

# Assessment of the physicochemical variables of a subtropical reservoir in the northwest of Argentina

Avaliação das variáveis físico-químicas de um reservatório subtropical no noroeste da Argentina

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**Abstract: Aim:** The Escaba dam is located in the south of the Tucumán province, Argentina, at 650 m above sea level. It has an extension of 541 ha. and a depth of 65 m and its tributaries are the Chavarría, Las Moras, El Chorro and Singuil rivers. The climate is mild with dry winters and rainy summers. The objective of this study was to characterize physicochemical parameters in the limnetic zone of the dam and the mouths of the tributaries to determine the water quality. **Methods:** Seasonal sampling was carried out between August 2010 and May 2012. Temperature, transparency, pH and electrical conductivity were field measured, whereas dissolved oxygen, biochemical oxygen demand (BOD<sub>5</sub>), major ion constituents and nitrogen and phosphate compounds were analyzed at the laboratory. **Results:** The water was classified as sodium-calcium-bicarbonate with neutral to alkaline pH, and thermal stratification during spring and summer. The water assayed was well oxygenated except for the bottom of the limnetic zone during the summer months. Lowest transparency was measured in the El Chorro River in November 2011 (0.12 m) and highest degree of transparency in the Singuil River during the winter of 2010 (4.1 m). The waters assayed showed weak mineralization with conductivities between 83 and 218  $\mu\text{S}\cdot\text{cm}^{-1}$ . Maximum BOD<sub>5</sub> value (183  $\text{mg}\cdot\text{L}^{-1}$ ) was measured in the Singuil River in spring 2010. Highest values for the different nitrogen compounds were as follows: 7  $\text{mg}\cdot\text{NO}_3^-\cdot\text{L}^{-1}$  at the bottom of the limnetic zone in August 2010, 0.07  $\text{mg}\cdot\text{NO}_2^-\cdot\text{L}^{-1}$  in the Las Moras River in May 2011 and 1.8  $\text{mg}\cdot\text{NH}_4^+\cdot\text{L}^{-1}$  in the Chavarría River in March 2011. During the summer of 2012 orthophosphate reached a value of 0.22  $\text{mg}\cdot\text{L}^{-1}$  at the bottom of the limnetic zone. The TN/TP ratio revealed that phosphate was generally the limiting factor and rarely nitrogen. **Conclusions:** Considering the TN, TP and transparency parameters the ecosystem was classified as hypertrophic. PCA allowed a seasonal differentiation of the sites, and components 1 and 2 classified the samples according to nutrient gradient, dissolved oxygen, BOD<sub>5</sub> and temperature.

**Keywords:** abiotic factors, water quality, Escaba dam, Tucumán, Argentina.

**Resumo: Objetivo:** A represa Escaba está localizada ao sul da província de Tucumán, a 650 metros de altitude, sua extensão é de 541 ha, tem 65 m de profundidade e seus afluentes são os Rios Chavarría, Las Moras, El Chorro e Singuil. O clima é temperado, com invernos secos e verões chuvosos. O objetivo do estudo foi caracterizar as propriedades físicas e químicas das águas limnéticas da represa e da foz dos seus afluentes, para interpretar a qualidade de suas águas. **Métodos:** Realizaram-se amostragens estacionais de agosto de 2010 até maio de 2012. As variáveis medidas *in situ* foram: temperatura, transparência, pH, condutividade elétrica, e no laboratório foram analisados: oxigênio dissolvido, demanda bioquímica de oxigênio (DBO<sub>5</sub>), íons principais, compostos nitrogenados e fosfatados. **Resultados:** O tipo de água é bicarbonatada-cálcica-sódica, de neutra a alcalina e detectou-se estratificação térmica na primavera e verão. Com exceção da zona limnética: fundo, nos meses mais quentes, as águas estiveram bem oxigenadas. Em novembro de 2011 no rio El Chorro, obteve-se o valor mais baixo de transparência: 0,12

m e o valor mais elevado foi de 4,1 m no rio Singuil no inverno de 2010. Observou-se uma mineralização fraca com condutividades que variaram entre 83 e 218  $\mu\text{S}\cdot\text{cm}^{-1}$ . A  $\text{DBO}_5$  atingiu o registro máximo de 183  $\text{mg L}^{-1}$  na primavera de 2010 no rio Singuil. Os valores mais altos dos compostos nitrogenados detectados foram: 7  $\text{mg NO}_3^- \cdot \text{L}^{-1}$  (zona limnética: fundo, agosto/2010), 0,07  $\text{mg NO}_2^- \cdot \text{L}^{-1}$  (rio Las Moras, maio/2011) e 1,8  $\text{mg NH}_4^+ \cdot \text{L}^{-1}$  (rio Chavarría, março/2011). No verão de 2012, o ortofosfato atingiu 0,22  $\text{mg}\cdot\text{L}^{-1}$  no fundo da zona limnética. A proporção NT/PT mostrou o fósforo como limitante, e o nitrogênio em raras ocasiões. **Conclusões:** O ecossistema analisado foi classificado como hipertrófico considerando NT, PT e transparência. O ACP permitiu uma diferenciação estacional dos sítios, os eixos 1 e 2 separaram as amostras de acordo aos gradientes dos nutrientes, oxigênio dissolvido,  $\text{DBO}_5$  e temperatura.

**Palavras-chave:** variáveis abióticas, qualidade da água, represa Escaba, Tucumán, Argentina.

## 1. Introduction

The Escaba reservoir is located in the Juan Bautista Alberdi department, about 110 km south of Tucumán city, the capital of the province of Tucumán. The dam was constructed between 1943 and 1948 (Bustanza et al., 2010). It is the fourth largest dam in the province at an altitude of 650 masl and with an area of approximately 541 ha, a volume of 138  $\text{hm}^3$ , and a maximum depth of 65 m (Locascio de Mitrovich et al., 1997; Fernández et al., 2007). The hydrographic system is represented by one of the most important basins in Tucumán, the Marapa River Basin, which mainly receives its water from this dam and belongs to the Salí-Dulce River Basin. The Escaba reservoir lies in a structural depression, limited by the Escaba mountain range in the east, the Los Llanos Cumbres (peaks) and the Quico mountain in the south and by the Las Higueras mountain range in the west. It receives its water from two main rivers with a permanent water regime, the Chavarría River in the north and the Singuil River in the south, and two smaller rivers, the Las Moras and El Chorro rivers, that flow into the reservoir in the west (Fernández et al., 2007). The Chavarría River originates on the Santa Ana plateau from where it flows southeast of the Narváez mountain. The rivers of this mountain traverse the mountain chain formed by the Churqui and Los Alisos mountains. The Singuil River originates in the Catamarca province, in the Atravesada range west of the Campo de Pucará and it flows west of the Narváez mountain where it receives water from numerous affluents from the Humaya range. Thanks to a tectonic discontinuousness it flows through the hilly area between the Narváez and the Balcosna mountains, receiving eastern tributary rivers from the Las Higueras range (Pantorrilla and Núñez Regueiro, 2006).

The lithology that can be observed around the reservoir is characterized by sandy tufa that in certain sectors can present clasts of pumice stone and fine tufa formations that alternate with tufa banks (Fernández et al., 2007).

The dam was built for several purposes: reduction in flooding, regulation of the water volume for irrigation, hydropower production, recreation and tourism development (Rearte, 1981). The main crops grown in the area are tobacco, citrus fruit and sugarcane.

The reservoir has annual cyclic hydrometric fluctuations that coincide with the marked dry season in the province. Between May and January the water level diminishes from its maximum level of about 30 m on average and from mid January the level starts rising until it reaches its maximum level again in May (Pantorrilla and Núñez Regueiro, 2006).

