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**Environmental Science and Pollution Research**

ISSN 0944-1344

Environ Sci Pollut Res  
DOI 10.1007/s11356-016-6646-9



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# Water quality in Atlantic rainforest mountain rivers (South America): quality indices assessment, nutrients distribution, and consumption effect

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**Abstract** The South American Atlantic rainforest is a one-of-a-kind ecosystem considered as a biodiversity hotspot; however, in the last decades, it was intensively reduced to 7 % of its original surface. Water resources and water quality are one of the main goods and services this system provides to people. For monitoring and management recommendations, the present study is focused on (1) determining the nutrient content (nitrate, nitrite, ammonium, and phosphate) and physiochemical parameters (temperature, pH, electrical conductivity, turbidity, dissolved oxygen, and total dissolved solids) in surface water from 24 rainforest mountain rivers in Argentina, (2) analyzing the human health risk, (3) assessing the environmental distribution of the determined pollutants, and (4) analyzing water quality indices ( $WQI_{obj}$  and  $WQI_{min}$ ). In addition, for total coliform bacteria, a dataset was used from literature. Turbidity, total dissolved solids, and nitrite ( $NO_2^-$ ) exceeded the guideline value recommended by national or international guidelines in several sampling stations. The spatial distribution pattern was analyzed by Principal Component Analysis and Factor Analysis (PCA/FA) showing well-defined groups of rivers. Both WQI showed good adjustment ( $R^2 = 0.89$ ) and rated water quality as good or excellent in all

sampling sites ( $WQI > 71$ ). Therefore, this study suggests the use of the  $WQI_{min}$  for monitoring water quality in the region and also the water treatment of coliform, total dissolved solids, and turbidity.

**Keywords** Rain forest · Rivers · WQI · Nutrients · Water pollution · Coliform bacteria

## Introduction

The influence of human activities in the environment is continuously influencing and changing the ecosystem conditions in different regions of the globe. High biodiversity sites or hotspots are becoming a main concern among developing countries due to the necessity to encourage a sustainable development and the lack of environmental management tools. Agricultural expansion and intensification that have accelerated since the 1960s have doubled crop production in many areas but, unfortunately, has come at a cost to the environment (West et al. 2013). Deforestation and land use change are also the main activities with a direct negative effect over the environment. This is also happening in the Atlantic Forest of South America, which is one of the most endangered rainforests on Earth, and exists only 7 % of its original cover (Di Bitetti et al. 2003). Land use change, fragmentation, and non-sustainable (or traditional) forest management are within the principal threats to this unique environment. The southern portion of the Atlantic Forest is located in northwestern Argentina (Misiones province) and neighboring areas of Brazil and Paraguay (Fig. 1). The Argentinean province of Misiones has the last largest continuous relict of Atlantic Forest, hence the responsibility and opportunity for the implantation of sustainable management practices. The few large fragments remain in locations where geological characteristics

Responsible editor: Kenneth Mei Yee Leung

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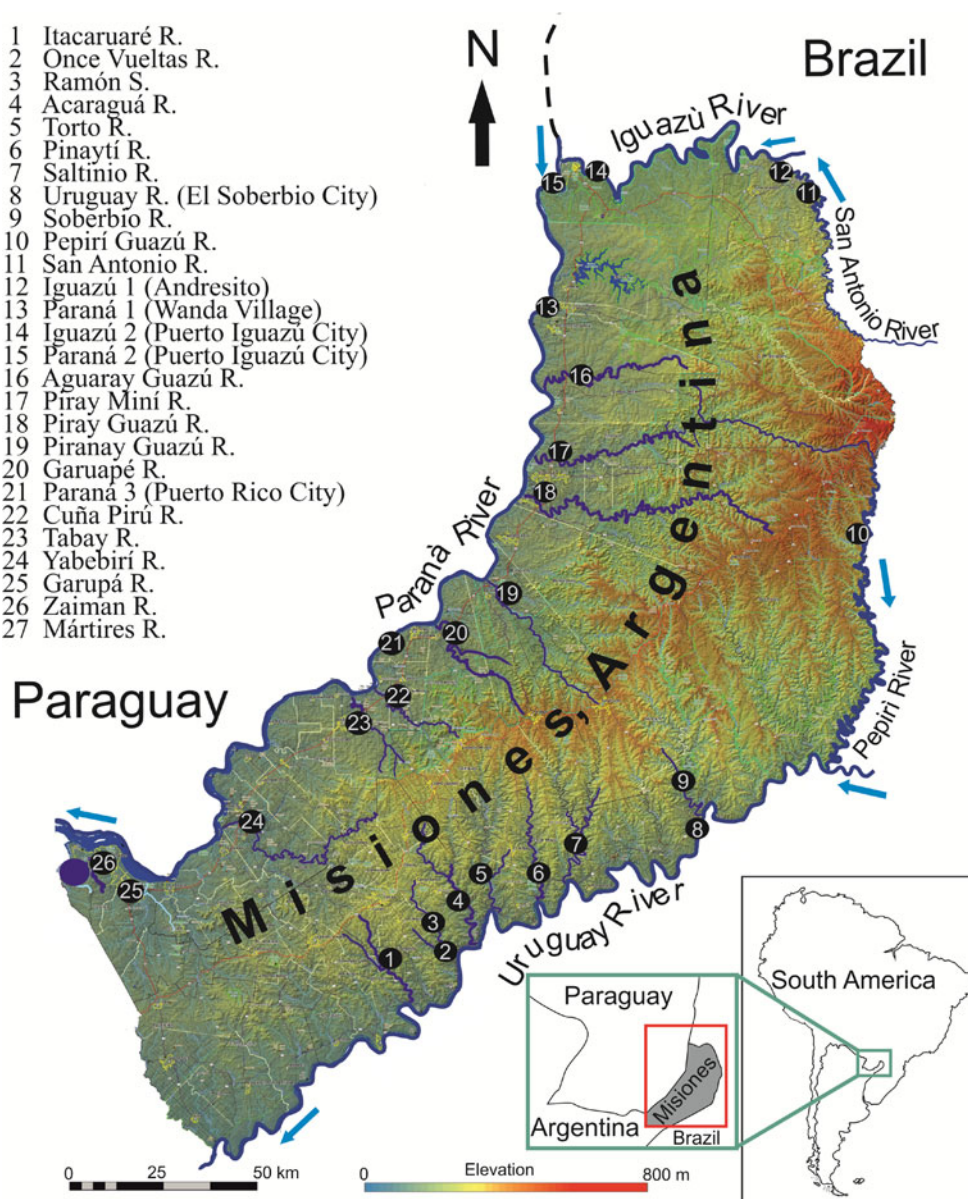
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**Fig. 1** Sampling sites of surface water, Misiones, Argentina. The arrows indicate the direction of water flow

- 1 Itacaruaré R.
- 2 Once Vueltas R.
- 3 Ramón S.
- 4 Acaraguá R.
- 5 Torto R.
- 6 Pinaytí R.
- 7 Saltinio R.
- 8 Uruguay R. (El Soberbio City)
- 9 Soberbio R.
- 10 Pepirí Guazú R.
- 11 San Antonio R.
- 12 Iguazú 1 (Andresito)
- 13 Paraná 1 (Wanda Village)
- 14 Iguazú 2 (Puerto Iguazú City)
- 15 Paraná 2 (Puerto Iguazú City)
- 16 Aguaray Guazú R.
- 17 Piray Mini R.
- 18 Piray Guazú R.
- 19 Piranay Guazú R.
- 20 Garupapé R.
- 21 Paraná 3 (Puerto Rico City)
- 22 Cuña Pirú R.
- 23 Tabay R.
- 24 Yabebirí R.
- 25 Garupá R.
- 26 Zaiman R.
- 27 Mártires R.



make human occupation particularly difficult (Silva et al. 2007; Ribeiro et al. 2009) or in protected areas.

