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Human health risk assessment and environmental distribution of trace elements, glyphosate, fecal coliform and total coliform in Atlantic Rainforest mountain rivers (South America)

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ABSTRACT

Trace elements (Ag, Al, As, Ba, Be, Cd, Co, Cr, Cs, Cu, Fe, Ga, Mn, Ni, Pb, Se, Sr, Ti, U, V and Zn), glyphosate and fecal (FC) and total coliform (TC) bacteria in surface water samples in 24 rivers from southern Atlantic rainforest (South America) were analyzed. The potential health risk of these trace elements, glyphosate and coliform to local population were assessed. Trace elements' (TE) concentrations were determined by ICP-MS, while the glyphosate was analyzed by HPLC. Determination of coliform was performed by dilution method and incubation. The results were then compared to national and international guidelines to diagnose the environmental situation. Only the Fe and Mn concentration were above the recommended limits by USEPA ($Mn = 500\ \mu g\ L^{-1}$) (USEPA, 2009) and WHO ($Mn = 400\ \mu g\ L^{-1}$). Based on TE concentrations, the Hazard Quotient and Hazard Index were calculated. The resulting indices suggest no risk to population. Glyphosate was below $200\ \mu g\ L^{-1}$ in all sites, except San Antonio River, where the concentration was $1600\ \mu g\ L^{-1}$. According to the USEPA, the glyphosate could present a low risk for children, but only in the San Antonio River during extreme floods. Based on the mean concentration of FCs, three of the 24 rivers were classified as high risk ($CFU\ 100\ ml^{-1} > 1000$) while the other study sites were intermediate ($100 > CFU\ 100\ ml^{-1} > 1000\ ml$). Inter-trace element correlation revealed the natural origin of Ba, Cu, Fe, Mn, V and Zn. Principal component analysis and factor analysis revealed that high levels of coliform were associated with urbanization and changes in land use.

1. Introduction

There is considerable evidence suggesting that elevated degradation and loss of habitats and species are compromising ecosystem services that sustain the quality of life for billions of people worldwide [10,15]. The continuous degradation of nature coupled with the growing human population (currently estimated at nearly 7.2 billion and projected to reach 9–10 billion by 2050) [15,50], suggest that the quality of human life may decrease considerably in the near future [10].

Surface water contamination proves to be one of the most concerning human effects on the environment. Industry, urbanization and agriculture often introduce various pollutants including heavy metals, bacteria, agrochemicals, and drugs [22,49,64,67]. These pollutants could have direct effects on human health, causing a wide variety of afflictions ranging from diarrhea to cancer [67]. In South America, urbanization has advanced dramatically in the last few decades, having drastic effects over native forests such as the Atlantic Forest.

The Atlantic Forest was one of the largest rainforests of the Americas, originally covering around 150 million ha, with great diverse environmental conditions. Its latitude ranges from approximately 5° to 29°, including both tropical and subtropical regions. The variation in forest composition found in this wide longitudinal range, caused by a decreasing rainfall regime further from the coast [42], is highly important to this diverse environment. Currently, most of the remaining Atlantic Forest remains in small fragments (<100 ha) that are isolated from each other [41,42]. The few large fragments remain in locations where geological characteristics make human occupation particularly difficult [42,47] or in protected areas. The southern portion of the Atlantic Forest is located in northwestern Argentina (Misiones province) and neighboring areas of Brazil and Paraguay. Only in the province of Misiones, the population increased 1.5% annually over the last few decades, with 1,101,593 inhabitants in 2010 [25]. The region serves a generally poor demographic with several communities ingesting river water directly. The situation is exacerbated for the indigenous people of the Mbyá Guaraní ethnic group where the population of 13,006 [25] live in the jungle under very poor health conditions.

Abbreviations: USEPA, United States Environmental Protection Agency; WHO, World Health Organization; ICP-MS, Inductively coupled plasma mass spectrometry; HPLC, High-performance liquid chromatography.

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New villages, urban centers and agriculture and livestock have led to deforestation. This data represents major concerns regarding the utilization of surface water for direct consumption and domestic use by population. Furthermore, the wastewater of these settlements is discharged to the same water bodies. Contamination of surface water with fecal-derived pathogens poses a significant threat to human health and represents an important barrier for the utilization of untreated river water for drinking or other domestic purposes [32].

Recently, some pollutants related to antrophic activities like heavy metals [16,18,27], fecal coliform [12,27], and agrochemical such as glyphosate [6,18], have been found in basins of the Atlantic Forest. Glyphosate is the most widely used herbicide in the Atlantic Forest and is manually applied for the cultivation of soybeans (*Glycine max*), tobacco (*Nicotiana tabacum*), tea (*Camellia sinensis*) and yerba mate (*Ilex paraguariensis*) [6,18]. This agrochemical is genotoxic and potentially carcinogenic to humans [20]. For this, it is necessary to evaluate the concentration of this element in water bodies.

Based on the above considerations, the objectives of the present study were: 1, to determine the content of trace elements (including toxic metals and arsenic), glyphosate (the pesticide most used) and fecal and total coliform bacteria 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, make management recommendations for the population affected by pollution.

This work identifies sites of risk to human health in the region of study, provides valuable information to guide environmental policy, and contributes to water management practices.

2. Materials and methods

2.1. Study area and social scenario evaluated

The study area is located among the highlands of the argentine province of Misiones, surrounded by subtropical rainforests with thermal seasonality and hydrological variation (Fig. 1). The region's major rivers are the Parana River (geographical border between Argentina and Paraguay), the Iguazú River (geographical border between Argentina and Brazil) and the Uruguay River (geographical border between Argentina and Brazil) [11]. 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 [17]. Additionally, most of the streams are originated by a great number of little wellsprings and small streams, which drain the excess of water from the central hills. Native vegetation, a typical characteristic of rain forest streams, can be found in stream margins. The climate is predominately rainy with high rain events [11]. During storm events, streams can vary their caudal very fast reaching 3 to 6 times their normal height However, they return to their normal state in a matter of days (2 or 3).

