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SPECIAL ISSUE

The environmental impact of Aguilar mine on the heavy metal concentrations of the Yacoraite River, Jujuy Province, NW Argentina

Alicia Kirschbaum · Jesica Murray · Emilce López · Ahinoam Equiza · Marcelo Arnosio · Geraldo Boaventura

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Abstract The Yacoraite River and its tributaries run down the eastern slope of the Aguilar Range. It is one of the tributaries of the Rio Grande, located in Quebrada de Humahuaca, a UNESCO World Heritage site. The Aguilar underground mine (Pb–Ag–Zn) is located in the upper reaches of the Yacoraite River drainage basin. The aim of this work is to characterize the presence of heavy metals in water and sediments of the Yacoraite River and to identify their sources. The analysis shows the seasonal variation of heavy metals concentration in water and their relation with the World Health Organization (WHO) limits established for human consumption. The Yacoraite basin is naturally anomalous in some metals and some elements, such as As which is controlled by the chemical composition of regional lithology. During the wet season, Al, Co, Mo and Pb concentrations in water samples are higher than during the dry season; in addition, these metals are also higher than WHO limit values. High enrichment factors for Ba, Mo, Pb, Zn and Cd were found in Casa Grande stream, indicating the direct influence of the mining activities. Cd, Pb and Zn are present in the Aguilar ore minerals, such as sphalerite and galena. Sediments collected during the dry season show a drastic increase in the concentration of As, Pb, Ba, Zn, Cd and Mn. The Müller geo-accumulation index in Casa Grande indicates that it is a *highly polluted* stream. The concentrations of As, Pb, Ba, Zn, Cd are also high in Yacoraite River: Security Quality Guidelines indicates *toxicity*. A decrease in enrichment factors and geo-accumulation indices observed in sediments indicates the occurrence of precipitation/adsorption processes in the river to restore the equilibrium composition. Strict environmental controls in Aguilar Mine are necessary to avoid the uncontrolled input of toxic metals in Casa Grande stream and Yacoraite River.

Keywords Heavy metals · Yacoraite River · Mining activity · Pollution · Argentina

A. Kirschbaum (✉) · J. Murray · E. López
Museo de Ciencias Naturales, Instituto de Bio y Geociencias del NOA, Universidad Nacional de Salta, Mendoza 2,
4400 Salta, Argentina
e-mail: alikir2003@yahoo.com.ar

J. Murray
e-mail: jesimurray@yahoo.com.ar

E. López
e-mail: emigemy@yahoo.com.ar

A. Kirschbaum · J. Murray · E. López
Consejo Nacional de Investigaciones Científicas y Técnicas,
Instituto de Bio y Geociencias del NOA, Salta, Argentina

A. Equiza
Ingeniería Sin Fronteras, Salta, Argentina
e-mail: ahinoam.equiza@isf.es

M. Arnosio
Universidad Nacional de Salta, Salta, Argentina
e-mail: marnosio@unsa.edu.ar

G. Boaventura
Instituto de Geociencias, Universidad Nacional de Brasilia,
Campus Universitário Darcy Ribeiro, Asa Norte, Brasília,
DE 70910-900, Brazil
e-mail: grbunb@unb.br

Introduction

Studies on the impact of pollution require a thorough knowledge of the natural geochemical background (i.e., baseline data) and information on the behavior of pollutants (Gaillardet et al. 2005). Contamination of freshwater streams and the consumption of high water volumes are the most important environmental problems in the mining activity (Nordstrom and Alpers 1999; Sánchez España et al. 2005; Herbert 2006; Lee et al. 2007; Navarro et al. 2008; Mighanetara et al. 2009). Several Pb–Ag–Zn mines are located in Northwest Argentina; some of them, such as Aguilar and Pirquitas are active, while others such as Concordia and Pan de Azúcar have been abandoned.

The aim of this study is to identify the influence of Aguilar's mining activity on the quality of water and sediments of the Yacoraite River drainage basin to advise a social organization (Red Puna) about the pollution level of the Yacoraite River. Red Puna represents a group of native communities from Northwest Argentina.

The Yacoraite River is one of the tributaries of the Grande River, which flows through Quebrada de Humahuaca, a UNESCO World Heritage site. The Aguilar Mine (Pb, Ag and Zn) has been active since 1936 and is located in the upper Yacoraite River basin. In this paper, heavy metal concentrations in water and sediments of the Yacoraite River and their tributaries are studied. The results provide information on the concentration of a group of heavy metals, determined in a sampling performed in 2009. It shows the seasonal variation of heavy metals concentration in water and their relation with the World Health Organization (WHO) values appropriate for human consumption. Sediment analyses show that Casa Grande Stream, directly influenced by mining activities, is significantly polluted and the comparison with United States Security Quality Guidelines (as Probably Effect Concentration, PEC indicates) show the need for remediation measures.

Study area

The Yacoraite River drainage basin drains the eastern flank of the Aguilar Hills; it is a tributary of the Grande River, located in Jujuy Province, Northwest Argentina. Grande River runs from north to south through the Quebrada de Humahuaca.