Changes in land use practices have affected the integrity and quality of water resources worldwide (Foley et al. 2005; Goldstein et al. 2012). In the Argentinean Patagonia, there is a strong concern about the ecological status of surface waters because these changes are rapidly occurring in the region (Miserendino et al. 2011), and the same situation is undergoing in the Argentinean Atlantic Forest. Recent studies (de Souza et al. 2013) showed that land use changes have resulted in large deforestation of rural landscapes, thus influencing transport of water and materials along the watersheds. In order to evaluate the water quality of aquatic systems, many countries have introduced a plan for monitoring and assessing the pollution effects (Pesce and Wunderlin 2000; Zampella et al.

2006; Silva and Jardim 2006). However, monitoring water quality and making qualitative and quantitative decisions based on real data have become a challenge for environmental management (Lermontov et al. 2009) and far more in developing countries where the lack of baseline information is a common denominator. The use of water quality indices (WQI) is a simple practice that overcomes many of the previously mentioned problems and allows the public and decision makers to receive water quality information. WQI also allows us to assess changes in the water quality and to identify water trends (Pesce and Wunderlin 2000; Wunderlin et al. 2001). A quality index is a unitless number that ascribes a quality value to an aggregate set of measured parameters. WQIs generally consist of sub-index scores assigned to each parameter by comparing its measurement with a parameter-specific rating

curve, optionally weighted, and combined into the final index. The construction of WQI requires first a normalization step, where each parameter is transformed into a  $0 \pm 100\%$  scale, with 100 representing the highest quality. The next step is to apply weighting factors that reflect the importance of each parameter as an indicator of the water quality (Pesce and Wunderlin 2000). The so constructed WQI gives a number that can be associated with a quality percentage, easy to understand for everyone, and based on scientific criteria for water quality. The WQIs are also conditioned by the quantity of analysis required and the cost to accomplish them (Santos Simoes et al. 2008), hence the necessity of specific WQIs to motivate sustainable management practices involving stakeholders and decision makers. Considering other research (Pesce and Wunderlin 2000; Sanchez et al. 2007; Nazeer et al. 2014), the use of WQI could be of particular interest for developing countries because they provide cost-effective water quality assessment as well as the possibility of evaluating trends. Biodiversity in freshwater ecosystems—rivers, lakes, and wetlands—is undergoing rapid global decline (Janse et al. 2015). Azrina et al. (2006) report that the richness and diversity indices were generally influenced by water quality (e.g., total suspended solids and conductivity). It has also been shown that an increase in the environmental availability of inorganic nitrogen usually boosts life production, firstly increasing the abundance of primary producers (Camargo and Alonso 2006). The nutrients also play an important role in the ecologic dynamics of rivers mostly related to eutrophication effects (Jarvie et al. 2008; Withers et al. 2011). WQI can be simplified considering only critical environmental variables that affect the quality of a certain aquatic body as a function of the soil use and occupation (Santos Simoes et al. 2008).

Based on the above considerations, the objectives of the present study were to (1) determine the physicochemical parameters and content nutrients (nitrate, nitrite, ammonium, and phosphate) in surface water from 24 rainforest mountain rivers in Argentina, (2) analyze the human health

risk, (3) assess and discuss the environmental distribution and origin of the determined pollutants, and (4) analyze WQI indices. The integrated analyses of the objectives provide a first step for management consideration and decision making.

## Materials and methods

### Study area and social scenario evaluated

The study area is located among the highlands of the Argentine province of Misiones, surrounded by subtropical rainforests (Atlantic Forest) (Fig. 1) with thermal seasonality and hydrological variation. The region's major rivers are the Paraná, Iguazú, and Uruguay Rivers (Cabrera and Willink 1982). The majority of the streams in the province of Misiones are highly influenced by the geology of the area, comprised mostly of basaltic soil that creates a large slope gradient (Frei et al. 2014). Additionally, most of the streams are originated by a great number of little wellsprings and small streams, which drain the excess water from the central hills. Native vegetation, a typical characteristic of rainforest streams, can be found in stream margins. The climate is predominately rainy with high rain events (Cabrera and Willink 1982). During storm events, the streams can vary drastically the caudal very fast, reaching three to six times the normal height and return to its normal state in a matter of days (2 or 3).

Vulnerable socioeconomic situation in the study area reveals the importance for the assessment of water quality. In Misiones and surrounding areas, the nearly 1.7 million inhabitants (INDEC 2010) commonly use rivers both for disposing wastewater and for direct consumption and domestic use in rural landscape. The situation is exacerbated for the indigenous people of the Mbyá Guaraní ethnic group where the population of 13,006 (INDEC, 2010) live in the forest under their traditional habits (Fig. 2).

**Fig. 2** Panoramic view of the rainforest (*above*) and Guaraní community (*below*) from Yabotí UNESCO Biosphere Reserve, Misiones, Argentina



## Sample collection and preparation

Water samples were collected by the same group of researchers according to standard procedures (APHA 2005) in three sampling periods: 12/3-12/4/2013, 2/11-2/12/2014, and 8/4-8/5/2014. Samples were drawn from 27 sampling stations located in 24 different streams and rivers (Fig. 1). The 27 sampling sites were chosen from the main sources of water for human consumption in the study areas.

Taking into account that the flow of the watercourses can vary greatly, all surface water samples were collected during the day within 24 h of each other. This ensured that weather conditions would not vary drastically.

All water samples for nutrients were collected manually at 0.3 m depth (USGS 2006) in the center of each river with 5 l opaque polyethylene-terephthalate bucket. Water subsamples for nitrate and nitrite were collected with 50 ml polyethylene-terephthalate falcon tubes, while for ammonium and phosphate these were collected with 500 ml opaque polyethylene-terephthalate bottles from a bucket. Following APHA methods, all containers were washed previously with distilled water and then rinsed with sample water. In all cases, air was removed from the containers. All samples were stored in darkness at 4 °C up and transported to the laboratory for analytical treatment within 32 h (APHA 2005).

## Physicochemical analysis and nutrient quantification

The temperature, pH, electrical conductivity, turbidity, dissolved oxygen (DO), and total dissolved solids (TDS) were measured at the sampling site using a multiparametric probe Horiba U-52.

The nitrate ( $\text{NO}_3^-$ ) concentration was determined by cadmium reduction method (Method 4500- $\text{NO}_3^-$  E) with a field portable colorimeter HACH DR890 (APHA 2005). The phosphate ( $\text{PO}_4^{3-}$ ) concentration was determined by molybdovanadate reaction (Method 4500-P) colorimetric method (APHA 2005). The nitrite ( $\text{NO}_2^-$ ) and ammonia ( $\text{NH}_4^+$ ) determinations were done by colorimetric (method 4500- $\text{NO}_2^-$ -B; method 4500- $\text{NH}_3$ -B, C, respectively) (APHA 2005) using a UV-Visible SHIMADZU UV 1601 spectrophotometer. The water samples were analyzed by triplicate.