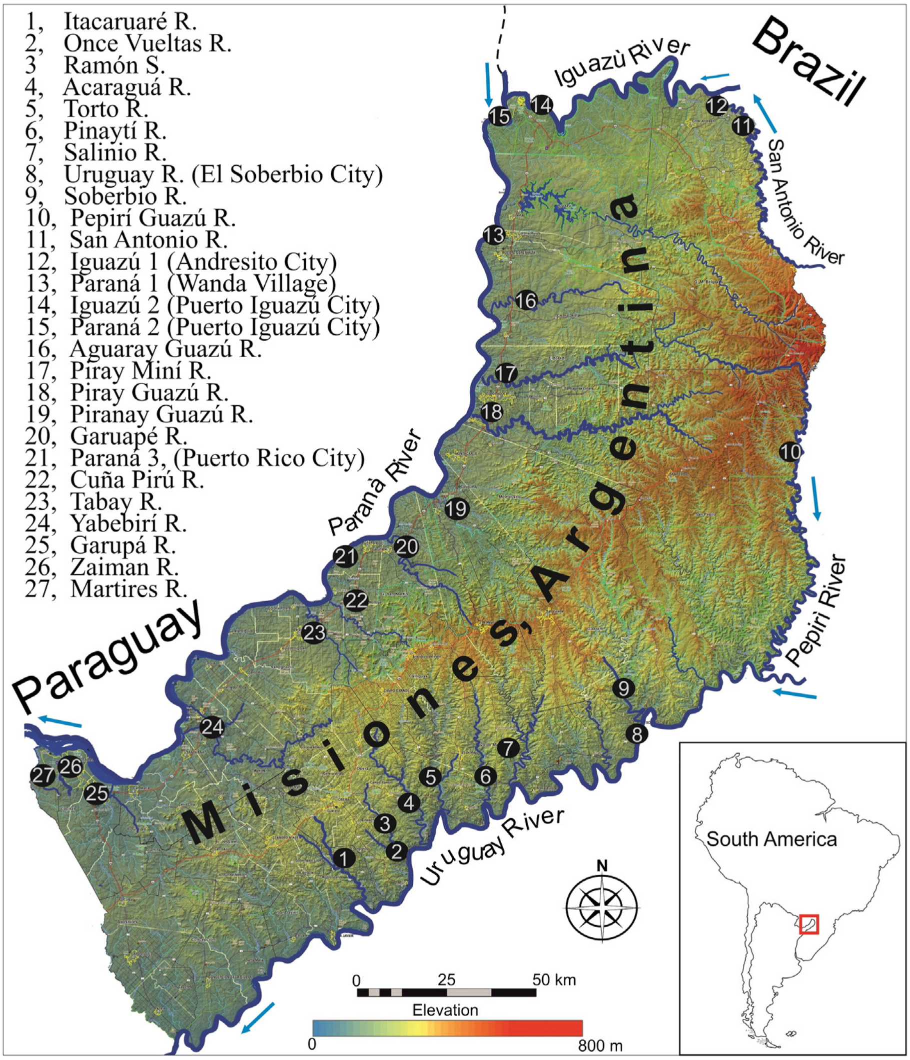

Fig. 1. Sampling sites of surface water, Misiones, Argentina. The arrows indicate the direction of water flow.

Due to the study area's generally poor population, services such as sewers, wastewater treatment and drinking water are absent. In Misiones and surrounding areas, the nearly 1.7 million inhabitants (native and non-native population) [25] commonly use rivers both for disposing wastewater and for direct consumption and domestic use.

2.2. Samples collection and preparation

Water samples were collected according to standard procedures [5] in four sampling periods: 12/3–12/4/2013, 2/11–2/12/2014, 6/9–6/10/2014, 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 drinking water in local areas.

Because 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. The flow of water from all sampling sites was normal except in the third sampling which was done a week after a rainfall event.

All water samples were collected manually at 0.3 m depth [59]. Water samples for trace elements were collected with 15 ml polyethylene-terephthalate falcon tubes and were acidified to 0.2% (v/v) (pH <2) with nitric acid (Merck® Pro Analysis) [5]. Subsequently, these were vacuum filtered through acid-treated Whatman GF/F glass fiber filters (0.45 mm) [5]. Water samples for glyphosate determination were collected with 500 ml opaque polyethylene-terephthalate bottles. Water samples for fecal and total coliform determination were collected with 125 ml polyethylene-tereftalate sterile containers and were refrigerated at 4 °C for up to 6 h before being processed in accordance with standardized protocols [5]. Collection, preservation, preparation and pretreatment of trace elements, microorganism and glyphosate in water were conducted according to APHA methods (2005).

In all cases, air was removed from the containers. All samples were stored in darkness at 4 °C up and immediately transported to the laboratory for analytical treatment [5].

2.3. Chemical analysis and bacterial quantification

2.3.1. Trace elements

Element concentrations (Ag, Al, As, Ba, Be, Cd, Co, Cr, Cs, Cu, Fe, Ga, Mn, Ni, Pb, Se, Sr, Ti, U, V and Zn) were determined by Inductively coupled plasma mass spectrometer (ICP-MS), using an Agilent 7500 (Agilent, Waldbronn, Germany) equipped with a Micro Mist nebulizer (Glass Expansion) and a quartz spray chamber. Water samples were analyzed with no previous digestion. The water samples for trace element determination were analyzed by triplicate. A water standard reference material (SRM 1640e; National Institute of Standards and Technology, NIST, USA) was analyzed to support quality assurance and quality control (QA/QC) of water sample measurements. Replicate analysis of these reference materials showed good accuracy, with recovery ranging from 82% to 121%. A blank was used to calibrate all measurements. The water used throughout the present study was obtained from a Milli-Q Academic water purification system (Heal Force PW VF, Shanghai, China) with a resistivity of 18.2 MOhm $*$ cm. Pro-analysis reagents were used throughout the study [44]. For each of the nine samples, a procedure blank and spike sample involving all reagents were run to check for interference and cross-contamination. In addition, scandium, yttrium, terbium and holmium were used as internal standards. Triplicate analyses of blanks, spike samples and reference materials differed from each other within an acceptable range of $\pm 15\%$. The sample results were reviewed and evaluated in relation to the corresponding QA/QC samples. Reported results have been corrected for the blanks. The detection limits (LOD) in μg L^{-1} based on three times the standard deviation of the blank signal was 0.01 for Ni, Ag, Be, Cd, Cs and Ti; 0.02 for Al, Mn and Sr; 0.03 for Cr; 0.05 for Fe; and 0.06 for As, Ba, Co, Cu, Ga, Pb, Se, U, V and Zn.

2.3.2. Glyphosate

Preservation, pretreatment and analyses of glyphosate were conducted according to Nollet [37]. Chromatographic separation and detection of glyphosate methodology employed by Le Fur et al. [28] was adapted. The derivation of the compound was performed with 0.5 ml of the sample solution, adding 0.5 ml of borate buffer 0.40 N at pH 10.0, adding 0.5 ml of OPA-MPA solution (ortho-phthalaldehyde and 3-mercaptopropionic acid), and 0.5 ml of FMOC (9-Fluorenylmethyl chloroformate) mark Sigma® pro-analysis quality. Subsequently, 2 ml of hexane were added to extract impurities. The aqueous phase was centrifuged at maximum speed for 2 min. After, an aliquot of 50 μL of the derived sample was injected in the HPLC system, Agilent model 1100 (Hewlett–Packard G1313A automatic injector; Hewlett–Packard detector FLD 1046A; Hewlett–Packard G1311A gradient pump; Hewlett–Packard G1316A thermostated column) containing a Hypersil APS-2 amino (NH_2) chromatography column (150×4.6 mm particle size 5 μm), photodiode array spectrophotometer monitoring at 240 nm and as mobile phase sodium phosphate buffer solution at 0.64 mmol (70%) and acetonitrile 30% at flow rate of 1.0 ml $\min^{-1}$ was used at a temperature of 25.0 °C.

A spike water sample with gryphosate was prepared from a standard solution of 96.7% purity, and served as the quality assurance and quality control (QA/QC) for the measurements. Replicate analysis of these reference materials showed good accuracy, with a recovery of 70.0%.

2.3.3. Fecal and total coliform bacteria

Pretreatment and quantification of bacteria in surface water samples were conducted according to standard methods [5]. Determinations of total and fecal coliform were performed by dilution method and incubation at 35–37 °C and 44–45°, respectively, using a culture oven (mark DALVO, model MCI44) and water bath (mark DALVO, model BMKI-22). Stove sterilization procedures were then performed (mark precision, model 16). The concentration of coliform is expressed in colony forming units per 100 ml (CFU 100 ml^{-1}).

2.4. Human health risk assessment

The levels of trace elements, glyphosate and fecal and total coliform concentration were compared with permissible limits set by Argentinean Food Codex (AFC), Argentinean National Guidelines for Human Consumption (ANGHC), the international guidelines of the United States Environmental Protection Agency (USEPA) and those of the World Health Organization (WHO). The levels of fecal and total coliform concentration were compared with permissible limits set by USEPA and WHO, while glyphosate was compared with guidelines by USEPA, WHO and ANGHC.