Paleozoic and Cenozoic low metamorphic grade rocks of continental and marine origin underlie the Yacoraite River valley. In the Yacoraite River upstream area, a Cretaceous calc-alkaline granite (Aguilar granite) outcrops, which is in part the host rock of the Aguilar mine ore deposit (Turner 1960; Russo and Serraiotto 1979; Geological Chart 2366 – IV, Argentinian Geological Survey).

The Aguilar Mining District is situated at 4,000 m a. s. l. and covers an area of 100 km^2. The most important mine is called The Aguilar (Fig. 1), which has been active since 1936. The exploitation methodology is mainly underground tunneling; Pb, Zn, Ag and Ba are the metals of interest and the ore minerals are primarily sphalerite, argentiferous galena, pyrite, pyrrotite and chalcopyrite. The mineral deposit is considered to be a Sedex complex and the mineralization appears in lenticular veins (Spencer 1950; Sureda 1999).

The climate in the study area is monsoonal, with 8 months of dry season; the annual precipitation fluctuates between 50 and 350 mm during the rainy season (mainly in summer). Near the Aguilar Mine, atmospheric precipitation is around 150 mm/year. The annual average temperature is 8.5–9.5°C with a minimum of some degrees below 0°C; one of the most conspicuous climatic characteristics is the usually high daily thermal fluctuation (Bianchi and Yañez 1992).

Methods

Sampling and analyses

The collection of samples was performed in 11 stations (Fig. 1; Table 1). CG1 and CG2 in the Casa Grande River is the nearest stream that drains water from the mine area. V and L in the Vizcarra and Lagunilla River are important Yacoraite River tributaries, Y1–Y5 in the Yacoraite River and, finally, G1 and G2, upstream and downstream the Yacoraite and Grande River confluence, respectively.

Water samples were collected in 2009 during the humid and dry seasons; sediment samples were collected in the dry season only.

Water samples for heavy metals analyses were filtered in the field with 0.45 μm Millex HV filtration units by using a syringe; the samples were then stored in 15 ml polyethylene centrifuge tubes and acidified to pH <2 with ultrapure concentrated HNO_3. Conductivity, pH, and temperature were determined in the field with multi-parametric Hanna equipment (code HI991300N).

The water samples collected during the rainy season were analyzed by a GmBH Spectro Analytical Instruments Spectroflame-Fvmo3 atomic emission spectrometer with plasma source, using a Meinhard nebulizador, in the Geochemistry Laboratory from Brasilia National University, Geosciences Institute. The samples collected during the dry season were analyzed by ICP-MS in Act-Labs (Canada).

River sediment samples were collected from sediment bars using plastic spoons and stored in plastic bags. At each station, representative sub-samples were taken to yield a composite sample of 2 kg. Sediments were dried at room temperature, and then analyzed by ICP-MS.

Statistical analysis

To identify the influence of mining activity on the concentration of metals in sediments and waters from Yacoraite River by using statistical analysis, sampling stations