The climate of the region is temperate with dry mild winters and warm, humid and rainy summers. Average annual rainfall is about 1,200 mm with highest precipitation in February (167 mm on average) and lowest in August (3 mm on average). The average annual temperature is 17.6°C. These climatic conditions are favored by the position of the mountain chains, which are perpendicular to the humid winds from the east and the southeast. These winds leave their humidity in Tucumán, and dry winds follow their way to the Catamarca province (Santillán de Andrés and Ricci, 1980).

The study area comprised the sub Andean foothills, a region characterized by the Yungas Eco-region. The natural vegetation of the area, especially close to the Chavarría and Singuil rivers, has been modified by diverse anthropic activities like crop cultivation and deforestation for fire wood and/or grassland for grazing. Currently, one of the principal ecological problems is cattle, because the animals feed on the forest vegetation and gradually deteriorate the forest, allowing the introduction

and installation of exotic species, mainly in the Chaco Forest.

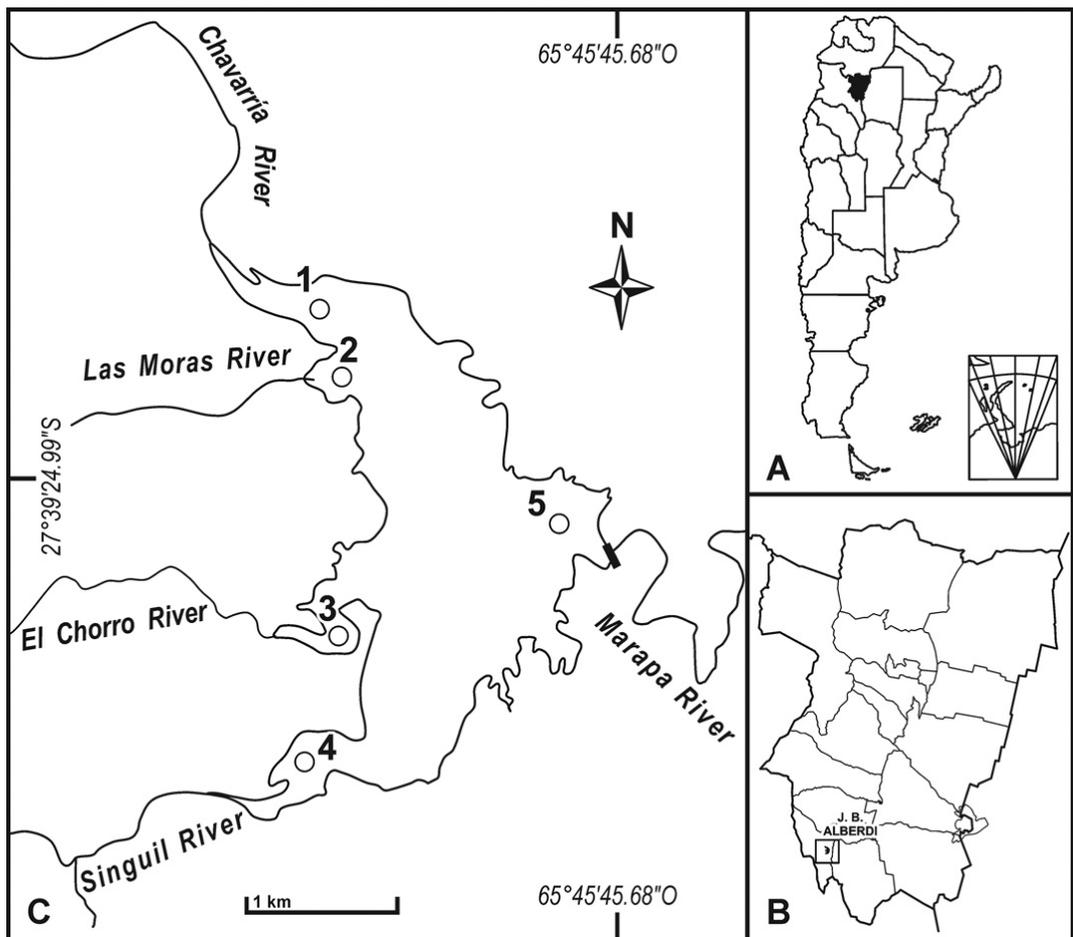
There are no systematic limnological reports on this dam and consequently, the current study allows us to know fluctuations in the abiotic factors of one of the most important lentic environments in the province of Tucumán. The objective of the current study was to analyze spatial-temporal variations in the physicochemical parameters of the Escaba dam and the mouths of the tributaries, the Chavarría, Las Moras, El Chorro and Singuil rivers, in order to determine the water quality. The results will help provide basic information to assess future biological studies and their interaction with physicochemical variations in the aquatic system.

## 2. Material and Methods

Eight seasonal sampling campaigns were carried out between August 2010 and May 2012 in the Escaba reservoir and the mouths of its tributaries. The sampling sites are given in Figure 1:

1-Chavarría River (27°38.803' S; 65°47.229' W), at 640 m altitude; 2- Las Moras River (27°39.020' S; 65°47.197' W), 617 m; 3- El Chorro River (27°39.984' S; 65°46.992' W), 632 m; 4- Singuil River (27°40.631' S; 65°47.102' W), 630 m; 5- limnetic zone (27°39.565' S; 65°45.954' W), 642 m. In the limnetic zone samples were taken at two depths: subsurface (0.20 m) and at the bottom; the depth of the latter site depended on the water level. Records on precipitation, water level and volume were provided by Hidroeléctrica Tucumán S.A., a hydroelectric company. It should be mentioned that the missing rainfall records for December 2010, March, April and December 2011, and April and May 2012 are the result of technical inconveniences. Similarly, the low hydrometric levels during November 2011 and 2012 did not allow us to sample the mouth of the Las Moras River.

To obtain a thermal profile the temperature was measured at 5 different levels in the limnetic zone of the dam, taking into account the maximum depth



**Figure 1.** A- Location of Tucumán, Argentina. B- Escaba Reservoir in Tucumán. C- Study area and sampling sites: 1- Chavarría River; 2- Las Moras River; 3- El Chorro River; 4- Singuil River; 5- Escaba reservoir (limnetic zone).

according to the season. Measurements were carried out in triplicate.

The following physicochemical parameters were measured *in situ*: transparency (Transp.; Secchi disk), depth, water temperature (T), pH and electrical conductivity (EC). These variables, except for transparency and depth, were measured with a portable digital multi-parameter water analyzer (Water Quality Meter 850081, Sper Scientific). The position of the sampling sites was obtained with a GPS (Garmin 48). Samples for dissolved oxygen (DO) were fixed *in situ* and 1.5 L plastic containers were used for chemical analyses of major ions, biochemical oxygen demand (BOD<sub>5</sub>), nitrogen compounds, orthophosphate and total phosphate, except for cations, which were sampled in caramel-colored glass flasks with 2 mL of 65% nitric acid. All samples were transported to the laboratory on ice and in the dark.

Major ions were measured in shallow water (August 2010 and 2011) and deep water (March 2011 and 2012), whereas all other parameters were determined every three months.

Physicochemical analyses were carried out according to APHA standard methods (APHA, 2005). Quality control of the sampling procedures and analytical determinations at the laboratory was carried out according to IRAM (Argentine Standards and Certification Institute) standards (29012-2, 1996; 29012-3, 1998; 301/ISO 17025, 2005). Piper-Hill-Langelier diagrams were constructed with mean values in mEq of major ions (HCO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup> and K<sup>+</sup>), using the RockWorks 15 program.

The relation between total nitrogen and total phosphorous (TN/TP) was calculated by the values (mg.L<sup>-1</sup>) obtained for each variable and its atomic weight (Margalef, 1983). Similarly, correlation analysis (Pearson coefficient:  $p < 0.05$  \* and  $p < 0.01$  \*\*) between physical and chemical variables was carried out using the SPSS program. Previously, data were logarithmically transformed, except for the pH.