## Consumption effect approach

Considering that part of the population, especially the indigenous, could drink water directly from water bodies, the levels of nutrients and physicochemical parameters were compared with permissible limits set by Argentinean Food Codex (AFC), the international guidelines of the United States Environmental Protection Agency (USEPA), and the World Health Organization (WHO).

## Water quality index (WQI) calculation

For the determination of the objective water quality index of the different watersheds studied, the following empirical equation was used (Pesce and Wunderlin 2000):

$$\text{WQI}_{\text{obj}} = k \frac{\sum C_i P_i}{\sum P_i}$$

where  $k$  is a subjective constant with a maximum value of 1 for apparently good quality water and 0.25 for apparently highly polluted water,  $C_i$  is the normalized value of the parameter, and  $P_i$  is the relative weight assigned to each parameter. In this work, such as in other studies reported in literature, the constant  $k$  was not considered in order not to introduce a subjective evaluation (Pesce and Wunderlin 2000; Sanchez et al. 2007). In relation to the parameter  $P_i$ , the maximum value of 4 was assigned to parameters of relevant importance for aquatic life as for example DO and TDS, while the minimum value (unity) was assigned to parameters with minor relevance such as for example temperature and pH. The values of total coliform bacteria were based on the results of Avigliano and Schenone (2015) (Table 2). The total coliform bacteria were determined in samples taken in the same sampling place and date.

Table 1 shows the values suggested for the parameters  $C_i$  and  $P_i$ , used in the calculation of WQI, which were based on European Standards (EU 1975). When the values of WQI are in the range of 0–25, the water must be classified as “very bad”; for a WQI value in the range of 25–50, the water is classified as “bad”; for WQI values in the range of 51–70, the water classification is “medium”; and finally, when the WQI values are within the range of 71–90 and 91–100, the water is classified as “good” and as “excellent,” respectively (Jonnalagadda and Mhere 2001; Sanchez et al. 2007).

Tracking and testing too many parameters is a difficult task to implement and also the cost-effectiveness effort. Quality criteria obtained by using some of the most predominant or easily measurable parameters also can be reported (Pesce and Wunderlin 2000; Akkoyunlu and Akiner 2012). In this study, dissolved oxygen, electric conductivity, turbidity, and total coliform were selected according to previous works (Pesce and Wunderlin, 2000), and considering the feasibility for implementation in the study area, a  $\text{WQI}_{\text{min}}$  was calculated:

$$\text{WQI}_{\text{min}} = \frac{(C_{\text{DO}} C_{\text{cond}} C_{\text{turb}} C_{\text{col}})}{4}$$

where  $C_{\text{DO}}$  is the value due to dissolved oxygen after normalization (Table 1),  $C_{\text{cond}}$  is the value due to electric conductivity after normalization (Table 1),  $C_{\text{turb}}$  is the value due to turbidity after normalization (Table 1), and  $C_{\text{col}}$  is the value due to total coliform after normalization (Table 1).

**Table 1** Parameters considered for WQI calculation

Parameter	Relative weight $P_i$	Normalization factor ( $C_i$ )										
		100	90	80	70	60	50	40	30	20	10	0
		Analytical value										
Ammonia	3	<0.01	<0.05	<0.10	<0.20	<0.30	<0.40	<0.50	<0.75	<1.00	≤1.25	>1.25
Conductivity	2	<750	<1000	<1250	<1500	<2000	<2500	<3000	<5000	<8000	≤12,000	>12,000
Dissolved oxygen	4	>7.5	>7.0	>6.5	>6.0	>5.0	>4.0	>3.5	>3.0	>2.0	≥1.0	<1.0
Nitrates	2	<0.5	<2.0	<4.0	<6.0	<8.0	<10.0	<15.0	<20.0	<50.0	≤100.0	>100.0
Nitrites	2	<0.005	<0.01	<0.03	<0.05	<0.10	<0.15	<0.20	<0.25	<0.50	≤1.00	>1.00
pH	1	7	7-8	7-8.5	7-9	6.5-7	6-9.5	5-10	4-11	3-12	2-13	1-14
Phosphate	1	<0.16	<1.60	<3.20	<6.40	<9.60	<16.0	<32.0	<64.0	<96.0	≤160.0	>160.0
TDS	2	<100	<500	<750	<1000	<1500	<2000	<3000	<5000	<10,000	≤20,000	>20,000
Temperature	1	21/16	22/15	24/14	26/12	28/10	30/5	32/0	36/-2	40/-4	45/-6	>45/≤6
Total coliform	3	<50	<500	<1000	<2000	<3000	<4000	<5000	<7000	<10,000	≤14,000	>14,000
Turbidity	2	<5	<10	<15	<20	<25	<30	<40	<60	<80	≤100	>100

Values in milligrams per liter, pH in pH units, temperatures in centigrade, turbidity in NTU, bacteria expressed in colony-forming units per 100 ml (CFU 100 ml<sup>-1</sup>), conductivity in microsiemens per centimeter (μS cm<sup>-1</sup>)

**Statistical analysis**

Statistics such as the median and standard deviation were calculated for all parameters (Table 2). To evaluate spatial distribution, data are represented in hydrographical maps. A Principal Component Analysis and Factor Analysis (PCA/FA) was applied to identify the contaminants that explain the higher proportion of variability and to evaluate the distribution patterns between sampling sites. The selection of axis for interpretation was performed using a screen plot (Hubert et al. 2009). The PCs are weighted linear combinations of the original variables and provide information on the most meaningful parameters, describing the whole dataset through data reduction with a minimum loss of original information (Varol and Şen 2012).

A cluster analysis was performed using the unweighted pair group method with arithmetic average (UPGMA) on a Euclidean distance matrix to assess dissimilarity among sites. In order to estimate the good fit between similarity matrix and the dendrogram, the coefficient of cophenetic correlation was calculated. A high cophenetic correlation suggests a good fit among the similarity matrix and dendrogram. Prior to Euclidean distance calculation, the data were standardized to have a mean of zero and a variance of one.

The regression method was used to evaluate the relation between the WQI<sub>obj</sub> and the WQI<sub>min</sub> (applying WQI as a regression variable) as suggested by Vryzas et al. (2007) and Akkoyunlu and Akiner (2012). Finally, the indices were compared using a non-parametric paired test (Wilcoxon test) in order to evaluate the existence of significant differences between the indexes.

Data processing was performed using INFOSTAT® statistical programs.

**Result and discussion**

**Physicochemical parameters and guideline values**

The physicochemical parameters are shown in Table 2. The average temperature value of all sampling stations was 25.3 ± 4.6 °C (range 23.0–27.0 °C). The highest temperature corresponds to Mártires sampling station. This water body is characterized by a slow current due to the influence of Yacyretá hydroelectric dam lake (biggest Argentinean hydroelectric dam).

The pH was neutral-basic within a range of 7.3–8.3 with an average value of 7.7 ± 0.4. According to WHO (2011), no health-based guideline value is proposed for pH. Although pH usually has no direct impact on consumers, it is one of the most important operational water quality parameters (WHO 2011). The AFC (2007) adopted the guideline values proposed by the USEPA in 2011 (pH 6.5–8.5) (Table 3). All the samples were in the recommended range proposed by both institutions.