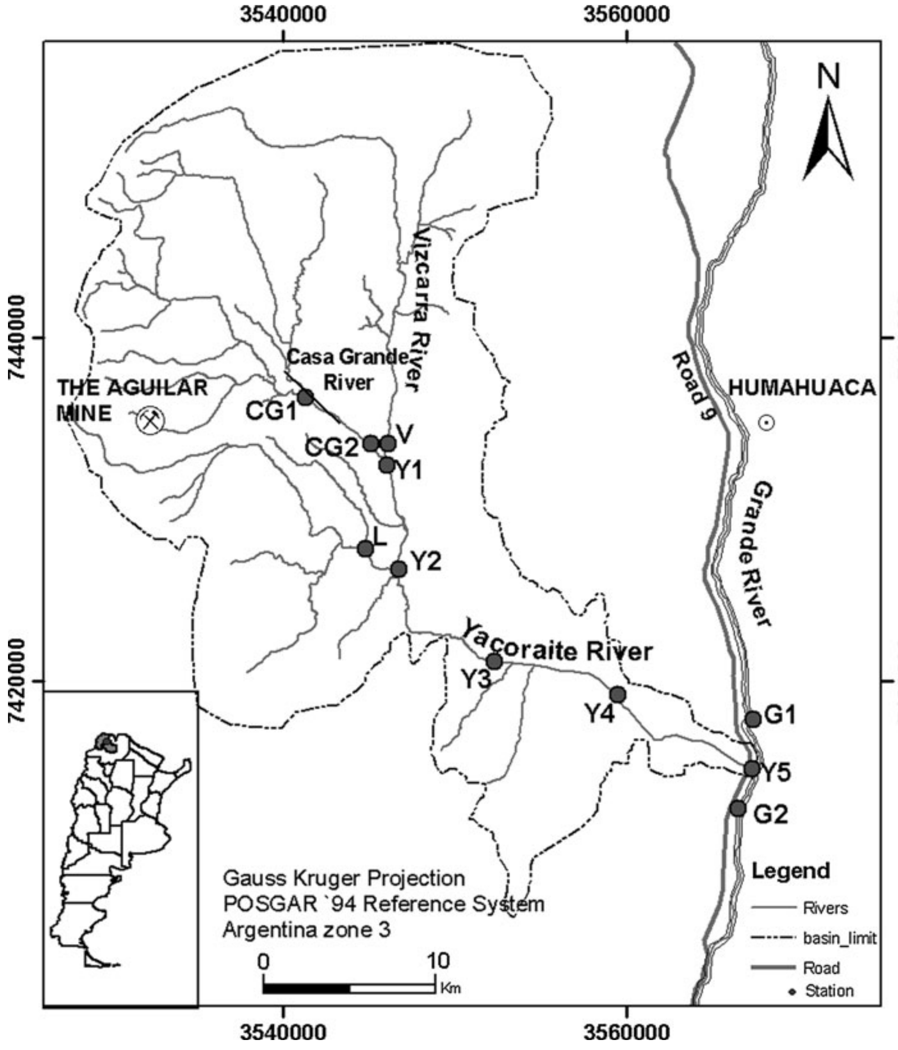

Fig. 1 Yacoraite River basin, sampling stations and Mine Aguilar location

Table 1 Description of sampling stations for water and sediment collection

Designation of stations in Fig. 1	Description
V	Tributary Vizcarra
CG1–sCG2	Tributary Casa Grande
L	Tributary Lagunilla
Y1	Yacoraite River after Vizcarra and Casa Grande confluence
Y2	Yacoraite and Lagunilla confluence
Y3–Y5	Yacoraite down stream
G1–G2	Grande River before and after its confluence with Yacoraite River

were grouped in three different sets: DI—directly influenced by mine drainage, integrated by the samples CG1, CG2 and Y1; these are the samples which are closest to the mine area. MI—moderately influenced by mine drainage: samples Y2, Y3, Y4, Y5 and G2, as they are influenced by mining drainage but are relatively far from the mine, and finally C—the control group, integrated by samples that are not affected by the mine drainage, such as V, L, and G1. Station G1, does not belong to the Yacoraite drainage basin and it was included in the control group.

As is often the case, water samples (dry season data) did not show a normal distribution. Therefore, the non-parametric Kruskal–Wallis test was used to detect significant differences between groups. Pearson and Spearman's Rho correlation coefficients were used to analyze the relation between pairs of variables. This analysis was only applied to water and sediment samples from the dry season (Table 3).

Results and discussion

Water analyses

The concentrations of heavy metals in filtered samples of river water are summarized in Table 2. It includes the

Table 2 Chemical analysis of water samples collected from Yacoraite River basin

Concentration (μg/L)	Station	V	L	CG1	CG2	Y1	Y2	Y3	Y4	Y5	G1	G2	WHO
As	WS	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	10
	DS	30.7	176	4.0	5.8	6.0	54	70.9	70.2	51.1	13.4	18.2	
Al	WS	LD	LD	ND	240	LD	240	ND	270	200	150	160	200
	DS	92	84	42	32	50	56	63	71	82	60	66	
Co	WS	40	60	ND	140	120	180	ND	110	120	80	100	NE
	DS	0.3	0.1	0.3	0.5	0.4	0.2	0.3	0.3	0.2	0.5	0.3	
Mo	WS	30	LD	ND	60	150	80	ND	50	50	30	60	70
	DS	5.9	1.9	8.6	4.2	4.7	3.5	3.6	3.4	3.5	1.7	2	
Pb	WS	210	130	ND	360	260	470	ND	250	350	240	240	10
	DS	3.8	2.3	7.9	2.7	2.2	1.1	1.2	1.0	0.9	1.2	0.9	
Cd	WS	LD	LD	ND	LD	LD	LD	ND	LD	LD	LD	LD	3
	DS	0.1	0.0	0.9	0.3	0.2	0.1	0.12	0.1	0.1	0.1	0.1	
Zn	WS	LD	LD	ND	LD	LD	LD	ND	LD	LD	LD	LD	3,000
	DS	90.1	16	70.8	30.4	41.5	41.6	19.4	27.4	25.6	27	79.6	
Mn	WS	LD	LD	ND	60	20	20	ND	140	30	20	LD	400
	DS	40.8	8.7	109	19.9	15.2	9.9	17.6	9	8.8	76.3	24.2	
Fe	WS	10	30	ND	230	LD	LD	ND	230	LD	50	60	300
	DS	300	120	80	140	170	160	80	100	140	170	160	

WS wet season, *DS* dry season, *ND* not determined, *LD* detection limit of ICP-OES analysis, *WHO* World Health Organization limit values for human consumption, *NE* not established

World Health Organization (WHO) recommended values for human consumption. Water pH measured in different sampling stations was circumneutral (between 6.0 and 7.0) and the electric conductivity measured was between 500 and 800 μS/cm; the mean temperature was 20°C.

Figure 2 shows the variation in metal concentration for water samples from the Yacoraite river basin; the figure also includes the WHO reference levels. In general, the concentration of aluminum (Al), cobalt (Co), molybdenum (Mo), and lead (Pb) are higher in the wet season than in the dry season.