Principal component analysis (PCA) was carried out with the following parameters: Temperature, depth, electrical conductivity, DO, BOD<sub>5</sub>, nitrate, nitrite, ammonium and orthophosphate (normalized and standardized values) using a correlation matrix. Data were processed using NTSYS (Rohlf, 1990).

### 3. Results

Table 1 shows minimum, maximum, and average records as well as the standard deviation

of the physicochemical variables of the Escaba reservoir and the mouths of the tributaries. The minimum values for the water level and the volume were obtained in January 2012 with 603 masl and 24.42 hm<sup>3</sup>, respectively, while maximum values were measured in May with 628 masl and 114.15 hm<sup>3</sup>. Water contribution, expressed in m<sup>3</sup>.s<sup>-1</sup>, oscillated between 1.59 in November 2011 and 56.23 in February 2011 (Figure 2A). Average precipitation fluctuated between 0.2 mm in September 2011 and 415.6 mm in February of the same year, which was also the month with most rainfall during the period assayed. A pronounced difference was observed between the summers of 2011 and 2012; the latter one was much drier. In addition, October 2011 was atypical because elevated rainfall was registered (Figure 2B).

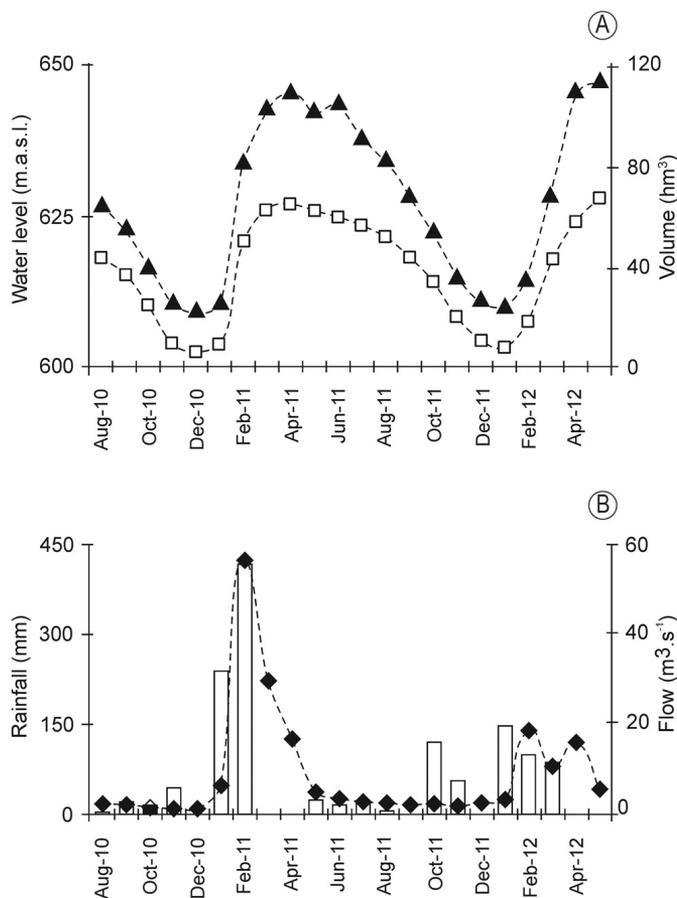
A great variability in the depth of the reservoir could be observed throughout the period studied. Periods with extremely low levels in November of both years (2010 and 2011) made it impossible to sample the mouth of the Las Moras River. The maximum depth in the limnetic zone was observed in May 2012 with 40 m, while the minimum depth, 18 m, was registered in November 2010. Depths in the river mouths greatly differed with values of 1.1 m in the El Chorro and Singuil rivers in November 2011 and 10 m in the Chavarría River in May 2011 and 2012 (Table 1). Table 2 shows a significant negative correlation between this variable and the pH.

Minimum transparency records fluctuated between 0.12 (El Chorro River, spring 2011) and 0.51 (limnetic zone, spring 2010), while maximum values varied more and oscillated between 1.5 and 4.1 m in the El Chorro and Singuil rivers in winter of 2011 and 2010, respectively (Table 1; Figure 3). This variable was correlated with the temperature ( $r = -0.72$ ;  $p < 0.01$ ), BOD<sub>5</sub> ( $r = -0.72$ ;  $p < 0.01$ ), potassium ( $r = -0.65$ ;  $p < 0.01$ ) and sodium ( $r = 0.47$ ;  $p < 0.05$ ).

Figure 4 shows the thermal profile in the limnetic zone demonstrating mixing periods in fall and winter and stratification periods in the warm months of both years assayed. The temperature of the selected sites showed a seasonal distribution with maximum values that were registered during the hot months and minimum values during the cold months (Table 1). Highly significant correlations were found between T and BOD<sub>5</sub>, potassium, transparency and bicarbonate and to a less extent with magnesium and nitrate (Table 2).

**Table 1.** Minimum (Min), maximum (Max), mean (Av) values and standard deviation (SD) of physical and chemical parameters of the Escaba reservoir and of the mouth of tributaries; (m/d: no data).