The average conductivity was 54.01 ± 12.3 μS cm<sup>-1</sup> with a range between 33.7 and 83.73 μS cm<sup>-1</sup>. The conductivity is not directly related to human health effects WHO (2011). In the study area were observed the lowest average conductivities of all La Plata basin (one of the largest basins in South America), observing that it increases as it flows to the south as the Paraná and Uruguay river approach the Paraná Delta, where the

**Table 2** Physicochemical parameters, nutrients, and WQI indices in surface water

Site	Temperature	pH	Conductivity	Turbidity	DO	TDS	NH <sub>4</sub> <sup>+</sup>	NO <sub>2</sub> <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	PO <sub>4</sub> <sup>3-</sup>	FC	WQI <sub>obj</sub>	WQI <sub>min</sub>
1 Itacuararé	23.6 ± 4.2	7.8 ± 0.8	87.7 ± 39.5	9.0 ± 5.8	8.5 ± 1.2	0.057 ± 0.03	0.018 ± 0.011	0.049 ± 0.037	0.33 ± 0.21	0.50 ± 0.46	220 ± 215	89	93
2 Once Vueltas	25.1 ± 5.0	7.6 ± 0.1	49.3 ± 22.9	25.1 ± 24.7	7.3 ± 0.4	0.032 ± 0.01	0.031 ± 0.019	0.049 ± 0.034	1.13 ± 0.93	0.80 ± 1.06	413 ± 728	86	88
3 Ramón	25.6 ± 5.8	7.5 ± 0.4	42.0 ± 4.6	15.4 ± 14.6	7.7 ± 0.4	0.027 ± 0.00	0.030 ± 0.000	0.052 ± 0.041	0.80 ± 0.44	0.70 ± 0.82	323 ± 526	83	83
4 Acaraguá	24.2 ± 4.7	7.4 ± 0.5	33.7 ± 0.0	11.5 ± 9.6	8.6 ± 1.2	0.022 ± 0.0	0.015 ± 0.007	0.045 ± 0.026	0.90 ± 0.36	0.57 ± 0.57	353 ± 500	86	88
5 Torto	26.2 ± 6.0	7.5 ± 0.3	37.7 ± 30.3	26.9 ± 35.1	7.8 ± 1.1	0.024 ± 0.02	0.035 ± 0.007	0.045 ± 0.022	1.43 ± 0.71	0.50 ± 0.52	877 ± 1324	84	85
6 Pindayí	24.1 ± 5.3	7.4 ± 0.3	53.0 ± 3.6	9.2 ± 7.1	8.1 ± 1.6	0.034 ± 0.00	0.020 ± 0.014	0.040 ± 0.016	1.57 ± 0.70	0.38 ± 0.38	343 ± 510	84	85
7 Saltinio	25.9 ± 6.0	7.4 ± 0.4	44.7 ± 6.4	16.5 ± 18.4	7.7 ± 0.8	0.029 ± 0.00	0.025 ± 0.007	0.041 ± 0.015	1.03 ± 0.68	0.47 ± 0.40	113 ± 64	84	88
8 Uruguay	25.0 ± 5.6	7.3 ± 0.4	46.7 ± 5.5	25.5 ± 18.2	9.5 ± 1.4	0.030 ± 0.00	0.023 ± 0.006	0.057 ± 0.031	1.33 ± 0.67	0.57 ± 0.42	543 ± 829	83	80
9 Soberbio	26.6 ± 6.4	7.4 ± 0.4	51.3 ± 4.2	9.0 ± 5.0	7.6 ± 0.7	0.033 ± 0.00	0.018 ± 0.011	0.046 ± 0.023	1.10 ± 0.20	0.33 ± 0.35	173 ± 227	87	73
10 Pepirí Guazú	25.0 ± 5.8	7.9 ± 0.6	71.3 ± 15.5	11.3 ± 11.8	9.0 ± 0.8	0.046 ± 0.01	0.012 ± 0.002	0.036 ± 0.015	1.17 ± 1.00	0.37 ± 0.15	453 ± 465	80	75
11 San Antonio	25.7 ± 4.5	7.4 ± 0.0	72.3 ± 11.6	14.8 ± 2.1	7.9 ± 1.5	0.047 ± 0.01	0.019 ± 0.010	0.061 ± 0.030	1.40 ± 0.26	0.48 ± 0.48	167 ± 110	90	95
12 Iguazú 1	24.2 ± 3.8	7.4 ± 0.2	36.0 ± 9.5	16.7 ± 12.2	7.6 ± 1.2	0.023 ± 0.01	0.015 ± 0.007	0.043 ± 0.002	0.87 ± 0.31	0.20 ± 0.20	110 ± 35	85	85
13 Paraná 1	26.1 ± 5.5	7.7 ± 0.5	50.0 ± 5.6	9.9 ± 12.0	7.3 ± 1.1	0.032 ± 0.00	0.014 ± 0.005	0.040 ± 0.008	0.77 ± 0.76	0.37 ± 0.32	347 ± 505	84	85
14 Iguazú 2	24.9 ± 7.1	7.9 ± 0.4	43.0 ± 2.8	5.9 ± 3.7	7.1 ± 1.6	0.028 ± 0.00	0.022 ± 0.012	0.056 ± 0.050	0.95 ± 0.07	0.20 ± 0.00	600 ± 784	80	78
15 Paraná 2	26.0 ± 4.2	7.6 ± 0.1	47.0 ± 8.5	20.4 ± 18.8	8.4 ± 1.6	0.031 ± 0.01	0.030 ± 0.008	0.065 ± 0.021	1.08 ± 0.57	0.25 ± 0.21	580 ± 797	81	78
16 Aguaray Guazú	24.7 ± 5.5	7.8 ± 0.2	56.3 ± 20.0	10.7 ± 8.1	7.6 ± 0.7	0.037 ± 0.01	0.014 ± 0.005	0.043 ± 0.026	1.00 ± 0.79	0.44 ± 0.44	467 ± 446	85	85
17 Piray Mimi	25.2 ± 5.3	7.9 ± 0.4	65.0 ± 3.6	13.1 ± 9.8	7.4 ± 0.6	0.042 ± 0.00	0.030 ± 0.010	0.042 ± 0.033	0.93 ± 0.87	0.41 ± 0.45	1593 ± 2605	80	78
18 Piray Guazú	25.9 ± 7.2	8.3 ± 0.6	55.0 ± 14.5	18.2 ± 17.4	7.4 ± 0.6	0.036 ± 0.01	0.014 ± 0.005	0.044 ± 0.036	0.87 ± 0.45	0.47 ± 0.50	621 ± 536	78	73
19 Piranay Guazú	26.7 ± 5.9	7.9 ± 0.3	62.3 ± 5.1	5.9 ± 2.9	7.2 ± 0.7	0.041 ± 0.00	0.015 ± 0.007	0.111 ± 0.070	0.87 ± 0.23	0.17 ± 0.15	1133 ± 1178	83	85
20 Garupé	23.0 ± 5.0	8.0 ± 0.4	67.0 ± 8.2	7.8 ± 5.8	8.0 ± 0.6	0.043 ± 0.01	0.012 ± 0.002	0.048 ± 0.026	0.77 ± 0.35	0.37 ± 0.32	620 ± 537	86	88
21 Paraná 3	25.9 ± 4.8	7.7 ± 0.2	50.3 ± 4.7	9.3 ± 7.2	7.3 ± 0.9	0.033 ± 0.00	0.014 ± 0.005	0.057 ± 0.019	0.80 ± 0.35	0.23 ± 0.21	327 ± 384	83	85
22 Cuña Pirú	26.1 ± 6.7	8.0 ± 0.3	62.0 ± 8.7	8.0 ± 4.0	7.9 ± 0.7	0.040 ± 0.01	0.014 ± 0.005	0.060 ± 0.040	0.73 ± 0.25	0.33 ± 0.31	594 ± 797	87	90
23 Tabay	23.0 ± 5.3	7.9 ± 0.3	54.7 ± 9.5	10.5 ± 5.3	8.3 ± 0.5	0.036 ± 0.01	0.015 ± 0.006	0.047 ± 0.034	1.87 ± 1.85	0.25 ± 0.35	643 ± 772	82	80
24 Yabebirí	26.2 ± 5.4	7.6 ± 0.2	64.7 ± 4.5	8.8 ± 3.7	7.3 ± 1.7	0.042 ± 0.00	0.017 ± 0.006	0.115 ± 0.138	1.60 ± 1.73	0.33 ± 0.29	233 ± 195	84	85
25 Garupa	25.8 ± 5.0	7.7 ± 0.4	45.7 ± 9.1	8.9 ± 4.9	7.4 ± 0.7	0.030 ± 0.01	0.014 ± 0.005	0.104 ± 0.053	0.60 ± 0.36	0.37 ± 0.32	990 ± 1322	79	78
26 Zaiman	25.7 ± 4.3	7.7 ± 0.4	53.7 ± 20.4	15.2 ± 9.6	7.4 ± 1.5	0.035 ± 0.01	0.040 ± 0.020	0.234 ± 0.115	2.40 ± 3.29	0.73 ± 0.87	710 ± 630	74	73
27 Mártires	27.6 ± 5.6	7.8 ± 0.2	56.0 ± 5.3	10.6 ± 1.6	6.8 ± 0.9	0.036 ± 0.00	0.014 ± 0.005	0.197 ± 0.077	0.83 ± 0.15	0.31 ± 0.25	1933 ± 2183	74	71
Mean	25.3 ± 4.6	7.7 ± 0.4	54.1 ± 12.3	13.1 ± 5.9	7.8 ± 0.6	0.035 ± 0.008	0.020 ± 0.008	0.068 ± 0.048	1.07 ± 0.45	0.41 ± 0.16	573 ± 430	83.0	82.5