Figure 2 only shows behavior of As for the dry season. The concentration of As in the Lagunilla stream (L) is three times higher than in other stations; this As enrichment is probably due to the chemical composition of the dominant lithology in the Lagunilla upstream reach. All Yacoraite River samples have similar As concentrations. Finally, in Grande River, As concentration increases after the confluence with the Yacoraite River. In the majority of the stations, As levels are higher than the WHO values (Fig. 2).

The Al concentration during the wet season becomes high in stations Y1–Y5 and decrease in G1 and G2 after the Yacoraite and Grande River confluence. During the dry season, stations V and L show the highest values (Fig. 2).

Co shows low concentrations during the dry season. In the rainy season, levels are five orders of magnitude higher and, hence, are higher than the WHO reference values; the tributary samples (V and L) show the lowest values, while CG2 and Yacoraite samples show the highest ones. The G2 sample increases its Co concentration after the Yacoraite confluence (Fig. 2).

Mo has low values for the dry season samples with a small increase in CG1 station. In the wet season the concentration is at least two orders of magnitude higher for all the stations; Y1 shows the highest concentration. The Mo values are lower than the WHO limits except for Y1 and Y2 samples, during the wet season (Fig. 2).

Pb has low concentrations in the dry season samples and is lower than the WHO limits. During the wet season all samples are higher than the WHO levels; lead concentration increases in all the samples, especially in CG2 and Y2 (Fig. 2).

Cd, Zn and manganese (Mn) show similar behavior in the dry and wet seasons; these metals show a peak in CG1 for the dry season. Moreover, the maximum concentration for Mn occurs in station G1, and for Zn in station V. All samples are lower than the limits established by WHO (Fig. 2).

Iron (Fe) contents are lower than the WHO limit in both seasons; in the dry season the Vizcarra tributary (V) has the highest concentration, and CG1 and Y3 the lowest ones. Concentrations in the wet season do not show a clear pattern.