Parameters	Chavarría River				Las Moras River				El Chorro River				Singuil River				Limnetic Zone (subsurface)				Limnetic Zone (bottom)							
	Min.	Max.	Av.	SD	Min.	Max.	Av.	SD	Min.	Max.	Av.	SD	Min.	Max.	Av.	SD	Min.	Max.	Av.	SD	Min.	Max.	Av.	SD	Min.	Max.	Av.	SD
Depth (m)	2	10	6.3	3.1	1.3	9	4.1	2.9	1.1	6	3	2	1.1	8.2	4.3	2.4	--	--	--	--	18	40	28.5	8.3	--	--	--	--
Transparency (m)	0.32	2.84	0.83	0.85	0.50	1.85	1.3	0.60	0.12	1.5	0.62	0.56	0.15	4.1	0.89	1.3	0.51	2.4	1.2	0.74	--	--	--	--	--	--	--	--
pH (upH)	7.9	9.5	8.7	0.70	8.3	9.5	8.8	0.62	7.8	9.3	8.6	0.62	7.8	8.6	8.4	0.39	7.8	8.9	8.3	0.51	7.3	8.2	7.6	0.43	--	--	--	--
EC ( $\mu\text{S}\cdot\text{cm}^{-1}$ )	83	203	132	46.8	89	130	109	18.6	93	203	136	43	89	186	143.8	36.1	95	218	140.4	49.2	94	191	132	42.5	--	--	--	--
T ( $^{\circ}\text{C}$ )	14.5	26	22.2	4	13.5	27	20.8	5.8	12.5	28	22	6	13	27	21	5.7	13	25	20.1	4.9	13	23	19.1	3.3	--	--	--	--
DO ( $\text{mg}\cdot\text{L}^{-1}$ )	7.2	14.3	10.6	2.8	7.8	14.3	11	2.1	4.5	14.5	10.2	3.4	5.2	10.2	8.5	1.8	5	10.8	7.3	2.0	2.7	9.1	5.3	2.3	--	--	--	--
BOD <sub>5</sub> ( $\text{mg}\cdot\text{L}^{-1}$ )	<5	56	--	--	<5	46	--	--	<5	59	--	--	<5	183	--	--	<5	16	--	--	<5	19	--	--	--	--	--	--
HCO <sub>3</sub> <sup>-</sup> ( $\text{mg}\cdot\text{L}^{-1}$ )	10	63	36.5	25.5	20	74	54.3	23.9	31	72	52.5	18.8	62	92	72.8	13.3	36	80	64	19.3	55	93	78.3	18	--	--	--	--
CO <sub>3</sub> <sup>2-</sup> ( $\text{mg}\cdot\text{L}^{-1}$ )	12	67	42.3	24.7	12	65	29	24.3	9	61	34.8	21.3	nd	27	--	--	nd	42	--	--	nd	31	--	--	--	--	--	--
SO <sub>4</sub> <sup>2-</sup> ( $\text{mg}\cdot\text{L}^{-1}$ )	<5	43	--	--	<5	9	--	--	<5	10	--	--	<5	32	--	--	<5	10	--	--	<5	9	--	--	--	--	--	--
Cl <sup>-</sup> ( $\text{mg}\cdot\text{L}^{-1}$ )	4	7	5.8	1.5	4	7	5.5	1.3	4	7	5.5	1.3	3	7	5.3	1.7	4	9	6	2.4	4	7	5.5	1.7	--	--	--	--
Na <sup>+</sup> ( $\text{mg}\cdot\text{L}^{-1}$ )	11	12	11.3	0.50	10	12	11.3	0.96	11	12	11.3	0.50	12	19	13.8	3.5	11	12	11.5	0.58	10	12	11	0.82	--	--	--	--
K <sup>+</sup> ( $\text{mg}\cdot\text{L}^{-1}$ )	2.5	4.5	3.3	0.87	2.4	4.4	3.5	0.91	2.6	4.2	3.5	0.77	2.6	6	4	1.6	2	3.3	2.7	0.57	2.3	4.1	3.1	0.74	--	--	--	--
Ca <sup>2+</sup> ( $\text{mg}\cdot\text{L}^{-1}$ )	13	24	17.5	5.1	12	37	21.5	11	14	27	20.8	6.7	10	30	22	9.8	13	23	17	4.2	12	29	20.3	9	--	--	--	--
Mg <sup>2+</sup> ( $\text{mg}\cdot\text{L}^{-1}$ )	3	4.8	4.2	0.85	3	5.2	4.2	0.94	3	4.7	4.1	0.78	4	5	4.4	0.49	3	5.4	4.5	1.1	3	5.1	4.2	0.94	--	--	--	--
NO <sub>3</sub> <sup>-</sup> ( $\text{mg}\cdot\text{L}^{-1}$ )	1	4	2.1	1.1	1	3	1.5	0.84	<0.5	3	--	--	<0.5	2	--	--	<0.5	5	--	--	1	7	2.9	2.1	--	--	--	--
NO <sub>2</sub> <sup>-</sup> ( $\text{mg}\cdot\text{L}^{-1}$ )	<0.007	0.06	--	--	<0.007	0.07	--	--	<0.007	0.03	--	--	<0.007	0.02	--	--	<0.007	0.06	--	--	<0.007	0.06	--	--	--	--	--	--
NH <sub>4</sub> <sup>+</sup> ( $\text{mg}\cdot\text{L}^{-1}$ )	<0.013	1.8	--	--	<0.013	0.05	--	--	<0.013	0.31	--	--	<0.013	0.37	--	--	<0.013	0.40	--	--	<0.013	0.96	--	--	--	--	--	--
PO <sub>4</sub> <sup>3-</sup> ( $\text{mg}\cdot\text{L}^{-1}$ )	0.02	0.08	0.04	0.02	0.02	0.03	0.03	0.01	<0.015	0.06	--	--	<0.015	0.14	--	--	<0.015	0.14	--	--	0.02	0.22	0.06	0.07	--	--	--	--
TN ( $\text{mg}\cdot\text{L}^{-1}$ )	<4	4	--	--	<4	10	--	--	<4	15	--	--	<4	13	--	--	<4	9	--	--	<4	7	--	--	--	--	--	--
TP ( $\text{mg}\cdot\text{L}^{-1}$ )	0.12	0.60	0.27	0.15	0.12	0.56	0.24	0.18	0.11	0.80	0.42	0.31	0.22	2.8	0.78	0.96	0.12	0.80	0.35	0.22	0.16	2.2	0.63	0.73	--	--	--	--



**Figure 2.** A- B. A. Fluctuation in water level (m.a.s.l.) (□) and volume (hm<sup>3</sup>) (▲); B. Variation in the rainfall (mm) (in bars) and water contribution (m<sup>3</sup>.s<sup>-1</sup>) (line).

**Table 2.** Correlation matrix of variables with \*\* p<0.01, \* p<0.05 significance levels.

	Depth	Transp.	pH	EC	T	DO	BOD <sub>5</sub>	HCO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup>	Ca <sup>2+</sup>	NO <sub>3</sub> <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>
pH													
T	-0.51*												
DO		-0.72**											
BOD <sub>5</sub>			0.62**										
HCO <sub>3</sub> <sup>-</sup>		-0.72**			0.70**								
CO <sub>3</sub> <sup>2-</sup>			-0.86**		-0.55**								
SO <sub>4</sub> <sup>2-</sup>			0.92**			0.59**		-0.71**					
Cl <sup>-</sup>				0.59**			-0.45*		-0.52**				
Na <sup>+</sup>		0.47*		0.47*					0.45*				
K <sup>+</sup>		-0.65**			0.78**		0.75**						
Ca <sup>2+</sup>				0.43*					-0.48*	0.72**			
Mg <sup>2+</sup>				0.61**	-0.42*		-0.48*		-0.51*	0.73**	0.65**		
NO <sub>3</sub> <sup>-</sup>			-0.43*		-0.30*				0.62**				
NO <sub>2</sub> <sup>-</sup>				-0.34*		-0.33*							
PO <sub>4</sub> <sup>3-</sup>				0.39**		-0.35*						0.36*	0.44**

The water assayed was neutral to alkaline as pH values oscillated between 7.3 at the bottom of the limnetic zone and 9.5 in the Chavarría and Las Moras rivers (Table 1). pH was correlated with carbonate ( $r=0.92$ ;  $p<0.01$ ), bicarbonate ( $r=-0.86$ ;

$p<0.01$ ), DO ( $r=0.62$ ;  $p<0.01$ ) and nitrate ( $r=-0.43$ ;  $p<0.05$ ).

Electrical conductivity oscillated between 83  $\mu\text{S}\cdot\text{cm}^{-1}$  for the Chavarría River in March 2011 and 218  $\mu\text{S}\cdot\text{cm}^{-1}$  in the subsurface limnetic zone in November 2011 (Table 1). EC was highly