Temperature in degrees Celsius (°C), conductivity in microsiemens per centimeter (μS cm<sup>-1</sup>), turbidity in NTU, dissolved oxygen (DO) in grams per liter, total dissolved solid (TDS) in grams per liter, nutrients in milligrams per liter, and fecal coliform bacteria (FC) in CFU 100 ml<sup>-1</sup>. FC were based on the results of Avigliano and Schenone (2015)



**Table 3** Permissible limits for drinking water according to different organisms

	pH	TDS (g l <sup>-1</sup> )	Turbidity (NTU)	NO <sub>2</sub> <sup>-</sup> (mg l <sup>-1</sup> )	NO <sub>3</sub> <sup>-</sup> (mg l <sup>-1</sup> )	NH <sub>4</sub> <sup>+</sup> (mg l <sup>-1</sup> )
AFC (2007)	6.5–8.5	–	3	0.1	45	200
USEPA (2011)	6.5–8.5	0.5	–	1	10	–
WHO (2011)	–	–	5	3	50	–

ACF Argentinean Food Codex, USEPA United States Environmental Protection Agency, WHO World Health Organization

conductivity is greater than 510 mS cm<sup>-1</sup> (Avigliano and Volpedo 2013). Other authors previously reported similar conductivity values in streams located in the Brazilian south (de Souza et al. 2013) where the native vegetation was replaced by crops (mean = 53 μS cm<sup>-1</sup>, range 13–100).

The TDS ranged between 0.02 and 0.06 g l<sup>-1</sup> with an average value of 0.035 ± 0.008 g l<sup>-1</sup>. Only Itacaruaré exceeded the guideline value recommended by USEPA (0.5 g l<sup>-1</sup>) (Table 3). TDS comprise inorganic salts (principally calcium, magnesium, potassium, sodium, bicarbonates, chlorides, and sulfates) and small amounts of organic matter that are dissolved in water. TDS in drinking water originates from natural sources, sewage, urban runoff, and industrial wastewater. Reliable data on possible health effects associated with the ingestion of TDS in drinking water are not available, and no health-based guideline value was proposed to WHO. However, the presence of high levels of TDS in drinking water may be objectionable to consumers (WHO 2011).

The turbidity ranged between 5.9 and 26.9 NTU, with an average of 13.1 ± 5.9 NTU, and it was higher than the proposed limits by AFC and WHO (3 and 5 NTU, respectively) (Table 3) in all sampling stations. Turbidity in water is caused by suspended particles or colloidal matter that obstructs light transmission through the water. It may be caused by inorganic or organic matter or a combination of the two (WHO 2011). To ensure effectiveness of disinfection, turbidity should be no more than 5 NTU and preferably much lower (WHO 2011).

The dissolved oxygen average was 7.8 ± 0.6 mg l<sup>-1</sup> (range 6.8–9.5). As temperature, Mártires station showed the lowest values of DO. de Souza et al. (2013) and Santos Simoes et al. (2008) reported similar dissolved oxygen levels in the same eco-region southeast of Brazil (3.6–9.1 mg l<sup>-1</sup>).

### Nutrients and guideline values

The highest values of nutrients (NH<sub>4</sub><sup>+</sup>, NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, and PO<sub>4</sub><sup>3-</sup>) were observed in Zaiman. The average values and ranges (mg l<sup>-1</sup>) were NH<sub>4</sub><sup>+</sup> = 0.020 ± 0.008, NO<sub>2</sub><sup>-</sup> = 0.068 ± 0.048, NO<sub>3</sub><sup>-</sup> = 1.1 ± 0.4, and PO<sub>4</sub><sup>3-</sup> = 0.41 ± 0.16.

According to WHO (2011), NH<sub>4</sub><sup>+</sup> and PO<sub>4</sub><sup>3-</sup> in drinking water is not of immediate health relevance, and therefore no health-based guideline value is proposed. However, toxicological effects related to NH<sub>4</sub><sup>+</sup> are observed only at exposures

above about 200 mg kg<sup>-1</sup> of body weight (b.w.) per day (WHO 2011). Considering that a typical argentine adult (65 kg) drinks 2.3 l of water daily (CESNI 2012), the NH<sub>4</sub><sup>+</sup> does not represent a risk to human health.