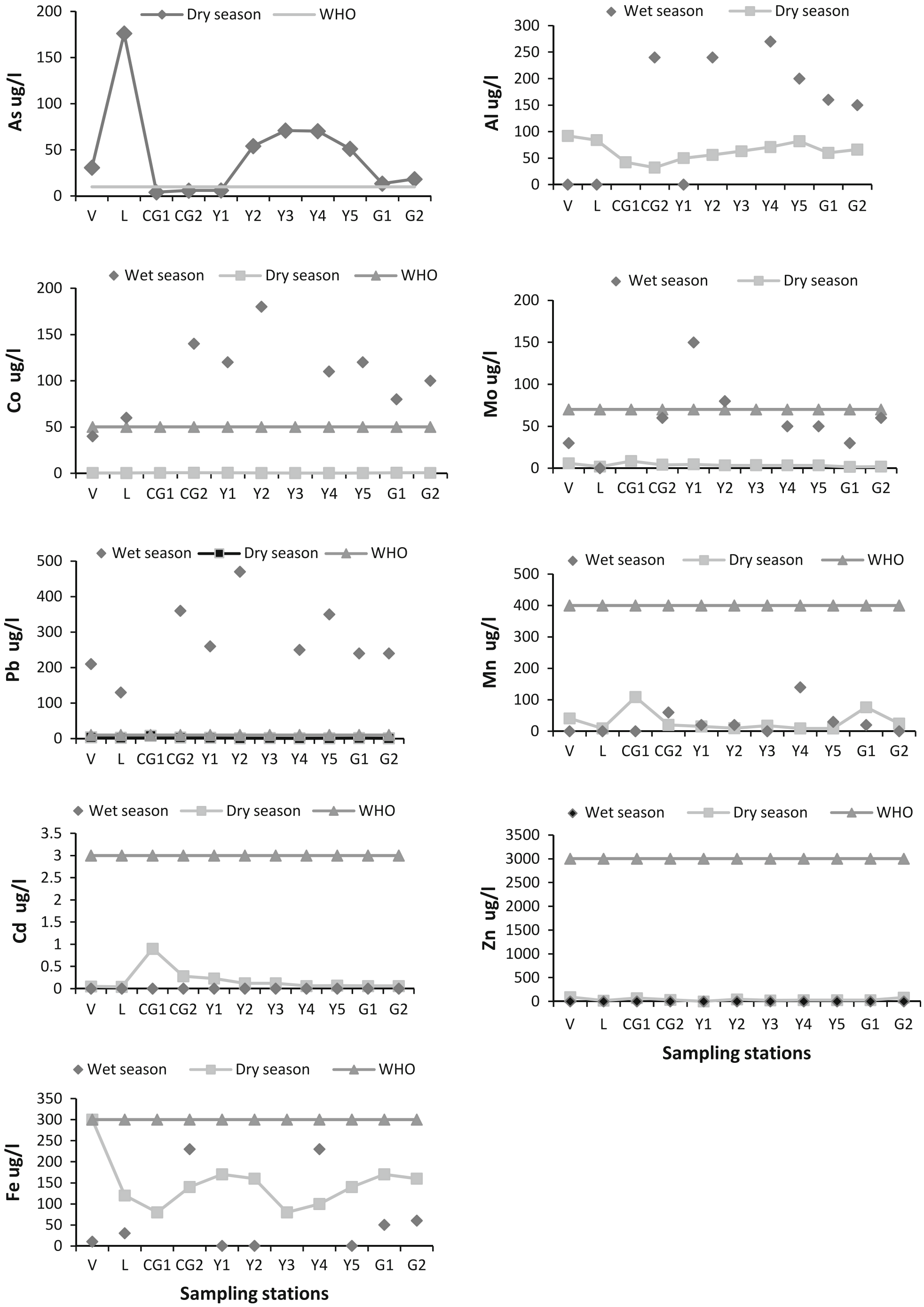

Fig. 2 Concentration of dissolved heavy metals for wet and dry seasons in water samples from the Yacoraite River basin. It also shows the recommended limits for human consumption, according to *WHO* (World Health Organization)

Sediment analyses

High concentrations of As, Ba, Co, Pb, Cd, Zn and Mn are observed in sediments for the station CG1. Then, in the remaining stations, Pb, Zn and Cd decrease; As, Ba and Mn increase in station Y3 and Co in station Y4. Fe does not show a linear pattern, the minimum values are in G1 and G2. The stations G1 and G2 show an important increase in Mn concentration. A high concentration of As is observed in all the samples, especially in CG1, probably due to the chemical composition of the dominant country rocks occurring in the area (Fig. 3).

Heavy metal concentrations in sediments (Table 3; Fig. 3) were compared with United States' Sediment Quality Guidelines (SQG) for metals in freshwater ecosystems, such as Threshold Effect Concentration (TEC) and Probably Effect Concentration (PEC). TECs provide an accurate basis for predicting the absence of sediment toxicity while PECs provide an accurate basis for predicting sediment toxicity. These parameters seek to define the

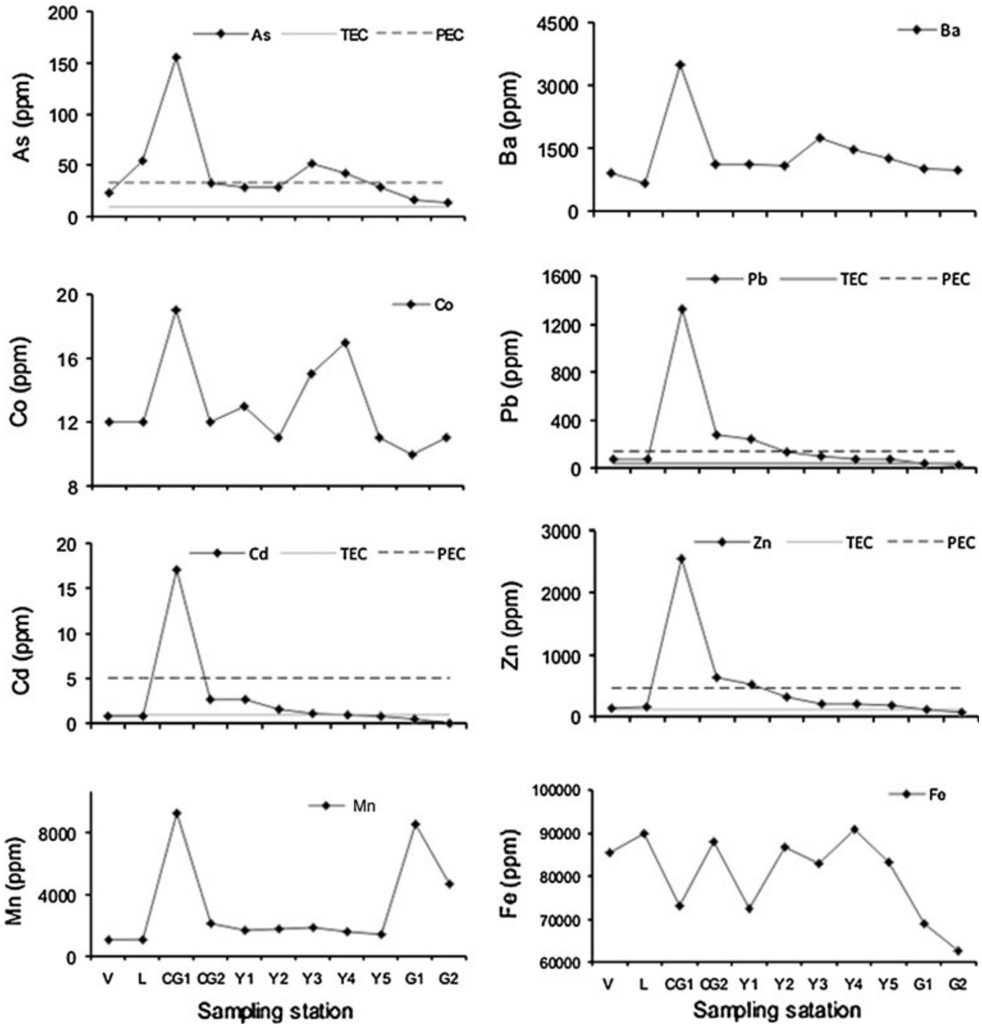

Fig. 3 Concentration of heavy metals in sediment samples for the Yacoraite River basin. *TEC* threshold effect concentration, *PEC* probably effect concentration (MacDonald et al. 2000)

concentrations of sediment-associated contaminants above which adverse effects on sediment-dwelling organisms are likely to be observed. They do not consider the potential for bioaccumulation in aquatic organisms nor the associated hazards to the species that consume aquatic organisms (i.e., wildlife and humans; MacDonald et al. 2000).