The estimation of intake in a human body through contaminant contact is estimated by chronic daily intake (CDI). The CDI value indicates the amount of chemical substance ingested [55] and was calculated by the following equation (Eq. (1)):

$$\mathrm{CDI} = \mathrm{C} \times \mathrm{IngR} \times \mathrm{EF} \times \mathrm{ED}/(\mathrm{BW} \times \mathrm{AT}). \tag{1}$$

Table 1
Parameters distribution for metal exposure and risk. Input data.

Parameter	Symbol	Unit	Value	Reference
Chemical concentration	C	μg/L	Value	
Body weight adult	BWA	kg	65	Del Pino et al.[14]
Bodyweight children	BWC	kg	20	Del Pino et al.[14]
Averaging time	AT	Day	ED x 365	USEPA [66]
Exposure frequency	EF	Day $year^{-1}$	365	USEPA [66]
Exposure duration adult	ED A	Year	70	USEPA [57]
Exposure duration children	ED C	Year	6	USEPA [57]
Ingestion rate of water adults	IngR (a)	L day^{-1}	2.3	CESNI [13]
Ingestion rate of water children	IngR (c)	L day^{-1}	1.4	CESNI [13]

Table 2
Concentration of trace elements in surface water (μg L^{-1}).

Site	Al				Ba				Cr				Cu				Fe				Sr			
	M	SD	Mi	Ma	M	SD	Mi	Ma	M	SD	Mi	Ma	M	SD	Mi	Ma	M	SD	Mi	Ma	M	SD	Mi	Ma
1	76.0	8.5	70.0	82.0	20.7	4.7	17.0	26.0	1.6	1.2	0.5	2.9	3.8	1.9	2.5	6.0	169.8	62.2	102.0	235.0	46.3	3.1	43.0	49.0
2	46.0	20.1	18.9	64.0	18.7	4.7	15.0	24.0	2.4	1.2	ND	3.7	3.6	2.8	0.4	7.2	133.0	77.7	37.0	218.0	32.0	7.5	25.0	40.0
3	50.8	41.3	9.0	107.0	16.8	3.5	13.0	21.0	1.7	1.5	ND	3.3	2.8	1.4	1.3	4.5	159.3	143.6	11.0	355.0	22.8	1.7	21.0	25.0
4	55.5	34.9	13.0	94.0	12.7	5.8	4.9	19.0	1.9	2.1	0.3	4.9	2.2	0.6	1.5	2.7	134.5	66.1	66.0	214.0	21.0	9.1	8.1	29.0
5	60.0	22.9	36.0	88.0	14.5	4.5	11.0	21.0	2.3	2.1	0.4	5.2	4.8	3.6	1.6	9.3	130.5	43.2	70.0	164.0	32.5	3.1	28.0	35.0
6	49.5	21.6	28.0	71.0	12.8	1.0	12.0	14.0	2.0	2.0	0.3	4.9	2.5	1.6	0.8	4.6	90.5	32.8	42.0	112.0	28.8	4.9	24.0	35.0
7	26.0	10.8	14.0	35.0	10.6	4.0	5.4	15.0	0.6	0.4	0.2	1.1	2.6	1.9	0.7	5.2	68.3	40.3	37.0	127.0	20.5	6.6	11.0	26.0
8	56.3	29.8	22.0	76.0	19.0	8.1	6.8	24.0	1.4	1.0	0.2	2.6	2.8	0.5	2.0	3.2	476.8	618.7	117.0	1403.0	22.3	9.3	9.0	30.0
9	47.3	20.5	21.0	65.0	9.8	2.7	6.5	13.0	1.7	2.0	0.2	4.5	2.3	1.3	0.9	4.0	64.3	19.8	39.0	80.0	24.5	9.5	11.0	33.0
10	53.5	35.0	21.0	89.0	16.5	4.2	12.0	22.0	1.6	1.5	0.4	3.8	2.9	1.7	1.1	5.1	94.3	63.7	49.0	188.0	30.8	1.3	29.0	32.0
11	41.7	13.3	33.0	57.0	26.0	8.0	21.0	38.0	1.8	1.5	0.3	3.8	3.9	2.6	1.9	7.5	314.8	113.8	250.0	485.0	36.8	1.9	34.0	38.0
12	45.7	27.2	15.0	67.0	24.0	9.6	11.0	34.0	2.0	2.5	0.2	5.6	2.9	1.7	1.9	5.5	182.0	108.7	50.0	315.0	22.5	7.6	12.0	30.0
13	36.7	16.5	20.0	53.0	30.8	7.6	24.0	40.0	1.5	1.4	0.2	3.5	3.3	1.7	2.2	5.9	237.3	221.9	63.0	558.0	29.0	3.2	25.0	32.0
14	41.7	31.3	13.0	75.0	25.3	13.7	14.0	45.0	2.5	2.5	ND	5.4	6.5	5.7	2.1	14.0	287.5	397.2	22.0	875.0	22.8	6.6	15.0	31.0
15	42.7	37.8	8.0	83.0	29.0	13.5	14.0	46.0	1.6	1.5	0.2	3.7	6.5	5.8	1.4	14.0	292.0	395.3	17.0	873.0	24.8	7.1	15.0	32.0
16	38.5	37.4	11.0	93.0	21.5	8.7	9.8	31.0	1.6	1.6	0.3	3.9	2.7	0.8	1.9	3.8	152.5	77.4	47.0	219.0	33.3	10.6	18.0	41.0
17	46.8	33.7	20.0	96.0	17.5	5.2	14.0	25.0	1.9	1.4	0.3	3.8	2.9	1.5	1.5	4.9	101.5	55.7	22.0	149.0	40.5	5.4	35.0	48.0
18	23.7	12.5	15.0	38.0	12.6	6.6	5.9	26.0	1.1	0.9	0.3	2.0	1.6	0.6	1.0	2.1	44.0	22.6	20.0	65.0	26.3	8.3	17.0	33.0
19	29.5	19.1	7.5	42.0	20.7	5.5	15.0	26.0	1.2	0.9	0.2	1.9	2.3	1.5	1.1	4.0	74.3	56.5	19.0	132.0	35.7	3.8	33.0	42.0
20	34.0	29.7	8.0	71.0	15.0	6.3	5.8	20.0	1.9	2.4	0.2	5.3	1.7	0.9	0.7	2.8	112.8	55.5	61.0	180.0	33.3	15.2	11.0	44.0
21	32.5	26.2	14.0	51.0	27.8	16.2	9.0	47.0	2.1	2.2	ND	4.5	2.8	2.8	0.6	6.9	336.3	404.6	19.0	792.0	24.3	10.0	11.0	32.0
22	21.7	17.8	9.1	42.0	22.3	10.4	8.1	31.0	2.9	4.4	0.2	9.5	2.2	1.7	1.3	4.7	125.0	103.6	27.0	267.0	32.5	13.4	14.0	46.0
23	44.8	33.5	21.0	93.0	23.0	3.2	20.0	27.0	2.4	2.8	0.2	6.5	2.3	1.1	1.5	3.9	194.8	98.6	79.0	320.0	35.3	6.8	30.0	45.0
24	41.8	30.9	14.0	70.0	22.0	9.8	11.0	30.0	1.6	1.7	0.2	4.0	2.5	0.5	1.9	3.0	139.0	60.0	52.0	188.0	32.5	11.8	15.0	41.0
25	41.3	24.4	17.0	69.0	27.5	7.0	17.0	32.0	1.7	1.7	0.2	4.1	2.5	0.7	1.9	3.4	147.0	83.2	31.0	223.0	29.3	7.4	19.0	36.0
26	36.3	24.1	16.0	63.0	36.3	5.7	28.0	40.0	2.5	3.4	0.3	7.6	3.7	1.3	1.7	4.8	266.0	168.2	37.0	442.0	33.5	7.2	27.0	43.0
27	45.5	33.4	16.0	81.0	29.8	11.4	13.0	38.0	2.2	2.5	0.2	5.7	3.1	1.2	2.0	4.8	124.8	83.9	31.0	201.0	30.3	12.3	13.0	42.0

ND = not detected; M = Mean; SD = standard deviation, Mi = minimum, and Ma = maximum.