Nitrate (NO<sub>3</sub><sup>-</sup>) is found naturally in the environment and is an important plant nutrient. It is present at varying concentrations in all plants and is a part of the nitrogen cycle (WHO 2011). The nitrate (NO<sub>3</sub><sup>-</sup>) values were below the recommended guideline by AFC, WHO, and USEPA (45, 50, and 10 mg l<sup>-1</sup>, respectively) for human consumption (Table 3). Nitrite (NO<sub>2</sub><sup>-</sup>) is not usually present in significant concentrations except in a reducing environment, as nitrate is the more stable oxidation state. It can be formed by the microbial reduction of nitrate and in vivo by reduction from ingested nitrate (WHO 2011). The nitrite (NO<sub>2</sub><sup>-</sup>) levels in this study were below the recommended guideline value by WHO and USEPA (3 and 1 mg l<sup>-1</sup>, respectively) (Table 3). On the other hand, the average values of Yabebirí, Garupá, Zaiman, and Mártires exceed the recommended value proposed by AFC (0.1 mg l<sup>-1</sup>). The information about nutrient concentration in water courses in Atlantic Forest is scarce (Table 4). The nutrient levels obtained in this study were compared with previous reports by other authors in different rivers and regions (Atlantic rainforest, urban, livestock, and agriculture areas). In general, the levels of NH<sub>4</sub><sup>+</sup> and PO<sub>4</sub><sup>3-</sup> found were similar to those reported for other rivers of Atlantic Forest in Brazil (da Silva and Sacomani 2001; Santos Simoes et al. 2008; de Souza et al. 2013), with the exception of the Paranapanema Basin where PO<sub>4</sub><sup>3-</sup> values up to 7.69 mg l<sup>-1</sup> have been reported. The NO<sub>3</sub><sup>-</sup> reported in this study were higher than those reported by de Souza et al. (2013) in an Atlantic Forest area replaced by urban areas. This is evidence that nutrient concentration varies among sampling sites in Atlantic Forest. These variations could be related to land use. However, to accomplish a strong relation further, more baseline information is needed.

### Spatial distribution patterns

Spatial patterns vary among the measured parameters and there are no evident generalizations (Fig. 3). However, some patterns can be pointed out. In the south of the province, a high density of sampling points with relatively low values of pH, dissolved oxygen, TDS, conductivity, and nitrite can be found.

**Table 4** Concentrations of nutrients ( $\text{mg l}^{-1}$ ) in surface water reported for previous studies

Water body	Country	Area type	$\text{NH}_4^+$	$\text{NO}_2^-$	$\text{NO}_3^-$	$\text{PO}_4^{3-}$	Reference
Parapanema Basin	Brazil	AR replaced by Rural Urban (Sao Pablo)	–	–	–	1.21–7.69	Henry and Gouveia 1998
Jacaré–Pepira River	Brazil	AR replaced by Rural (Sao Pablo)	0.003–0.05	–	0.006–0.6	–	de Souza et al. 2013
Pardo River	Brazil	AR replaced by agriculture and industry	–	–	–	0.15–0.79	da Silva and Sacomani 2001
Macuco and Queixada Rivers	Brazil	AR replaced by agriculture and rural areas	–	–	–	0.01–0.42 <sup>a</sup>	Santos Simoes et al. 2008
Piray Mini River	Argentina	AR	0.03	0.042	0.93	0.41	This study
Acaraguá River	Argentina	AR and agriculture and livestock areas	0.015	0.045	0.9	0.57	This study
Zaiman River	Argentina	Urban and suburban	0.04	0.23	2.4	0.73	This study

AR Atlantic rainforest

<sup>a</sup> Determinate as total phosphorus

The Middle West region of the province showed low and intermediate values of conductivity, turbidity, dissolved oxygen, TDS, ammonia, and phosphate. In general, relatively high values of conductivity and TDS were found in the sampling points situated northeast and in the southern region of the study area (San Antonio, Pepirí Guazú, and Itacaruaré).

All the nutrients showed relatively high values in the southwest of the province, near Posadas City (e.g., Zaiman River). With the exception of nitrite, nutrients were also high in the southeast.

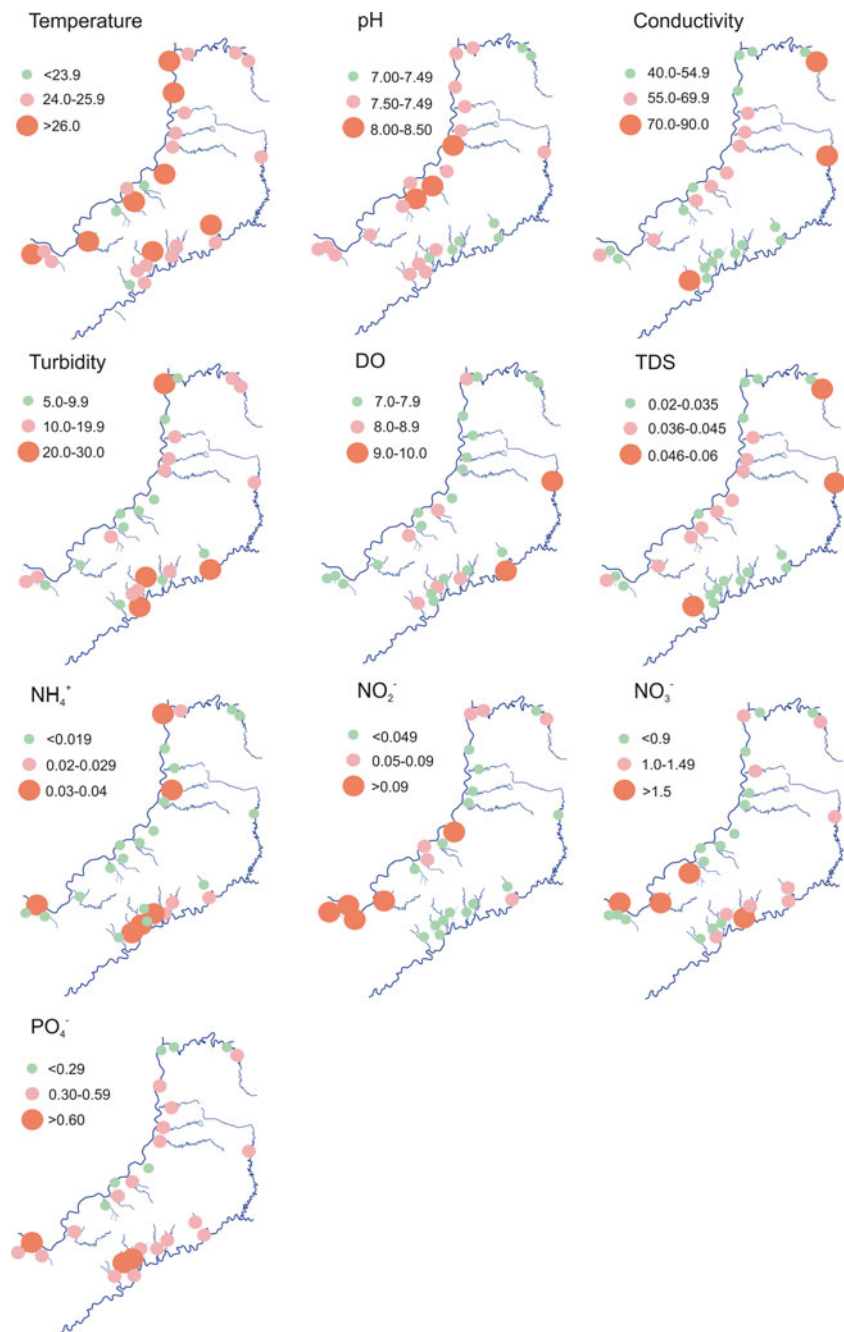
Eutrophication of inland and coastal waters is a widespread environmental problem caused by the increased cycling and fluxes of phosphorus (P) and nitrogen (N) associated with urbanization, deforestation, and intensification of agriculture (Jarvie et al. 2008; Withers et al. 2011). Eutrophication in rivers is most prevalent under low-flow conditions when residence times are greatest, and the role of major point sources in maintaining high nutrient concentrations, especially P, during summer low flows is now well documented (Withers et al. 2011). This is not an isolated matter if we consider that the Paraná River and its tributaries flow to Yacyretá Dam Lake and the Uruguay River and its tributaries to a future Dam lake in the same region. On the other hand, in high water conditions, the water quality can also be affected. For example, within the study area, glyphosate concentrations were associated with high water events (Armas et al. 2007; Freire et al. 2012; Avigliano and Schenone 2015). Even more, it has been observed that there is an increase in nutrients (Chaves et al. 2009) and fecal coliform (da Silva and Sacomani 2001; Avigliano and Schenone 2015) related to the runoff.