TEC and PEC are given for As, Pb, Cd and Zn; these metals show concentrations above PEC in some stations. Pb and Zn are above PEC in CG1, CG2 and Y1 stations. As shows similar or higher values than PEC in almost all the stations, especially in CG1. Cd concentration is also higher than PEC in station CG1.

Enrichment factor (EF)

To evaluate the anthropogenic impact on the Yacoraite River sediments, EF was calculated using Fe as the conservative reference element. Commonly, geochemical normalization of heavy metal data to a conservative element such as Al and Fe is employed to identify anomalous metal concentrations (Zhang et al. 2009). In this case, Fe was used because Al was not analyzed. EF is expressed as follows (Davutluoglu et al. 2011):

$$\mathrm{EF} = (\mathrm{Me/Fe})_{\mathrm{sample}}/(\mathrm{Me/Fe})_{\mathrm{background}}$$

where $(\mathrm{Me/Fe})_{\mathrm{sample}}$ is the metal to Fe ratio in the sample of interest and $(\mathrm{Me/Fe})_{\mathrm{background}}$ is the natural background value used for the metal to Fe ratio in the Earth's crust. The background values utilized were those from Taylor and MacLennan's (1985) average shale: 650 ppm for Ba; 23 ppm for Co; 1 ppm for Mo; 20 ppm for Pb; 85 ppm for Zn; 800 ppm for Mn and 50.500 ppm for Fe. Cd EF values were calculated using the reference value from Taylor (1964): Cd 100 ppm.

EF values between 0.5 and 1.5 suggest that the trace metals may be entirely from crustal materials or natural weathering processes while EF values greater than 1.5 suggest that a significant portion of trace metal is delivered from non-crustal materials (Zhang and Liu 2002, Praveena et al. 2008).

EF values for Yacoraite River basin are in Table 4 and Fig. 4. Values for Vizcarra stream are between 0.3 and 2.1;

Table 3 Chemical analysis of sediment samples collected on dry season from the Yacoraite River basin

Station (ppm)	Detection limit (ppm)	V	L	CG1	CG2	Y1	Y2	Y3	Y4	Y5	G1	G2	TEC	PEC
As	2	23	55	155	32	29	28	52	42	29	13	16	9.79	33
Ba	3	903	671	3,480	1,110	1,130	1,090	1,730	1,450	1,250	968	996	NS	NS
Co	1	12	12	19	12	13	11	15	17	11	11	10	NS	NS
Mo	2	<2	<2	3	<2	<2	<2	<2	<2	<2	<2	<2	NS	NS
Pb	5	67	73	1,330	280	237	127	91	74	71	21	37	35.8	128
Cd	0.5	0.7	0.7	17	2.7	2.6	1.5	1.1	1	0.8	<0.5	0.5	0.99	4.98
Zn	1	145	166	2,560	621	518	311	211	197	173	70	110	121	459
Mn	0.01 (% MnO)	1,084	1,084	9,294	2,091	1,704	1,781	1,859	1,626	1,394	8,519	4,647	NS	NS
Fe	0.01 (% Fe_2O_3)	85,286	89,904	72,902	87,875	72,343	86,615	82,977	90,883	83,117	68,985	62,408	NS	NS

NS not specified, *TEC* threshold effect concentration, *PEC* probable effect concentration (MacDonald et al. 2000)

Table 4 Enrichment factor values calculated for metals in sampling stations

	V	L	CG1	CG2	Y1	Y2	Y3	Y4	Y5	G1	G2
Ba	0.8	0.6	3.7	1.0	1.2	1.0	1.6	1.2	1.2	1.1	1.2
Mo	ND	ND	2.1	ND	ND	ND	ND	ND	ND	ND	ND
Pb	2.0	2.1	46.1	8.0	8.3	3.7	2.8	2.1	2.2	0.8	1.5
Cd	2.1	2.0	58.9	7.8	9.1	4.4	3.3	2.8	2.4	ND	2.0
Zn	1.0	1.1	20.9	4.2	4.3	2.1	1.5	1.3	1.2	0.6	1.0
Co	0.3	0.3	0.6	0.3	0.4	0.3	0.4	0.4	0.3	0.4	0.4
Mn	0.0	0.0	0.4	0.1	0.1	0.1	0.1	0.1	0.0	0.4	0.2