The values and description of the different parameters are summarized in Table 1.

Non-carcinogenic risks were assessed by estimating the Hazard Quotient (HQ), calculated as the quotient between the exposure through ingestion and the oral reference dose (RfD) (Eq. (2)) [52,57].

$$\mathrm{HQ} = \mathrm{CDI}/\mathrm{RfD} \tag{2}$$

The RfDs used to calculate the HQ and HI values were: 0.009, 0.003, 0.14, 10, 0.003, 0.04, 0.3, 0.6 and 0.21 mg kg^{-1} per day for V, Cr, Mn, Fe, Ni, Cu, Zn, Sr and Ba, respectively [52,54,57]. No oral RfD values were provided for Al and Pb by the USEPA. The provisional tolerable weekly intake (PTWI) levels established by the World Health Organization (WHO) and FAO/WHO were used in place of RfDs for non-carcinogenic risk assessment. The PTWI values used were 1 mg kg^{-1} per day for Al [65] and 0.0036 mg kg^{-1} per day for Pb [26] (only RfDs of the components exceeding the detection limit are reported).

The Hazard Index (HI), which is defined as the total risk [55], was obtained by summing the HQs of each element (Eq. (3)) [55].

$$\mathrm{HI} = \sum \mathrm{HQi}, \quad \text{where i represents the HQ of each element} \tag{3}$$

Calculations were based on the USEPA [55] methodology, performed for 2 subpopulation groups: adults (as general population) and children (as especially sensitive group), separately. The exposed populations to trace elements is assumed to be safe when HQ or HI <1 [55].

As an approach to exposure categorization of fecal coliform, it has been used the defined disease risk for drinking water based on categories of indicator organism measured in 100 ml samples: 0, safe; 1–10, low risk; 11–100, intermediate risk; 101–1000, high risk; and 1000, very high risk [19,63]. The risk for glyphosate intake was estimated with the guide values by USEPA (100 μg Kg^{-1} of body weight per day) [58].

2.5. Statistical analysis

Several statistics, such as the median, standard deviation, minimum and maximum were calculated for all parameters (Table 1). This information was presented in tables and bar graphics. Correlation analysis was used to determine the relationship between trace elements' concentrations in water. The regression coefficient was designated as r. 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 [23]. The PCs are weighted linear combinations of the original variables and provide information on the most meaningful parameters, describing the whole data set through data reduction with a minimum loss of original information [60].

Data processing was performed using SPSS 17.00 and INFOSTAT statistical programs.

3. Result and discussion

3.1. Water characteristics and guideline values

3.1.1. Trace elements

The Ag, As, Be, Co, Cd, Cs, Ga, Se, Ti and U concentrations were below detection limit in all sampling sites.

The Al, Ba, Cr, Cu, Fe, Sr, Pb, Mn, Ni, V and Zn concentrations in all sampling sites are shown in Table 2. The mean levels of Al, Ba, Cr, Cu, Pb, Ni and Zn were below the recommended maximum levels established by AFC [1] (Al = 200, Ba = 1000, Cr = 50, Cu = 1000, Pb = 50, Ni = 25, Zn = 5000 μg L^{-1}). Furthermore, Al, Ba, Cr, Cu, Pb, Ni, and Zn were below the recommended maximum levels established by USEPA [53] (Al = 200, Ba = 2000, Cr = 100, Cu = 1300, Pb = 15, Zn = 5000 μg L^{-1}) and WHO [62] (Ni = 70 μg L^{-1}).

The Fe and Mn concentrations in all sample sites ranged from 19.8 to 1403 and 2.5–144.0, respectively (Table 2). Fe is one of the most

Pb				Mn				Ni				V				Zn			
M	SD	Mi	Ma	M	SD	Mi	Ma	M	SD	Mi	Ma	M	SD	Mi	Ma	M	SD	Mi	Ma
0.3	0.1	0.2	0.4	13.8	3.9	9.4	17.0	1.5	0.8	0.6	2.2	3.8	1.0	3.2	4.9	31.8	36.7	7.5	74.0
3.2	4.4	0.4	9.7	12.5	10.9	2.5	28.0	2.9	1.7	ND	4.8	1.6	0.9	0.5	2.7	14.4	5.6	7.7	21.0
2.6	2.5	0.3	5.0	16.3	4.7	11.0	20.0	2.9	3.3	0.7	7.8	1.8	0.8	1.3	3.0	32.6	31.6	8.3	77.0
2.5	2.9	0.5	6.8	11.0	2.9	8.3	15.0	1.5	0.8	0.6	2.5	1.5	0.9	0.4	2.6	19.5	15.3	7.9	42.0
3.7	4.4	0.6	10.0	13.3	6.9	7.2	23.0	2.0	1.7	0.5	4.1	2.4	0.7	1.8	3.0	23.5	12.4	12.0	39.0
1.9	1.8	0.1	3.8	9.9	3.0	7.2	13.0	2.2	1.4	ND	3.1	1.7	0.2	1.5	1.9	19.9	11.3	6.5	33.0
2.2	2.0	0.1	4.1	8.1	2.4	5.3	11.0	1.3	0.9	ND	2.3	1.4	0.6	0.7	2.1	18.4	12.6	6.4	36.0
4.3	4.9	0.4	11.0	25.0	9.2	18.0	38.0	1.2	0.5	ND	1.6	2.1	1.3	0.3	3.5	20.5	16.3	5.5	41.0
2.1	1.9	0.2	4.0	7.3	1.2	6.2	8.8	1.5	1.1	ND	2.5	1.6	0.5	0.9	2.2	16.4	12.7	6.7	35.0
2.0	1.8	0.3	3.6	17.7	11.0	6.8	33.0	1.5	0.7	ND	2.0	2.1	0.3	1.7	2.4	18.3	12.9	8.1	37.0
1.3	0.9	0.3	2.5	53.8	46.9	24.0	123.0	1.5	1.0	ND	2.4	4.0	2.3	2.2	7.3	20.0	9.8	11.0	33.0
1.3	0.8	0.2	2.1	26.4	14.1	8.4	39.0	1.6	1.6	ND	3.4	1.9	1.3	0.2	3.4	17.9	14.2	4.5	35.0
1.5	1.1	0.3	2.4	29.5	44.4	5.8	96.0	1.3	0.5	0.9	2.0	2.4	2.1	0.7	5.5	16.7	14.5	6.5	38.0
2.4	3.0	0.2	6.8	58.7	74.0	13.0	144.0	2.6	2.7	0.5	6.4	3.0	3.6	0.6	8.3	42.0	31.1	15.0	76.0
2.3	3.0	0.2	6.8	67.7	86.0	17.0	167.0	2.5	2.7	0.4	6.4	3.0	3.4	0.6	8.0	33.6	31.4	5.5	76.0
1.0	0.8	0.4	2.2	10.7	8.9	1.9	23.0	1.2	0.8	0.4	2.2	2.2	0.7	1.3	3.0	15.4	14.8	4.8	37.0
1.3	1.4	0.2	3.4	27.1	22.5	8.2	52.0	1.3	0.9	0.2	2.1	2.8	0.8	2.2	4.0	17.1	10.9	8.2	33.0
1.2	0.9	0.3	2.1	6.3	6.7	1.5	14.0	0.6	0.3	0.2	0.8	1.6	0.2	1.5	1.8	16.9	16.7	4.9	36.0
1.1	1.2	0.1	2.5	11.9	10.1	3.2	23.0	1.1	0.9	0.3	2.1	2.0	0.5	1.5	2.5	29.4	21.0	6.1	47.0
0.8	0.5	0.3	1.5	6.5	4.4	2.3	11.0	1.2	1.1	0.4	2.9	1.6	0.8	0.4	2.1	21.9	16.2	8.7	40.0
0.8	0.4	0.3	1.0	45.9	70.4	1.2	127.0	1.0	1.0	0.2	2.4	2.5	2.8	0.4	6.5	21.0	12.5	11.0	35.0
0.9	0.6	0.1	1.3	7.3	4.9	2.4	14.0	1.7	2.1	0.4	4.9	1.6	0.7	0.7	2.2	18.2	16.7	2.5	35.0
0.9	0.5	0.2	1.5	8.5	4.2	2.8	13.0	1.5	1.3	0.6	3.5	1.4	0.2	1.2	1.7	23.7	13.2	6.8	39.0
1.0	0.6	0.5	1.8	25.6	11.9	9.5	38.0	1.4	0.7	0.6	2.2	1.8	0.8	0.7	2.5	27.3	7.4	17.0	34.0
1.4	1.1	0.2	2.6	14.2	8.2	7.1	25.0	1.3	0.7	0.6	2.2	1.5	0.5	0.8	1.9	23.5	12.3	11.0	36.0
2.1	1.6	0.3	3.6	51.0	28.3	10.0	75.0	1.8	1.6	0.5	4.0	1.5	0.3	1.1	1.9	20.1	10.1	9.4	31.0
1.7	1.6	0.3	3.8	11.6	2.3	10.0	15.0	1.9	0.9	1.0	2.9	1.4	0.7	0.4	2.1	21.1	13.2	7.4	39.0