Multivariate analyses like factor analysis (FA) and y clusters allow to evaluate the relation between sampling sites with many parameters simultaneously. The values of the four main principal components from the FA are given in Table 5. The total variance for the four factors in surface water was 79 %.

The first factor (F1) explains 32 % of total variance and is positively related to the variables turbidity and pH (Table 5). Factor 2 (F2) accounts for 20 % of the total variance and has strong positive weight for dissolved oxygen and negative weight for temperature. Factor 3 (F3) explains 18 % of the total variance and has strong positive weight for TDS and conductivity. Factors 2 and 3 represent some physicochemical characteristics in the study area. Factor 4 (F4) explains 9 % of the total variance and has strong positive weight for  $\text{NO}_3^-$  and  $\text{PO}_4^{3-}$ . This factor mainly represents the some nutrients contents in the study area. Figure 4 displays a plot of sample scores on the bi-dimensional plane defined by the first four components. In this plot, an association between  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  and points 2, 3, 5, 6, 7, and 14 (Once Vueltas, Ramón, Torto, Pindaytí, Saltinio, and Iguazú 2) was observed (Fig. 4a). Moreover, an association between temperature and points 15, 17, 24, and 27 (Paraná 2, Piray Mini, Yabebirí and Mártires) was observed, while turbidity was associated with site 8 (Uruguay) (Fig. 4a). On the other hand, an association between the TDS and conductivity in points 1 and 11 (Itacaruaré and San Antonio) was observed, while  $\text{NO}_3^-$  and TDS were associated with sites 8, 10, and 20 (Uruguay, San Antonio, and Garupé) and  $\text{PO}_4^{3-}$  and  $\text{NH}_4^+$  were associated with sites 1, 2, and 17 (Itacaruaré, Once Vueltas, and Piray Mini) (Fig. 4b). In general, multivariate association patterns are related with the graphic patterns in Fig. 3.

The cophenetic correlation coefficient (UPGMA dendrogram) was 0.76, suggesting a good fit between the similarity matrix and the matrix derived from the dendrogram. The similarity analysis showed the existence of at least five main different groups (Fig. 5). In the cluster analysis, the Zaiman and Mártires Rivers showed a separation from the rest of the groups (Fig. 5). These rivers run through the capital city of the province with 323,739 inhabitants (Posadas City) (INDEC 2010). Along the margins of the rainforest are several

**Fig. 3** Geographic distribution of the physicochemical parameters and nutrients in the study area



settlements with no effluent treatment upstream of the sampling points. In addition, both rivers are affected by Yacyretá hydroelectric dam lake. Avigliano and Schenone (2015) showed for these rivers the highest values of total coliform for the study region, these being directly related to the untreated urban runoff. Moreover, the highest concentration of total coliform matches with the relatively high levels of nutrients observed in the present study.

The Acaraguá River also showed a separation from the rest of the groups (Fig. 5). This river showed the lowest mean values of electric conductivity and TDS of all studied sites.

The Acaraguá River begins in the center of the province and runs through small crops in between Atlantic Forest islands including private reserve areas. In this river, it has been observed that there are relatively low values for all parameters (Figs. 3 and 4) and native forest is present in the margins along all the extension of the river.

The rest of the sites were grouped into two clusters (1 and 2) (Fig. 5). Cluster 1 includes the Uruguay River and three affluents (Torto, Ramón, and Once Vueltas), and all these rivers flow southeast of the study area (less than 10 km in-between) and showed moderate to high values of turbidity,

**Table 5** Eigenvalues of the factor analysis and physicochemical parameters and nutrients

	e1	e2	e3	e4
Temperature	-0.31	0.30	-0.39	-0.10
pH	-0.38	-0.20	0.15	0.21
Conductivity	-0.27	-0.19	0.56	0.23
Turbidity	0.35	0.03	-0.16	0.17
DO	0.36	-0.17	0.43	0.01
DTS	0.45	-0.15	-0.23	0.43
NH <sub>4</sub> <sup>+</sup>	0.10	0.55	0.14	-0.29
NO <sub>2</sub> <sup>-</sup>	-0.19	0.39	-0.10	0.68
NO <sub>3</sub> <sup>-</sup>	0.06	0.43	0.29	0.32
PO <sub>4</sub> <sup>3-</sup>	0.20	0.38	0.35	-0.17

DO dissolved oxygen, TDS total dissolved solids

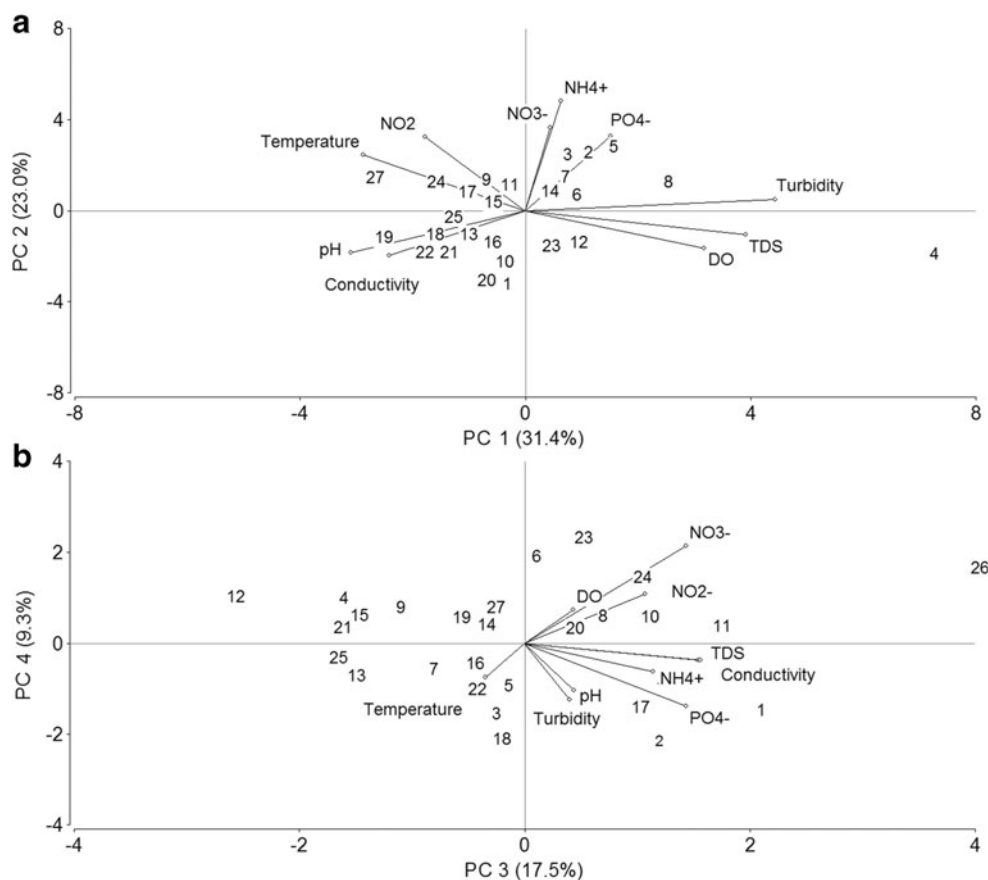
NH<sub>4</sub><sup>+</sup>, and PO<sub>4</sub><sup>-3</sup> (Table 2 and Fig. 3). The association between these rivers and NH<sub>4</sub><sup>+</sup> and PO<sub>4</sub><sup>-3</sup> is also represented in the results obtained in the FA (Fig. 4). Cluster 2 can be divided into two main groups (Fig. 5) which includes rivers with different origins in the study region. The 2a group is composed of Tabay, Garuapé, Itacaruaré, and Pepiri Guazú Rivers. The first two rivers tribute to the Paraná River, while the other two to the Uruguay River. The 2b group can be divided into two