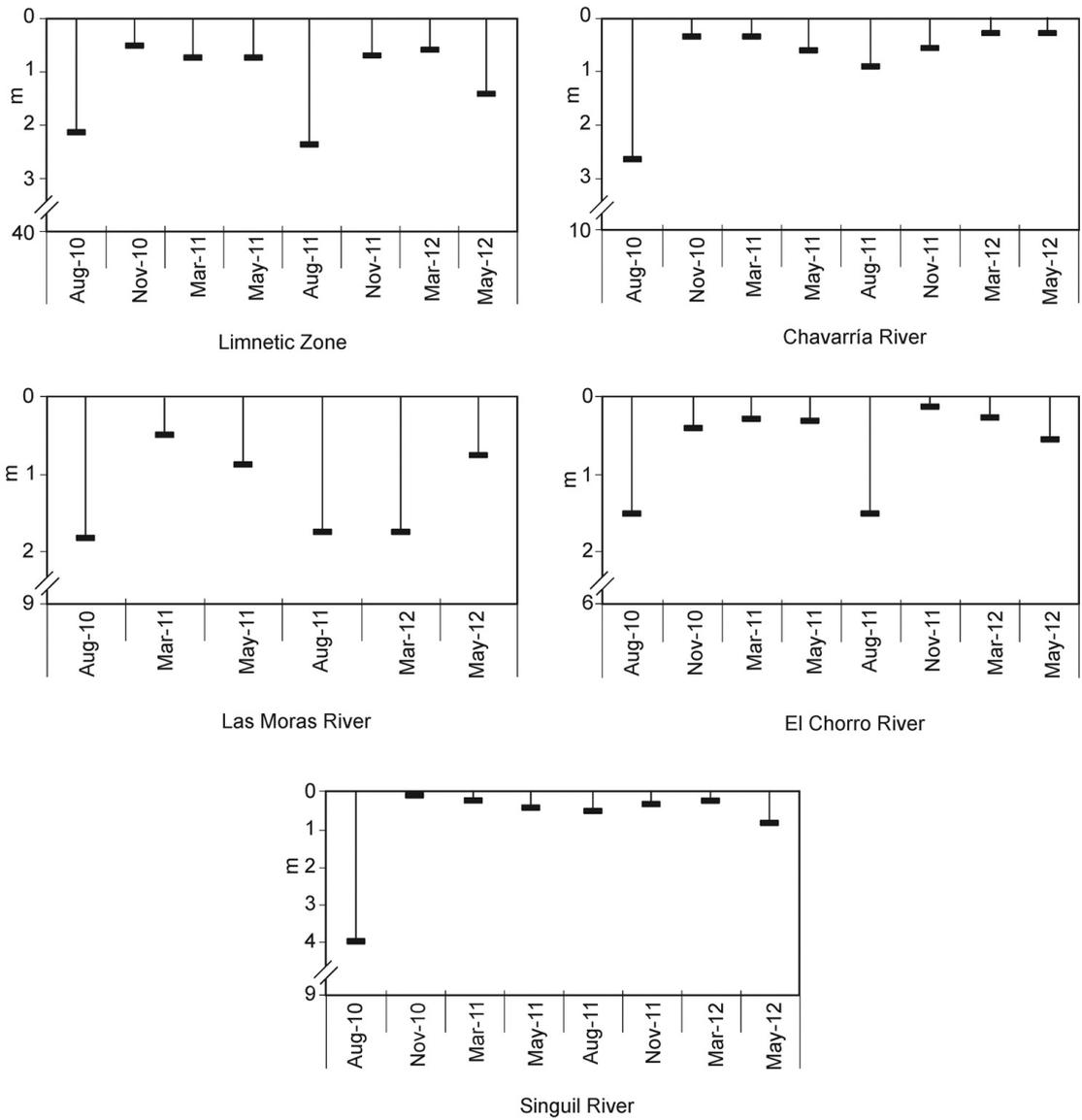


Figure 3. Variation in transparency in the limnetic zone and the mouth of the tributaries.

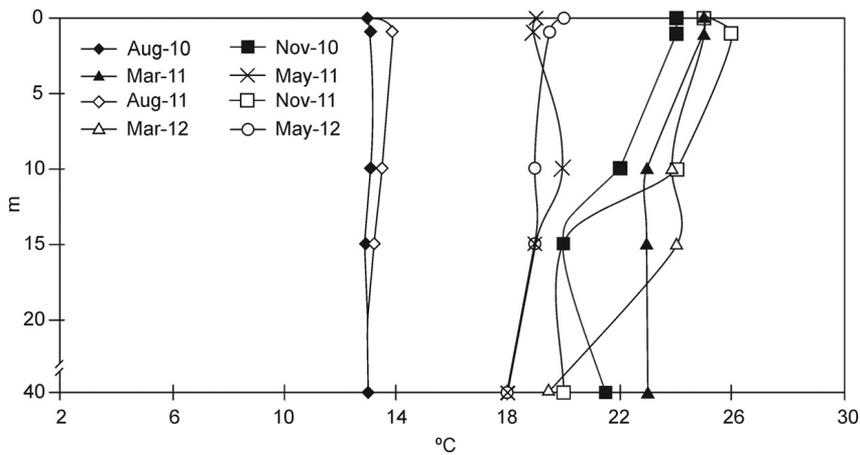


Figure 4. Thermal profile of the limnetic zone of the reservoir.

significantly correlated with chloride, magnesium and phosphate and significantly with sodium, calcium and nitrite (Table 2).

During the hot months minimum values for dissolved oxygen were observed in the limnetic zone (bottom), reaching 2.7 mg.L<sup>-1</sup> in the fall of 2012, while were well oxidized during the remaining seasons, reaching 10.8 mg.L<sup>-1</sup>. In the mouths of the tributaries DO values fluctuated between 6.5 and 14.5 mg.L<sup>-1</sup>, except for November 2011 when minimum values of 4.5 and 5.2 mg.L<sup>-1</sup> were registered in the El Chorro and Singuil rivers, respectively (Figure 5). The DO was correlated with the pH ( $r=0.62$ ;  $p<0.01$ ), carbonate ( $r=0.59$ ;  $p<0.01$ ), sulfate ( $r=0.44$ ;  $p<0.05$ ), nitrite ( $r=-0.33$ ;  $p<0.05$ ) and orthophosphate ( $r=-0.35$ ;  $p<0.01$ ).

BOD<sub>5</sub> measurements of all sites assayed were  $\leq 5$  mg.L<sup>-1</sup> in the winters of 2010 and 2011 and in the fall of 2012. In May 2011 values  $\leq 5$  mg.L<sup>-1</sup> were obtained in the limnetic zone and in the Chavarría River, while BOD<sub>5</sub> values for the other tributary mouths oscillated between 10 and 49 mg.L<sup>-1</sup>. The maximum value, 183 mg.L<sup>-1</sup>, was registered in the Singuil River in spring 2010. In summer BOD<sub>5</sub>

values in the mouths of the tributaries greatly differed; in 2011 they fluctuated between 46 and 51 mg.L<sup>-1</sup>, except for the Chavarría River with 20 mg.L<sup>-1</sup>, while in 2012 the records oscillated between 6 and 22 mg.L<sup>-1</sup>, and only the El Chorro River reached a value of 59 mg.L<sup>-1</sup>. For the last two years, values of 8 and 12 mg.L<sup>-1</sup> were measured in the limnetic zone (Figure 5). BOD<sub>5</sub> was correlated with the temperature, potassium and transparency ( $p<0.01$ ) and chloride and magnesium ( $p<0.05$ ) (Table 2).

According to the Piper-Hill-Langelier diagrams the ionic composition of the waters of the reservoir and its tributary mouths was sodium-calcium-bicarbonate (Figure 6). The HCO<sub>3</sub><sup>-</sup> concentration oscillated between 10 mg.L<sup>-1</sup> in the Chavarría River and 93 mg.L<sup>-1</sup> at the bottom of the limnetic zone, both measured in the summer of 2012. The Ca<sup>2+</sup> values fluctuated between 10 mg.L<sup>-1</sup> in the Singuil River and 37 mg.L<sup>-1</sup> in the Las Moras River in March 2011 and 2012, while the Na<sup>+</sup> concentration maintained rather stable (10-12 mg.L<sup>-1</sup>) throughout the period assayed, except for the Singuil River in August 2010, when the maximum value (19 mg.L<sup>-1</sup>)