abundant metals on earth and it is an essential element for the normal physiology of living organisms [64]. Nevertheless, in high concentrations Fe may be toxic [64]. The Fe mean concentration was above the recommended maximum value by AFC, USEPA and WHO (Fe = 300, μg L^{-1}) [1,53,64] in the San Antonio and Paraná Rivers (sites 11 and 15). Additionally, the maximum concentration of Fe exceeded recommended limits on several sites including Ramón, San Antonio; Iguazú 1; Paraná 1 and Paraná 2 (sites 3, 11, 12, 13, 15) (Table 2). The Mn maximum concentration in San Antonio Paraná 2 and Paraná 3 (sites 11, 15 and 21) (Table 2) was above the recommended value proposed by AFC (Mn = 100 μg L^{-1}). However, Mn values were below the recommended limits by USEPA (Mn = 500 μg L^{-1}) [53] and WHO (Mn = 400 μg L^{-1}) [64].

The Al, Fe and Mn are a naturally occurring mineral in surface and groundwater, but human activities contribute much to their introduction into water [51]. High levels of Al, Fe and Mn have been observed in the Argentinean rainforest soil [29,61]. In this sense, the presence of these elements in water cannot be attributed to anthropic sources, but are an effect of runoff.

High concentrations of Pb are found downstream of this research's study area [8,43]. This relates directly to effluents from large cities located on the basin [43]. The As and V level was low compared with other regions of Argentina, as the Pampan Plain, where these elements exceeds 400 μg L^{-1} and 290 μg L^{-1}, respectively [8,45].

The presence of Cr in water in the study area is of natural origin and relates to the basaltic rock type [17]. Frei et al. [17] has reported a Cr range between 0.8 and 2.8 μg L^{-1} in Piray Miní and Iguazú 2 (sites 17 and 14). These values are within those obtained in this study.

The Sr and Ba occurrence is of natural origin from the La Plata Basin. Levels are related to the salinity of the water with more abundance found in fresh water environments [8,9].

The concentration of elements that exceed the guideline values (Fe and Mn) in this study were compared to those reported by other authors in more detail (Table 3). Similar concentrations of Fe, were reported for Paraibuna River (Atlantic Forest, Brazil) [27], La Plata River (Uruguay and Paraná Rivers are the main affluent of the La Plata river) [8] and Chenab River (Pakistan) [36] (Table 3). Fe and Mn levels were relatively low compared to other water bodies such as the Chascomús Lagoon (Argentina) [45] and Bara River (Pakistan) [35]. The Bara River is associated with elevated concentrations of Fe and Mn due to industrial development [35]. High concentrations of Mn were reported in the Chenab River (Pakistan) in comparison with this study [36]. Fe concentrations in this study were much higher than those observed in the Mississippi River [46], although Mn mean levels were generally lower. This shows that the levels of Fe and Mn found in this study are generally lower than those reported for other water bodies contaminated by industrial development.

The inter-metal relationships provided interesting information on metal sources and pathways. The Pearson's correlation coefficient matrix for the elements is given in Table 4. Correlations highly significant were found among Fe–Mn (r = 0.70), Fe–Ba (r = 0.56), Fe–Cu (r = 0.54), Mn–Ba (r = 0.64), Mn–Cu (r = 0.74), V–Cu (r = 0.59), V–Mn (r = 0.58), and Zn–Cu (r = 0.6) (Table 4). In accordance to Pekey et al. [39], correlations between elements as Ba, Cr, Cu, Fe, Pb and Zn could indicate that they have similar anthropogenic sources, mainly represented by the paint industry. It is well known that soils in the study area are rich in Fe and Mn salts [17,29,61]. Therefore, Fe–Mn high correlation may be related to the natural high levels of these elements in the soil [17,29,61]. The correlation between elements such as Ba, Cu, V and Zn and others from natural origin like Fe and Mn might indicate that in the study area, the origin would be related to the soil characteristics. Concordant with our results, there have been relatively high reported concentrations of Ba, Cu, V and Zn in soil samples within the study area. Muhammad et al. [34] discovered a positive correlation between Zn and Mn for Pakistan, but this may be due to an anthropic source related to mining.

3.1.2. Glyphosate

The glyphosate level was below 200 μg L^{-1} in all sites and sampling campaigns excluding the third sampling in San Antonio River (site 11),

Table 3
Concentrations of Fe and Mn in surface water samples (μg L^{-1}) reported for previous studies.

Water body	Country	Fe	Mn	Reference
Chenab River	Pakistan	180	280	Nickson et al. [36]
Bara River	Pakistan	1290–1750	777–850	Nazif et al. [35]
Rio de la Plata River	Argentina	681	25.6	Avigliano et al [8]
Chascomús Lagoon	Argentina	7620	245	Schenone et al. [45]
Mississippi River	USA	9.6	78	Shim et al. [46]
Krishna River	India	157.2	11.9	Arunachalam et al. [7]
Paraibuna River	Brazil	24–790	–	Kuhlmann et al. [27]
Paraná River	Argentina	284	58.7	Present study
San Antonio River	Argentina	314,8	53.8	Present study

where the concentration was 1600 μg L^{-1}. During the third sampling, the San Antonio River was the most affected by heavy rains from Brazil's rain forest. The water level was three times the normal height. This explains the high concentration of glyphosate, which came from the runoff of the crop area from the neighboring country (State of Paraná province, Brazil). Glyphosate peaks in surface water were previously reported by other authors during storms. For example, Armas et al. [6] and Freire et al. [18] reported maximum concentration during storms in Sao Paulo and State of Paraná province (Brazil), respectively. Hanke et al. [21] registered similar results in Switzerland.