ND not determined

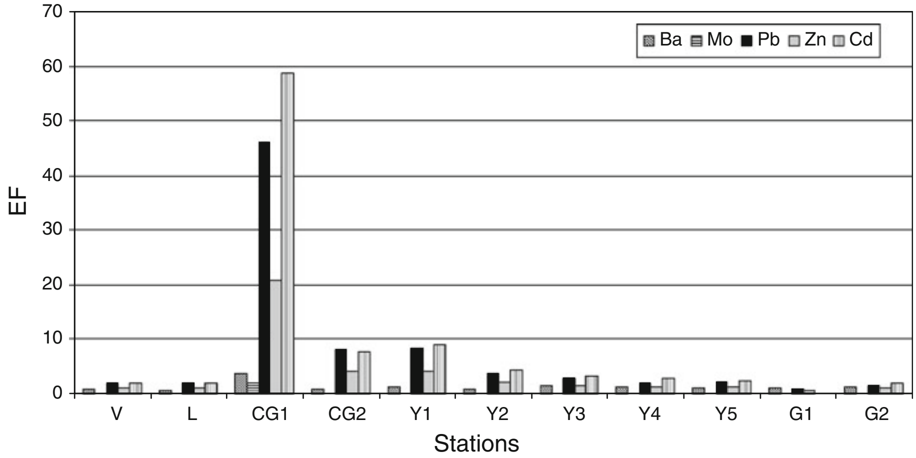

Fig. 4 Variation of Enrichment Factor for metals in sediments of Yacoraite River drainage basin

Table 5 Geo-accumulation Index of Müller (1979) for metal concentration in sediments

	V	L	CG1	CG2	Y1	Y2	Y3	Y4	Y5	G1	G2
Ba	−0.1	−0.5	1.8	0.2	0.2	0.2	0.8	0.6	0.0	0.0	0.0
Co	−1.5	−1.5	−0.9	−1.5	−1.4	−1.6	−1.2	−1.0	−1.6	−1.6	−1.8
Mo	ND	ND	1.0	ND	ND	ND	ND	ND	ND	ND	ND
Pb	1.2	1.3	5.5	3.2	3.0	2.1	1.6	1.3	−0.5	−0.5	0.3
Zn	0.2	0.4	4.3	2.3	2.0	1.3	0.7	0.6	−0.9	−0.9	−0.2
Mn	−0.1	−0.1	3.0	0.8	0.5	0.6	0.6	0.4	−0.87	2.8	2.0
Fe	0.2	0.2	−0.1	0.2	−0.1	0.2	0.1	0.3	3.8	−0.1	−0.3

ND not determined

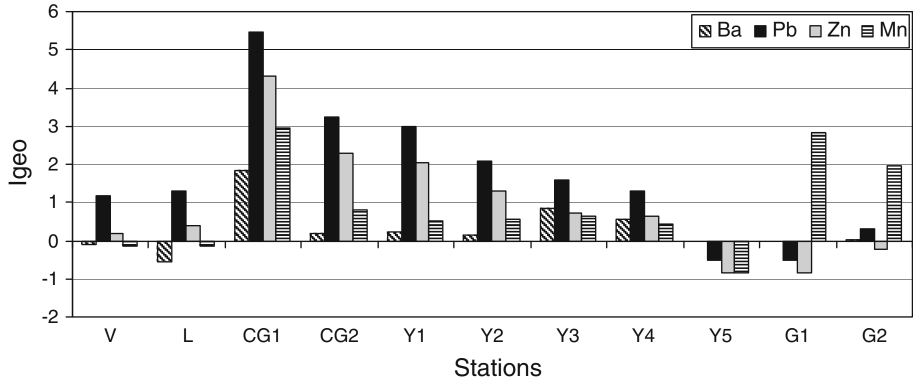

Fig. 5 Variation of geo-accumulation index for metals in sediments of Yacoraite River basin

these are slightly higher than the EF established by Zhang and Liu (2002) as natural background weathering. Vizcarra stream is not influenced by mining activity, but high enrichment factors are related to a regional metal anomaly. In this sense, trace metals in station Vizcarra are interpreted as originating in crustal material sources, while trace metals in stations CG1, CG2, Y1, Y3, Y3, Y4 and Y5 are related to the influence of Aguilar mine as an anthropogenic source.

The highest EF levels for Ba, Mo, Pb, Zn and Cd are found in CG1 indicating the influence of the mining activities in Casa Grande stream. Metals, such as Cd, Pb and Zn, occur in ore minerals in Aguilar Mine such as sphalerite and galene (Sureda 1999).

G1 and G2 stations belong to the Rio Grande basin and their EF values are ≤ 1.5; the trace metals concentrations are considered to be supplied by crustal materials (Fig. 4).