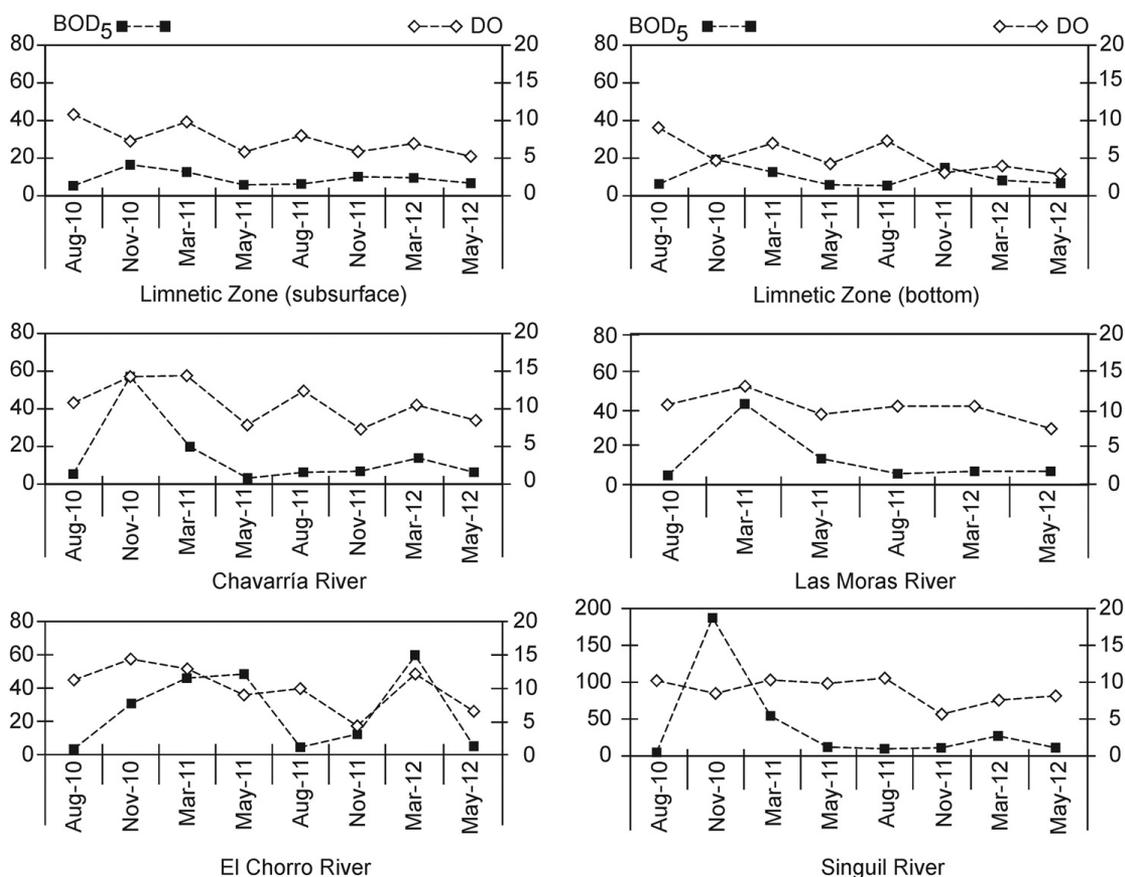
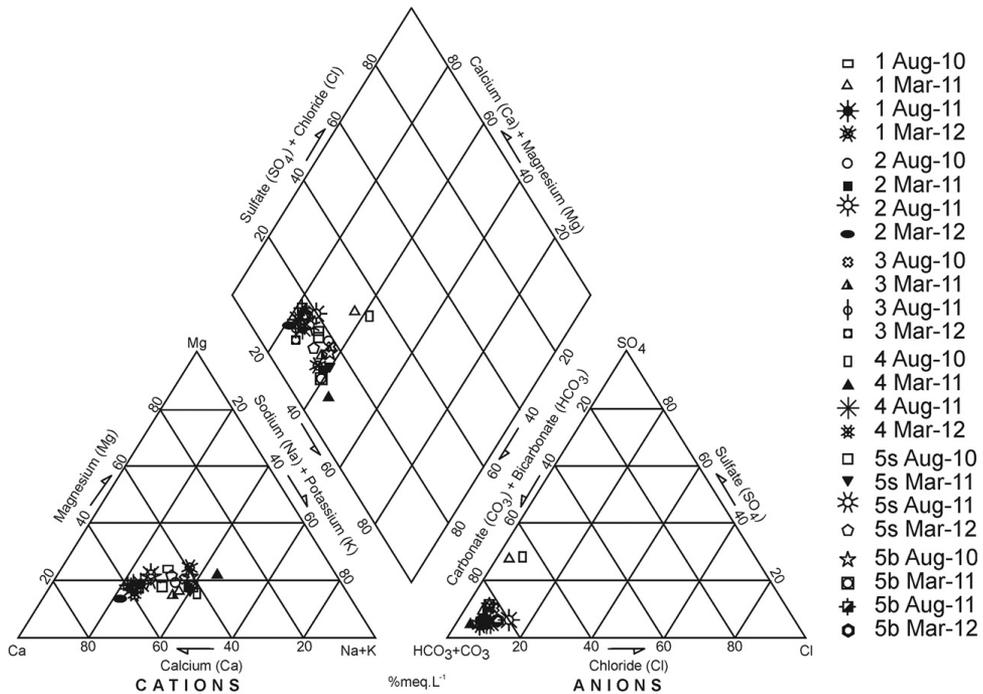


Figure 5. Variation in dissolved oxygen (DO) (mg.L<sup>-1</sup>) and biochemical oxygen demand (BOD<sub>5</sub>) (mg.L<sup>-1</sup>).



**Figure 6.** Piper-Hill-Langelier diagrams of the sampling sites.

was observed. Regarding the other ions assayed,  $Mg^{2+}$  concentrations were slightly higher than  $K^+$  concentrations. In relation to  $SO_4^{2-}$  and  $Cl^-$  concentrations, the first was found in low and high water levels in 2010 and 2011 and the inverse effect was observed in winter of 2011 and summer of 2012.

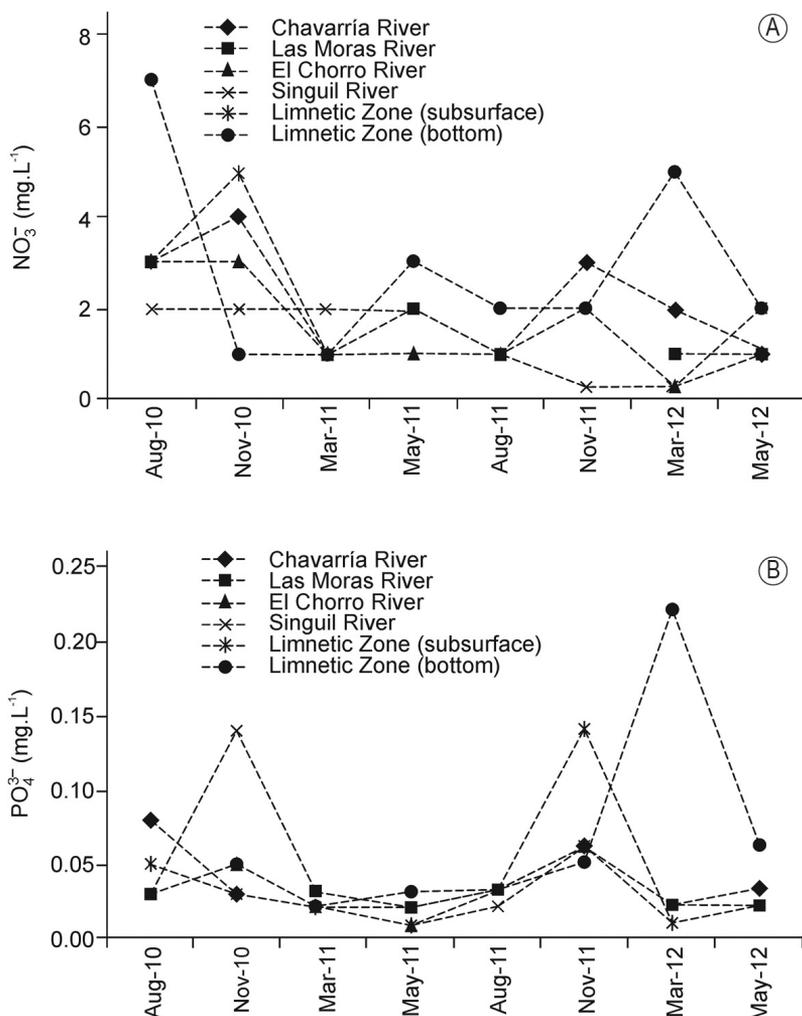
Correlations between anions and cations were highly significant ( $p < 0.01$ ) with  $r = -0.71$  between  $HCO_3^-/CO_3^{2-}$ ,  $r = -0.52$  for  $SO_4^{2-}/Cl^-$  and  $r = 0.65$  between  $Mg^{2+}/Ca^{2+}$ . Furthermore, both  $SO_4^{2-}$  and  $Cl^-$  showed correlations with  $Ca^{2+}$  and  $Mg^{2+}$  and  $SO_4^{2-}$  also correlated with  $Na^+$ . Similarly, Table 2 shows other associations of the major ion constituents with electrical conductivity,  $BOD_5$ , DO, pH, temperature and transparency.