The glyphosate concentration in water from the San Antonio River is related to soybean crops. In this river, the Argentine margin is covered by native forest while, in the Brazilian margin, there are extensive soy plantations [18]. In the State of Paraná (Maringá Stream and Pirapó River), glyphosate concentrations up to 2024 μg L^{-1} were reported [18].

Glyphosate is considered to exhibit low toxicity [64]. Under usual conditions, the presence of glyphosate in drinking water does not represent a hazard to human health. For this reason, the WHO considers deemed the establishment of a formal guideline value unnecessary. Instead, considering toxicity studies in rats, the USEPA established a guideline value of 700 μg L^{-1} [53] for drinking water or 0.1 μg Kg^{-1} of body weight (b.w.) per day [58]. The level recommended by ANGHC [3] is 300 μg L^{-1}. According to these guidelines, the concentration found in the third sampling taken from the San Antonio River exceeds recommended limits for drinking water. This value is significant because the local population ingests water directly.

3.1.3. Fecal and total coliform

According to the WHO and USEPA standards for public drinking water, total and fecal coliform cannot be present in 100 ml of water samples (CFU = 0 100 ml^{-1}) [53,64]. In the study, the fecal and total coliform concentrations ranged respectively from 0 to 4300 and 40 to 24,000 CFU 100 ml^{-1} in all samples sites (Fig. 2). In this sense, the mean concentration of fecal coliform was above the recommended maximum levels for drinking water in all sites (Fig. 2). Moreover, the mean fecal coliform was above the recommended levels established by the ANGHC and USEPA (126 CFU 100 ml^{-1}) [4,56] for recreational use in all site. Additionally, maximum values observed for fecal coliform exceeded the recommended limits by WHO [65] for crop irrigation (1000 CFU 100^{-1} ml) in most sites.

Overall, our results exceed the concentration of total and fecal coliform bacteria from other rivers of the world, polluted mainly by domestic waste (Table 5). For example, in some rivers in urban areas of other developing countries, concentrations ranged from 12 to 240 CFU 100 ml^{-1} (Table 5). However, similar results were reported for Paraibuna River associated with the Atlantic Forest in Brazil, with up to 2300 CFU 100 ml^{-1} [27] (Table 5). High concentrations of fecal coliform in the study area most likely relate to the recent population increase (from 290,000 in 2001 to 1,097,829 in 2010; [25]). Most of the small villages located within the rainforest do not have effluent treatment systems. These communities discharge their effluents directly into watercourses or grounds cameras. Consequently, the underground chambers pollute nearby streams and rivers. Moreover, almost all of the rivers studied are in contact with livestock activities, which are mainly in the margins of the rivers and streams. In this sense, agricultural enterprises could provide fecal coliforms to the rivers [31].

In some rivers such as the Pepirí Guazú, Aguaray Guazú and Yabebirí (sites 10, 16 and 24), there was little urban influence and a relatively high concentration of fecal coliform. These may have originated from a combination of agricultural activities, domestic animals and wildlife. In conservancy areas and sections of the catchment area used for pastoralism, large herds of animals graze, and their waste is likely to find its way into rivers, where they contribute to elevated levels of coliforms. High levels of total coliformin in natural forest areas from Tanzania have been previously reported by other authors [32] (Table 5).

3.2. Human health risk assessment

3.2.1. Trace elements

Concentrations of trace elements in water were used to assess human exposure through oral intake. Two population groups were considered: adults and children. Fig. 3 summarizes the HQ and HI index of trace elements through consumption of drinking water in the study area.

In all sites, the mean HQ index values for Al, Ba, Cr, Cu, Fe, Mn, Ni, Pb, Sr, V and Zn for adults ranged from $7.7E^{-04}$ to $2.7E^{-03}$, $1.7E^{-03}$ to $6.1E^{-03}$, $7.4E^{-03}$ to $3.4E^{-02}$, $1.4E^{-03}$ to $5.8E^{-03}$, $1.6E^{-04}$ to $1.7E^{-03}$, $1.6E^{-03}$ to $1.7E^{-02}$, $7.1E^{-03}$ to $3.4E^{-02}$, $2.9E^{-03}$ to $4.2E^{-02}$, $1.2E^{-03}$ to $2.7E^{-03}$, $5.5E^{-03}$ to $1.6E^{-02}$ and $1.7E^{-03}$ to $5.0E^{-03}$. Mean HQ index values for Al, Ba, Cr, Cu, Fe, Mn, Ni, Pb, Sr, V and Zn for children (all sites) ranged from $1.5E^{-03}$ to $5.3E^{-03}$, $1.1E^{-02}$ to $3.1E^{-02}$, $1.4E^{-02}$ to $6.7E^{-02}$, $3.2E^{-03}$ to $3.4E^{-02}$, $3.1E^{-04}$ to $3.3E^{-03}$, $1.4E^{-02}$ to $6.8E^{-02}$, $2.8E^{-02}$ to $1.1E^{-01}$, $3.4E^{-03}$ to $9.8E^{-03}$, $2.4E^{-03}$ to $5.4E^{-03}$, $3.3E^{-03}$ to $1.2E^{-02}$ and $5.8E^{-03}$ to $8.3E^{-02}$, respectively. HQ maximum (adults and children) for sites 1, 11, 12, 13, 16–27 was Cr, for sites 4, 5, 7, 8, 9, 10 and 15 was Pb, for sites 2, 3, 6 and 14 for Ni, respectively.

The mean HI index values for all site ranged from $4.8E^{-02}$ to $1.3E^{-01}$ and $2.5E^{-02}$ to $8.3E^{-02}$ for adults and children, respectively. According

Table 4
Pearson's correlation between difference trace elements for all sampling sites.

	Al	Ba	Cr	Cu	Fe	Mn	Ni	Pb	Sr	V	Zn
Al	1.00										
Ba	−0.15	1.00									
Cr	0.07	0.36	1.00								
Cu	0.27	**0.40***	0.25	1.00							
Fe	0.15	**0.56***	0.19	**0.54***	1.00						
Mn	−0.04	**0.64***	0.19	**0.74***	**0.70***	1.00					
Ni	0.31	0.09	0.45	**0.60***	0.09	0.25	1.00				
Pb	0.32	−0.22	0.10	0.35	0.29	0.10	0.48	1.00			
Sr	0.22	0.17	0.19	−0.03	−0.18	−0.11	−0.15	−0.48	1.00		
V	0.35	0.23	−0.02	**0.59***	0.43	**0.58***	0.07	−0.13	0.40	1.00	
Zn	0.22	0.21	0.06	**0.60***	0.25	0.42	0.42	0.02	−0.01	0.37	1.00

*Significant differences ($p < 0.05$).

