to mix the whole water column.

The Reconquista River at its origin has good water quality and is similar to the water in the reservoir. The reservoir can be thought of as a facultative pond where the wind promotes the mixture and oxygenation of the water column. It is this oxygenation process that would contribute to the degradation of the organic matter and the chemical transformation of nitrogen compounds from reduced forms to oxidized ones (Faleschini and Esteves 2011). However beyond the reservoir, the input of different types of effluents downstream produces a fast decrease in water quality that causes a reduction in dissolved oxygen concentration and an increase in several contamination parameters such as suspended particulate organic/inorganic matter ratio, BOD_5, COD, and nitrite, ammonia, and phosphorus concentration. As a result, Reconquista 2 site shows a high level of pollution.

It is important to mention that prior to the sampling of summer 2010, there was a very important flood which produced a rise in water level at the reservoir of about 1 m. Immediately after this event, we observed a decrease in the concentration of suspended materials, nutrients, dissolved solids, chlorophyll-*a*, and metals, as well as a reduction in dissolved oxygen at all sampling sites. Thus, the flood event caused a homogenization and decrease in the variability of the water bodies (Vilches et al. 2011). This is shown in the left of Fig. 5 where we observed that the sites sampled in summer 2010 are aggregated.

Although the concentration of heavy metals shows random variations with values lower than the limits for recreational activities and water quality for human use according to Buenos Aires province legislation, a significant increase in the concentration of chromium was registered at Reconquista 2 site in comparison with the previous sampling site (Mann–Whitney, $p=0.022$). This is caused by the presence of industries upstream which spill effluents into the river with little or no previous treatment. On the other hand, high concentrations of arsenic are present in the Pampean soils due to their volcanic origin and are therefore are not related to anthropogenic activities as mining or agriculture (Rosso et al. 2011). The streams receive the arsenic from the first aquifer which has frequent connection with them, resulting in higher concentrations of arsenic than expected; this is the case of the Durazno and La Choza streams. However, in the reservoir, there is a diminution of arsenic concentration, possibly due to the precipitation of arsenic salts such as ferric arsenate, the interaction with humic substances, or the absorption of arsenate by algae (Harper and Kingham 1992; Mucci et al. 2000; Romero et al. 2004; Taggart et al. 2004).

The presence of a reservoir usually reduces the wide fluctuations of physical and chemical parameters such as hardness and alkalinity (Love 1967); however, we found that the variability of these parameters in the reservoir water was similar to the variability of the streams.

The reservoir receives water from three streams with different water quality. Our results suggest that the Roggero reservoir has a depuration role that increases water quality by physical and chemical changes particularly by decreasing the suspended particulate organic/inorganic matter ratio, increasing the water oxygen concentration and the transformation of inorganic nitrogen to forms less toxic to organisms. Luna et al. (2002) asserts that the increase in hydraulic residence time at the reservoir favors the sedimentation and decomposition of organic compounds allowing the depuration processes. However, the well-being of the river downstream the dam is critically poor due to the presence of point and nonpoint sources of pollution from human settlements and industries without depuration stations or with inadequately functioning depurations systems that reverse the amelioration of water quality that occurs at the reservoir within a few kilometers.

Acknowledgments This study was supported by the Agencia Nacional de Promoción Científica y Tecnológica through the PICT 2007–00371 and Universidad Nacional de Luján. We thank the "Reserva Municipal Los Robles", Martín Da Silva, Eduardo Zunino, Carolina Rodriguez Castro, and Renata Menendez-Helman for their collaboration in the field surveys; the owners of the field near the La Horqueta sample site; and Lucy Bridgman for the language review. We also thank the anonymous reviewers.

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