Maximum  $NO_3^-$  concentrations were observed in August and November of 2010 at all the sites studied, reaching  $7 \text{ mg.L}^{-1}$  at the bottom of the limnetic zone, whereas minimum records were obtained in March of 2012, except for the Chavarría and Las Moras rivers (Figure 7A). Compared with other nitrogen compounds,  $NO_2^-$  concentrations during most of the period assayed were less than  $0.007 \text{ mg.L}^{-1}$ , except for May in 2011 and 2012. During the first year values oscillated between  $0.02$  and  $0.07 \text{ mg.L}^{-1}$  for the Singuil and Las Moras rivers, respectively, and during the 2<sup>nd</sup> year they varied between  $0.01$  for the El Chorro

River and  $0.06 \text{ mg.L}^{-1}$  in the subsurface area of the limnetic zone. The minimum  $NH_4^+$  value was less than  $0.013 \text{ mg.L}^{-1}$  and it was mostly observed during November 2010, May 2011 and 2012 and August 2011. In general, values oscillated between  $0.02 \text{ mg.L}^{-1}$  (Chavarría River, August 2010 and May 2011; Las Moras River, August 2010, subsurface limnetic zone, August 2010) and  $1.8 \text{ mg.L}^{-1}$  (Chavarría River, March 2011). All sites showed an increase in  $NH_4^+$  during spring 2011, which differed this season from the other months assayed. Correlations were observed between  $NO_3^-$  and pH / temperature /  $PO_4^{3-}$  ( $r = -0.43$ ,  $-0.30$  and  $0.36$ , respectively;  $p < 0.05$ ).  $NO_2^-$  was associated with  $SO_4^{2-}$  ( $r = 0.62$ ;  $p < 0.01$ ), EC ( $r = -0.34$ ;  $p < 0.05$ ) and DO ( $r = -0.33$ ;  $p < 0.05$ ).  $NH_4^+$  was only correlated with orthophosphate ( $r = 0.44$ ;  $p < 0.01$ ).

Figure 7B shows that in general orthophosphate values were less than  $0.05 \text{ mg.L}^{-1}$  and maximum values fluctuated between  $0.14 \text{ mg.L}^{-1}$  (Singuil River, November 2010 and the subsurface of the limnetic zone, November 2011) and  $0.22 \text{ mg.L}^{-1}$  (bottom of the limnetic zone, March 2012).  $PO_4^{3-}$  correlated with  $NH_4^+$  ( $r = 0.44$ ;  $p < 0.01$ ), EC ( $r = 0.39$ ;  $p < 0.01$ ),  $NO_3^-$  ( $r = 0.36$ ;  $p < 0.05$ ) and DO ( $r = -0.35$ ;  $p < 0.05$ ).

In 80% of the samples the total nitrogen / total phosphorous ratio (TN/TP) varied between 26 and



**Figure 7.** A -B. A. Nitrate fluctuation in the limnetic zone and the mouth of the tributaries and B. Concentrations of orthophosphate in the limnetic zone and the mouth of the tributaries.

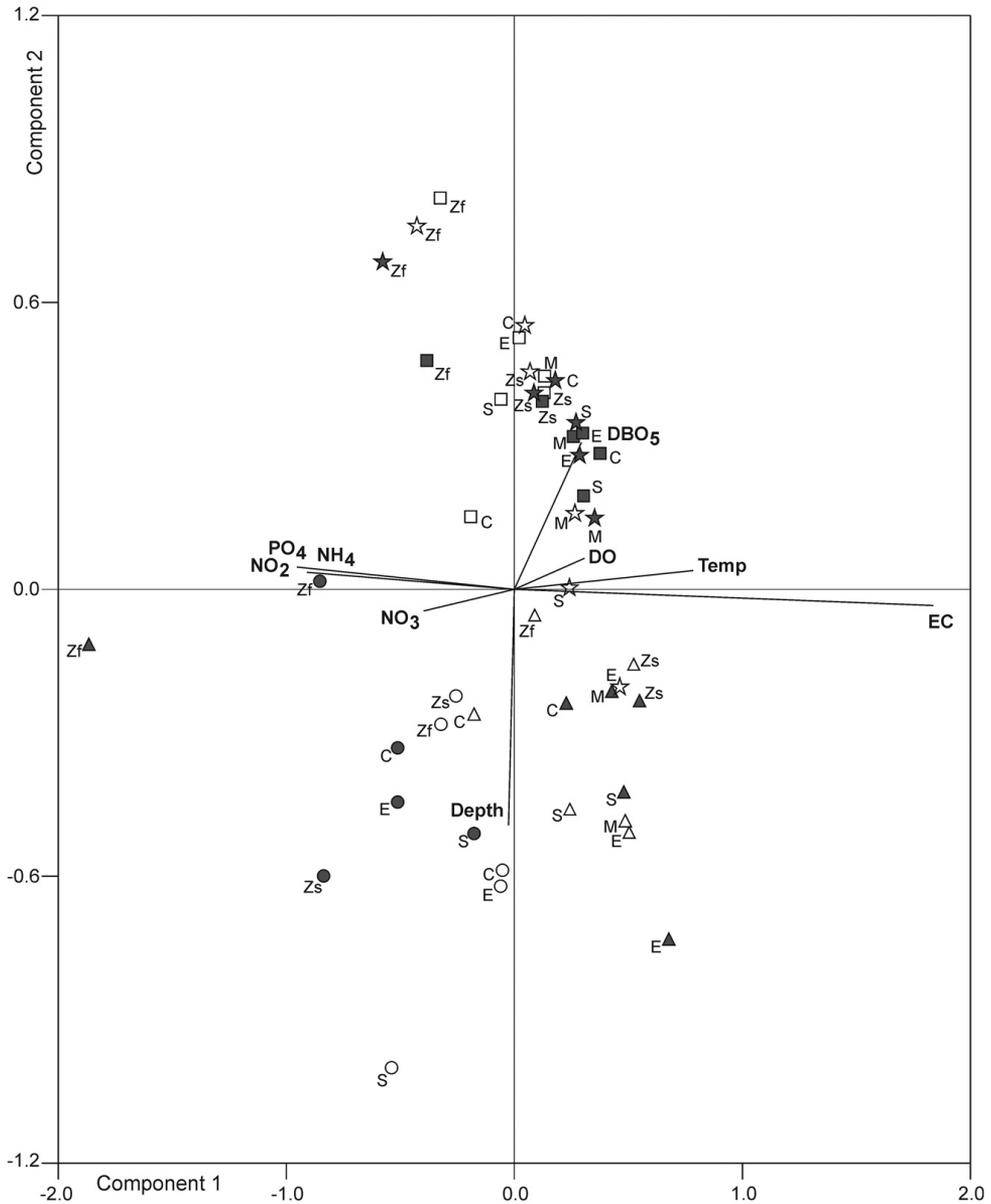
158 and the lowest value (4) was recorded at the bottom of the limnetic zone in May 2011.