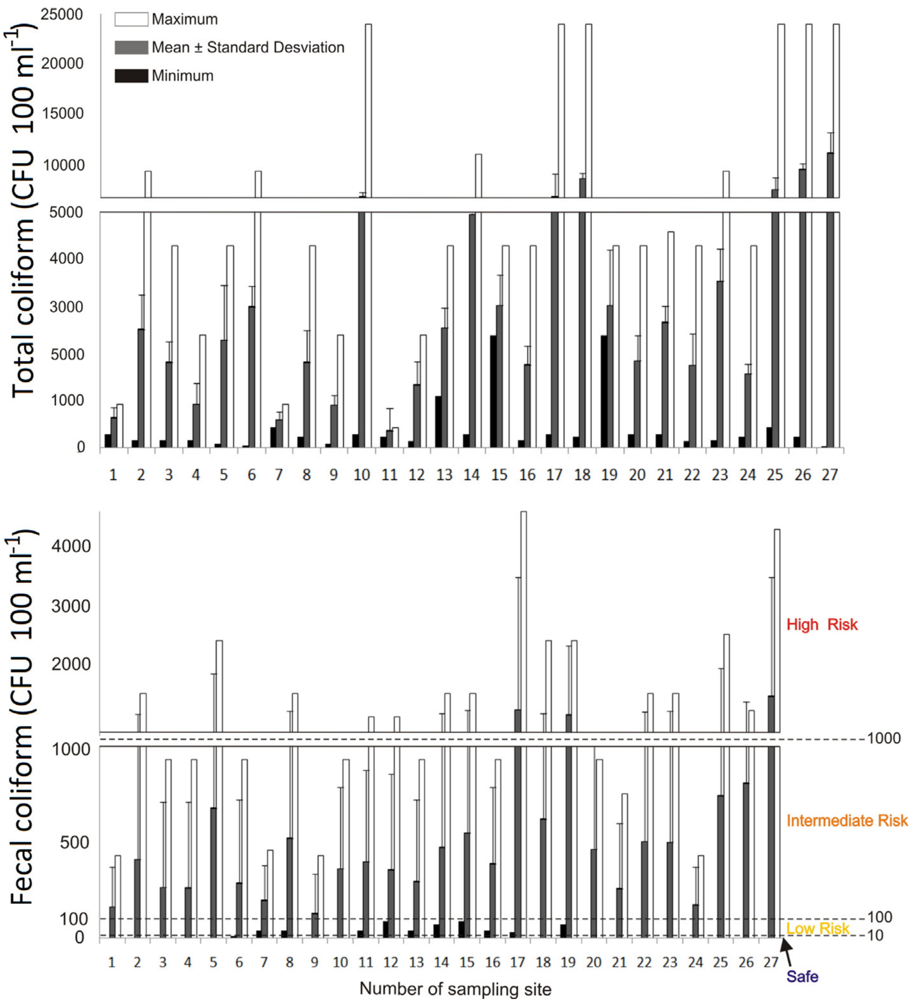

Fig. 2. Mean, standard deviation, minimum and maximum for fecal and total coliforms determined in all sampling sites. The dotted lines indicate the limits of the risk ranges considered.

the HQ and HI indices for all elements and sites suggest no risk to population (HQ, HI <1). However it is important to state that indigenous peoples maybe ingesting higher levels of metals considering that water samples were filtrated before the measurement, therefore metals in the water particles are not included in the analysis. While the majority of the sampled water bodies were characterized by clear water with relatively low turbidity levels (<5 NTU) (Avigliano and Schenone, data unpublished), after storms and rain events turbidity levels increase considerably (>200 NTU) (Avigliano and Schenone, data unpublished). As a consequence suspended solids increase due to the runoff water. This phenomenon could lead to an underestimation of some elements, especially those related to the soil composition such as Fe, Mn and Al when analyzing direct intake values. In this regard, we recommend evaluating in the short term future the effect of runoff on the incorporation of trace elements in the study area and its implications on human health.

3.2.2. Glyphosate

According to the USEPA [58], the lower limit associated with health risk for glyphosate is 100 μg Kg^{-1} of body weight (b.w.) per day. Given these values, a 65 kg person must consume more than 4.04 L day^{-1} of water from San Antonio River to have health problems. Considering that a typical Argentine adult drinks 2.3 L of water daily [13], the glyphosate does not represent a risk to human health. However, taking into account the weight of a 6 year old child (20 kg), the daily consumption of water from the San Antonio River during significant rain events should not exceed 1.25 L rain events in order to prevent risk. Although

Table 5
Concentrations of fecal and total coliforms (CFU 100 ml^{-1}) in surface water samples reported for previous studies.

Water body	Country	Area type	Fecal coliform	Total coliform	Reference
Haraz River	Iran	Urban	110–170	–	Pejman et al. [38]
Jiquirica River	Brazil	Suburban	700	2500	Ponce-Terashima et al. [40]
Gomti river	India	Urban	12	23	Singh et al. [48]
Douala lagoon	Cameroon	Urban	220–240	180–240	Akoachere et al. [2]
Mara River	Tanzania	Forest	<100	147–764	Matano et al. [32]
Paraibuna River	Brazil	Atlantic Rainforest	–	6–23,000	Kuhlmann et al. [27]
Mártires River	Argentina	Urban	0–4300 (mean = 1540)	40–24,000 (mean = 11,113)	Present study
Pepirí Guazú	Argentina	Atlantic Rainforest	0–930 (mean = 364)	290–24,000 (mean = 6789)	Present study

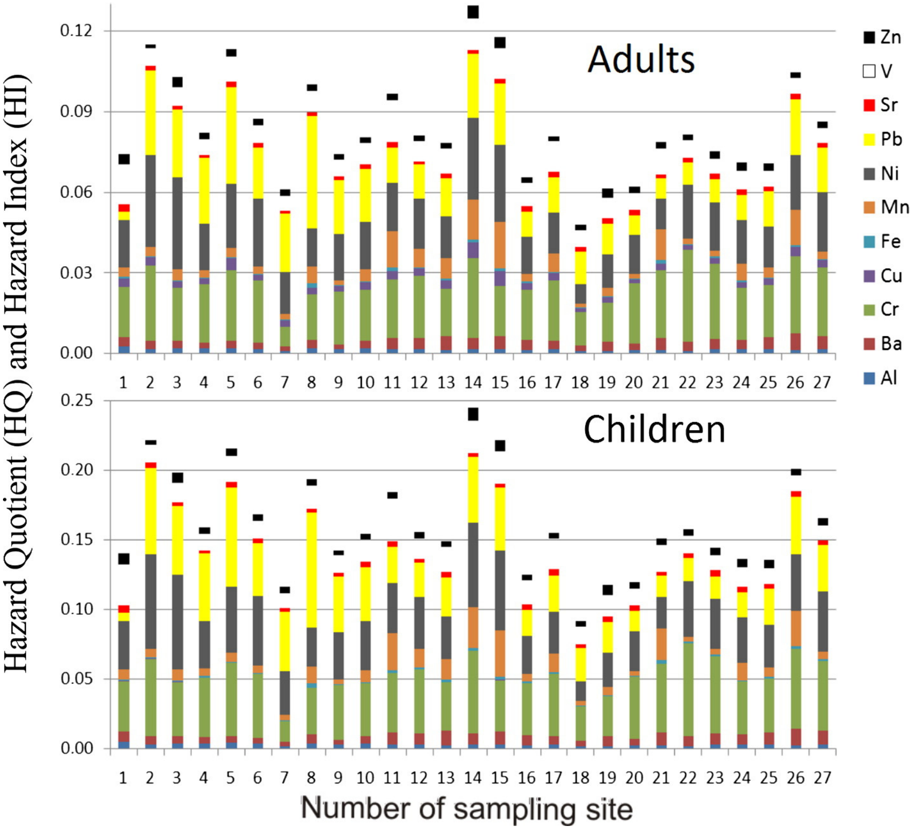

Fig. 3. Hazard Quotient (HQ) and Hazard Index (HI) for adults and children for sampling sites. Whole bars represent the HI and bar fractions (different colors) show HQ index of each element.

a child drinks about 1.4 L day^{-1}, the risk by glyphosate consumption is low because high levels were observed only during infrequent, extreme floods in the San Antonio River. Recently, the International Agency for Research on Cancer (IARC; Lyon, France) assessed the carcinogenicity of glyphosate in humans and concluded that it induces a positive trend in the incidence of a rare tumor (renal tubule carcinoma). For this reason, they classified this substance as probably carcinogenic to humans [20,24]. Hence, it is necessary to monitor the levels of glyphosate in the studio area to ensure the population health.