subgroups (2bi and 2bii) (Fig. 5). The 2bii subgroup grouped together two sampling points in Paraná River and seven affluents to the Paraná River (west-east direction), while the subgroup 2b1 grouped together affluents from the Paraná and Uruguay Rivers, and a sampling point in the Paraná River (Paraná 2) with high similarity in-between.

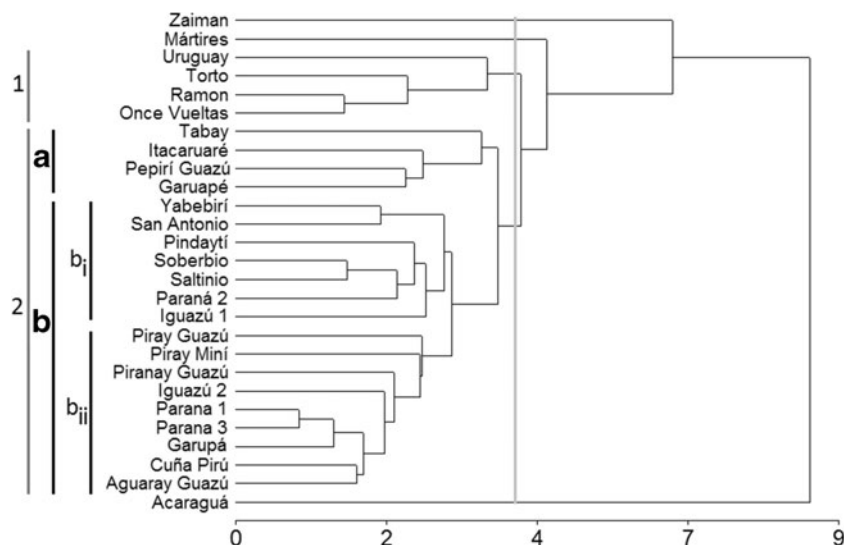
### Water quality indices

According to the WQI<sub>obj</sub> values (Table 2), water quality was rated as good in all sampling sites (WQI<sub>obj</sub> = 71–90), with the exception of Itacaruaré which was rated as excellent (WQI > 91). The regression of the two indices WQI<sub>obj</sub> and WQI<sub>min</sub> was significant ( $p < 0.0001$ ) with a good adjustment ( $R^2 = 0.89$ ), and there were no significant differences between values for both indices (Wilcoxon test,  $W = 714$ ,  $p > 0.6$ ). This shows that the WQI<sub>min</sub>, with only four parameters, is as efficient to represent water quality in the region as the WQI<sub>obj</sub> with 11 parameters. The use of the WQI<sub>min</sub> will reduce drastically the operative costs for monitoring. The use of regional WQI has become an important matter for the evaluation of water resources in different regions of the world (Pesce and Wunderlin 2000; Lumb et al. 2011; Akkoyunlu and Akiner 2012; Gebrehiwot et al. 2013). The lack of basic information

**Fig. 4** Scores of river water samples on the bi-dimensional plane defined by the first four factors (the most representative)



**Fig. 5** UPGMA cluster based on physicochemical parameters and nutrients in all sampling sites



or baseline studies added to the need for local capacities and small budget create a wide field for the exploration of easier indices (e.g.,  $WQI_{min}$ ) with local acceptance in developing countries (Pesce and Wunderlin 2000).

### Monitoring and management

In relation to management, the results obtained create a baseline and a diagnosis of the situation of the water quality and possible solutions for monitoring accounting for local capacities and budget. On the other hand, the spatial information presented is highly valuable to determine the exposition of water quality to vulnerable communities. Furthermore, some recommendation can be made so far like the need for a water treatment before its consumption to decrease the values of TDS and NTU, especially in the sampling sites where these values were above the recommended guidelines.

When considering nutrient, only the  $NO_2^-$  in Yabebirí, Garupá, Zaiman, and Mártires were above the recommended guidelines; however, these rivers are near urban areas and people do not use water directly from the source. The study suggests the use of the  $WQI_{min}$ , with the aim of controlling temporarily the water quality and to be used as a tool for fast reaction when abnormalities are detected.

One other crucial point is to consider the necessity to include fecal coliform in the monitoring actions due to the high levels reported in this region. It has to be pointed out that coliform bacteria could play a substantial role in the calculation of the WQI indices (Lumb et al. 2011).

### Final considerations and conclusions

The present study explores for the first time the water quality of a wide number of mountain streams and big rivers from the

last relict of continental Atlantic Forest in the world. It also presents the information for consumption and the possible health effect, showing low to no risk for consumption considering nutrients.

The higher values of physicochemical parameters such as DO and temperature were related to rivers influenced by urban areas and the possible effect of Yacyretá Dam (e.g., Mártires River). Nutrients were associated with urban areas and dam effect (e.g., Mártires, Zaiman, and Garupá Rivers). The cluster and PCA analysis showed defined groups of rivers and streams with similar characteristics which facilitate the management alternatives when approached by stakeholders and policymakers.

As a biodiversity hotspot, this particular ecosystem has an intimate relation to water quality not only from the optic of contamination but also as a provider of ecosystem services (water resources). The results showed good water quality when considering the  $WQI_{obj}$  and  $WQI_{min}$ . The authors would like to remark the importance of applying simple indices as a first approach to evaluate water quality in order to be realistic with the situation of the region. The use of  $WQI_{min}$  is recommended for monitoring water quality in the region and also the water treatment of coliform, TDS, and NTU. The study area is under development pressure, turning native forest areas into production landscapes, hence the urge for monitoring and data collection.

**Acknowledgments** This research was funded by The Ministry of Ecology and Renewable Natural Resources of Misiones Province, Fundación Bosques Nativos Argentinos para la Biodiversidad and Consejo Nacional de Investigaciones Científicas (CONICET). We are also greatly indebted to D. Bucafusco, L. Diaz, G. Comte, R. Barassi, M. Torrents, and J. R. Vida for their invaluable collaboration for the sampling logistic. We thank the Editor and anonymous reviewers for their constructive comments, which helped us to improve the manuscript.

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