PCA showed that the first three components explained 62% of the variability of the data, which contributed 23, 21 and 18% of the total variance. Axes 1 and 2 contributed to a separation of the sites according to the seasons. The spring samples were arranged towards the left lower quadrant and the summer samples towards the right lower quadrant, except for the bottom of the limnetic zone in March 2012. On the contrary, samples corresponding to fall and winter were separated towards the upper quadrants. The variables that contributed to Axis 1 were orthophosphate, dissolved oxygen (DO), nitrate and ammonium (intra-set correlation coefficients: -0.82, 0.59, -0.57, -0.56, respectively). In component 2, BOD<sub>5</sub> and temperature contributed with correlation

coefficients of -0.86 and -0.79, respectively (Figure 8).

#### 4. Discussion

The Escaba reservoir has annual hydrometric fluctuations that coincide with the seasonal rainfall that show two well-defined periods in the Tucumán province: high water level (summer-fall) and low water level (winter-spring). Variations in water level, volume and flow coincided with those observed in other lentic environments in the province (Tracanna et al., 2006; Seeligmann and Tracanna, 2009, among others). During the period assayed the differences in the water level of the lake were similar to those described by Pantorrilla and Núñez Regueiro (2006), even though precipitations recorded for the summer of 2011 triplicated values observed during the same season in 2012. Maximum transparency was registered in winter,



**Figure 8.** Principal Components Analysis (PCA) of the limnetic zone and of the mouth of tributaries of Escaba Reservoir in relation to physical and chemical variables (C = R. Chavarría; M = R. Las Moras; E = R. El Chorro; S = R. Singuil; Zs = limnetic zone (subsurface); Zf = limnetic zone (bottom)). (Winter/2010 = □; Spring/2010 = ○; Summer/2011 = △; Autumn/2011 = ☆; Winter/2011 = ■; Spring/2011 = ●; Summer/2012 = ▲; Autumn/2012 = ★).

which coincides with the low water level period, while the decrease in this variable observed in spring and summer could be attributed, among other factors, to the increase in suspended solids, which agrees with studies on other reservoirs in Tucumán, like Dr. C. Gelsi (Tracanna et al., 2006) and La Angostura (Seeligmann and Tracanna, 2009), and the influence of algae (Margalef, 1983; Ordoñez Salinas, 2010). This agrees with the strong negative correlation between temperature and transparency (Table 2).

According to Margalef (1983) the reservoir can be characterized as warm monomictic with thermal stratification in spring-summer, a classification that can be applied to the majority of the artificial reservoirs in central and northern Argentina (Boltovskoy and Foggetta, 1985; Locascio de Mitrovich et al., 1997; Bazán, et al., 2004; Salusso, 2005; Tracanna et al., 2006; Seeligmann and Tracanna, 2009, among others).

The highest pH values observed close to the surface of the dam could be directly related

to the CO<sub>2</sub> consuming photosynthesis process which produces an increase in the pH values. In different lakes around the world a relation has been observed between to high pH values and the capacity of certain phytoplankton members like *Ceratium*, *Anabaena* and *Microcystis* capture CO<sub>2</sub> (Mancini et al., 2011). The elevated pH values could be related to the dominance of *Ceratium hirundinella* (OF. Müll.) Dujardin, observed during most of the months studied (Martínez De Marco et al., 2011; Taboada et al., 2011). The strong positive correlation between the pH and carbonate would be related to pH values higher than 8.5; above this value carbonate concentrations begin to increase (Weiner, 2008).

With regard to electrical conductivity and according to the classification by Rodier (1990), the water presented mild mineralization during most of the assay period. This is the result of the fact that salts of the crystalline metamorphic basement rocks are hardly dissolved by precipitation and besides, at this stage the water has covered very little distance to be in significant contact with the sediment. Thus, conductivity is exclusively determined by dissolution of the minerals that characterize the lithology of the region. Similarly, the sodium-calcium-bicarbonate classification of this reservoir agrees with the relative composition of fresh water bodies around the world (Margalef, 1983), which would be the result of the incongruent dissolution of plagioclase. On the other hand, this variable only allowed a temporary differentiation which influenced mainly high temperatures and hence increases evaporation in the late periods of drought, which can be demonstrated with the inverse relationship between the water level and the conductivity. This result coincides with observations in the Campo Alegre reservoir (Borja, "pers. com.", 2011) and for other bodies of water.

Dissolved oxygen is an important parameter to determine the water quality. The oxygen concentration in the limnetic zone during the hot months presented a gradient with a higher concentration in the epilimnion and a deficit in deeper strata without reaching anoxic conditions, which was in agreement with the stratification of the reservoir. This diminution could be attributed to the degradation process of organic matter, caused by a considerable accumulation of dead vegetation and elevated temperatures (Peralta and León, 2006, among others). These results agree with the higher pH values measured close to the surface of the dam because of the photosynthesis process that

releases oxygen to the medium during the summer months (Weiner, 2008). This is confirmed by the significant positive correlation found between the pH and dissolved oxygen. During the mixing period the oxygen concentration in the water column maintained stable.

In general, BOD<sub>5</sub> measured in the mouths of the rivers and in the limnetic zone was higher than 8 mg O<sub>2</sub>.L<sup>-1</sup>, which is characteristic for highly contaminated aquatic environments (Orozco Barrenetxea et al., 2008). Highest BOD<sub>5</sub> levels were detected during the summer months which coincided with the lowest transparency values of the water and consequently with the highest levels of organic matter. Part of this material is generated by diverse human activities like agriculture, cattle breeding and domestic activities in the area. This variable behaved similarly to that in the Dr. C. Gelsi and Río Hondo reservoirs, while the BOD<sub>5</sub> values for the La Angostura reservoir could be considered acceptable all year round in the entire water column (Locascio de Mitrovich et al., 1997; Seeligmann and Tracanna, 2009; Tracanna et al., 1999, 2006, among others).

The concentration of the majority of the nitrogen and orthophosphate compounds tend to follow seasonal patterns, diminishing during spring and summer as a result of the increase in biological activity (Margalef, 1983; Vila Pinto, 2003, among others), which agrees with our results during the summer and at several sites during spring. In most of the cases NH<sub>4</sub><sup>+</sup> values did not exceed recommendations for aquatic life. Nitrate was generally higher than 1 mg.L<sup>-1</sup> which would indicate contamination by agricultural practices (both crop growing and livestock). Nitrite was in most of the cases below the accepted level for normal biota development, as the mainly oxidizing environment most likely favored its oxidation to nitrate (Weiner, 2008).

Natural phosphorous is scarce, because it is predominantly found in insoluble salts, which makes its bioavailability difficult and hence, it behaves as a limiting nutrient for algal growth compared with nitrogen and carbon that naturally exist at higher concentrations. The critical threshold of inorganic phosphate for algal bloom can be as low as 0.005 to 0.01 mg.L<sup>-1</sup>, but it is more frequently around 0.05 mg.L<sup>-1</sup> (Weiner, 2008). In the current study most of the data obtained were below this value. The low levels registered could be the result of the fact that the pH values measured were not adequate to release phosphorous from the sediment

and in addition, there are no important external phosphorous sources. On the other hand for atomic nitrogen/phosphorous ratios > 17, phosphorous behaves as a limiting factor, whereas at ratios < 10, nitrogen is limiting (Conzonno, 2009). The samples from the Escaba reservoir (limnetic zone and mouth of the rivers) generally showed phosphorous as the limiting factor and only in a few cases nitrogen. The ecosystem studied can be classified as hypertrophic considering TN, TP and transparency (Secchi disk) parameters and according to the trophic classification by Conzonno (2009).

Interpretation of principal component analysis (PCA) only allowed seasonal ordination of the sites. The results obtained confirmed that the temperature affected the physical mixture of the water column and that the hydrological cycle favored the nutrient concentration in low waters. In conclusion, it could be said that the physicochemical variables in this dam are regulated by seasonal changes and thermal stratification.

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