3.2.3. Coliform

Fecal contamination of drinking water is the major pathway of infection for humans and several studies correlate the concentration of fecal coliform with diarrhea [19]. However, the threshold, above which there is a significant risk of diarrhea, is not yet clear. For example, the current WHO guidelines recommend that drinking water that is safe for human consumption should have no detectable amounts (FCU = 0.100 ml^{-1}). On the other hand, Moe et al. [33] evaluated the effect of contaminated source water on diarrhea in the Philippines and found no evidence of an association between CF and diarrhea at the 1 total coliform (counted as *Escherichia coli*) threshold level. However, significant associations with diarrhea were observed at the 1000 total coliform level. Singh et al. [48] reported similar results in a study developed in India. In this sense, some authors suggest that a tolerant drinking water level (beyond the 1 total coliform threshold) might be acceptable in developing countries, where better quality sources are not accessible [33,48]. Contrary, Gruber et al. [19] found an elevated risk of diarrhea at a total coliform threshold of 1. These results support current WHO guidelines, regardless of location.

In this study, based on the mean concentration of FCs, the Piray Miní, Piranay Guazú and Mártires Rivers (17, 19 and 27) were classified as high risk (CFU 100 ml^{-1} > 1000) (Fig. 2). The other study sites were classified as intermediate risk (100 > CFU 100 ml^{-1} > 1000 ml) (Fig. 2). No study site was classified as low risk or safe. However, according to the observed maximum levels, 15 sites (55.5%) were classified as high risk, while 12 sampling sites were classified as intermediate risk (45.5%) (Fig. 2). According to mean and maximum levels the direct consumption of water from the rivers and streams without any treatment (basic purification treatments) is not recommended as all sites exceed the WHO guidelines.

3.3. Environmental distribution patterns

The values of the four main principal components from the component factor analysis (FA) are given in Table 6. The total variance for the four factors in surface water was 74%. The first factor (F1), explains 29% of total variance and is positively related to the variables Cu, Mn and Fe. This factor represents the natural presence of Fe, Cu and Mn the study

Table 6
Eigenvalues of the factor analysis for trace elements and total and fecal coliform.

	F1	F2	F3	F4
TC	0.003	**0.50**	0.29	0.08
FC	0.20	**0.52**	0.23	0.17
Al	0.16	−0.25	−0.07	**0.51**
V	0.32	−0.07	**−0.48**	0.06
Cr	0.19	0.20	0.17	0.28
Mn	**0.43**	0.09	−0.06	−0.32
Fe	**0.37**	−0.05	−0.02	**−0.35**
Ni	0.29	−0.17	0.34	0.33
Cu	**0.46**	−0.05	0.5	0.08
Zn	0.32	−0.06	−0.06	0.10
Sr	0.002	0.27	**−0.45**	**0.47**
Ba	0.30	**0.41**	0.05	−0.21
Pb	0.14	−0.29	**0.51**	0.05

F = factor analysis. TC, total coliform; and FC, fecal coliform. Values of dominant trace elements in each factor are reported in bold.

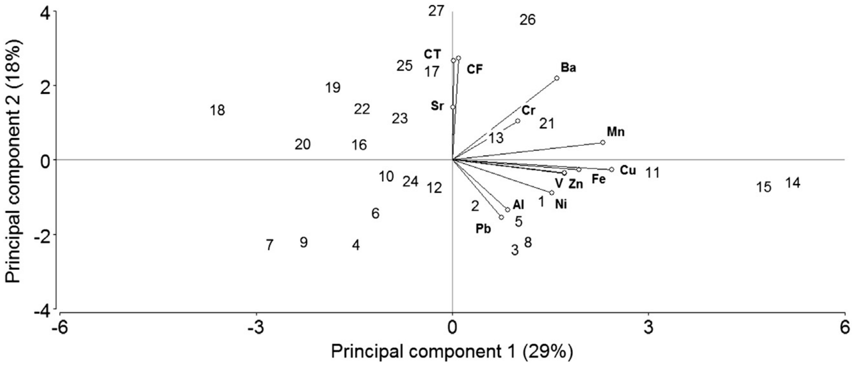

Fig. 4. Scores of river water samples on the bidimensional plane defined by the first two factors (the most representative).

area. Factor 2 (F2), accounts for 18% of the total variance and has strong positive weight for fecal and total coliform and Ba. This factor represents the natural presence of Ba and pollution from domestic waste and sewage. Factor 3 (F3), explains 15% of the total variance and has strong positive weight for Pb, and negative weight for V and Sr. This factor represents the natural mineral contents in the study area and the occurrence of Pb. Factor 4 (F4), explains 12% of the total variance and has strong positive weight for Al and Sr, and negative weight for Fe. This factor also represents the natural mineral contents in the study area. Fig. 4 displays a plot of sample scores on the bi-dimensional plane defined by F1 (mineral contents natural) and F2 (contents natural and anthropogenic contamination). In this plot, an association between the Cu, Mn and Fe and the points 11, 14 and 15 (San Antonio, Iguazú 2 and Paraná 2) was observed, while total and fecal coliform were associated with sites 17, 25, 26 and 27 (Piray Miní, Garupá, Zaiman and Mártires).

These rivers run through the capital city of the province with 323,739 inhabitants (Posadas city) [25]. Along the margins of the rainforest are several settlements with no effluent treatment upstream of the sampling points.

3.4. Management policy recommendations

Taking into account all the data mentioned above along with the behavior of the local population, the recommendations are based on simple strategies for reducing the probability of direct water ingestion from the streams and rivers analyzed, along with an intensification of the monitoring capacity. Results highlight coliform bacteria as the main concern. Consequently, campaigns to raise awareness of this problem should be encouraged. Due to the infrastructure of the vulnerable population, an alternative such as UV is not recommended due to the lack of regular electricity supply. For onsite treatment purpose, boiling or chlorination would be the most cost-effective way to overcome the problem.

4. Conclusions

With a few exceptions (Fe and Mn), the current concentrations of metals in samples of water collected in study area were generally in accordance to the quality standards set by national and international guidelines. The health risk assessments like HQ and HI indices indicated that the drinking water would be safe for human consumption. The statistical analysis provided powerful basis for identification and classification of various sources of trace elements. Glyphosate levels found were above the limits for human consumption except in the San Antonio River during extreme floods. In this case, the glyphosate could present a low risk for children. Here, the concentration of fecal coliform was above the national and international recommended maximum levels established in all sites (Fig. 2). The water from the studied streams and rivers is not recommended for direct human consumption, considering that all sites in average were above the WHO guidelines and the 55% exceed 1000 CFU/100.

It is noteworthy that the approaches employed in this study contain some possible uncertainties. The RfD obtained from USEPA and WHO might not be specific to South America. The average concentration of each metal was applied to evaluate the risk level for local residents in a punctual collection. More efforts are needed in order to obtain more data for each basin and to analyze the direct effect of rainfall and flash floods in the study area.

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