Geo-accumulation index (I_{geo})

Another commonly used method to evaluate the heavy metal pollution in sediments is the geo-accumulation index (I_{geo}) introduced by Müller (1979). I_{geo} is expressed as follows:

Table 6 I_{geo} guide level values for pollution intensity determination (Müller 1979) and I_{geo} values for unpolluted sediments according to the local background

I_{geo} (Müller 1979)	I_{geo} (this paper)	Pollution intensity
≤0		Background concentration
0–1	0–1.2	Unpolluted
1–2	1.2–2	Moderately to unpolluted
2–3		Moderately polluted
3–4		Moderately to highly polluted
4–5		Highly polluted
>5		Very highly polluted

Table 7 Kruskal–Wallis statistic test results

Parameter	Statistic	*P* value
Al	6.59394	**0.0369951**
Cd	8.23566	**0.0162798**
Co	3.92727	0.140347
Mo	4.2618	0.118731
Pb	7.63636	**0.0219677**
Zn	0.678788	0.712202
Mn	1.7697	0.412777
Fe	1.83642	0.399233

In bold are the parameters with significant statistic differences

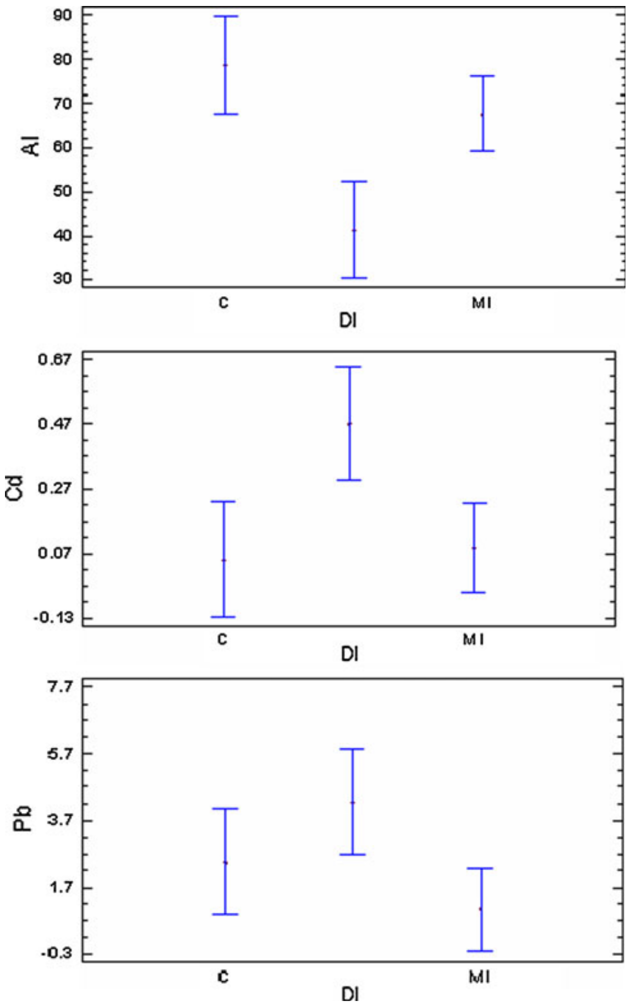

Fig. 6 Kruskal-Wallis graph *C* control group, *DI* directly influenced by mining activity group, *MI* moderately influenced group. Mean and Fisher's least significant difference 95.0%

$$I_{geo} = \log(2)\, C_n / 1.5\, B_n$$

where C_n = measured concentration of the metal (n) in the sediment sample, B_n = geochemical background value concentration of the metal (n). Factor 1.5 is the background matrix correction due to lithogenic effects. The calculated values for the Yacoraite fluvial sediments are given in Table 5; the background values used in this paper were those from the average shale by Taylor and McLennan (1985). The Vizcarra tributary (station V) is not influenced by the mining activity; it shows $I_{geo} \leq 1.2$. In this paper, this value is considered as the local I_{geo} guide level that indicates unpolluted sediment samples.

The I_{geo} of Müller for the Yacoraite drainage basin sediments indicates that station V is unpolluted; station L is moderately polluted to unpolluted; CG1 is very highly polluted; CG2 is moderately to highly polluted; Y1 and Y2 are moderately polluted; Y3 and Y4 moderately to unpolluted; Y5 has the background concentration in metals. Finally, G1 and G2 are moderately polluted; nevertheless, a study of the heavy metal concentrations in Grande River and its tributaries is necessary to determinate if the Mn anomaly is due to anthropogenic pollution or is the natural background.

An important decrease in EF and the I_{geo} index is observed in the 20 km that span from CG1 to Y5 stations (Figs. 4, 5), indicating precipitation/adsorption processes in the river to recuperate the equilibrium geochemical composition.

According to the I_{geo} Index, CG1 is the most polluted sample. This station also has high enrichment factors of 58 for Cd, 46 for Pb, 20 for Zn, 3.7 for Ba and 2.1 for Mo. Moreover, the concentrations of As, Ba, Co, Pb, Cd, Zn and Mn are above PEC Security Quality Guidelines. PEC coefficient indicates that CG1 sediments are toxic to sediment-dwelling organisms (MacDonald et al. 2000).

Statistical analysis

The Kruskal–Wallis test was applied to water samples collected during the dry season to corroborate the proposed grouping of samples in DI, directly influenced; C, control; MI, moderately influenced is statistically significant. As a result, differences for Al, Cd and Pb between the medians

Table 8 Pearson correlation coefficients

	Log Al	Log Cd	Log CE	Log Co	Log Fe	Log Mn	Log Mo	Log Pb	Log Zn
Log Al		**−0.8294**	0.2600	**−0.6305**	0.3003	−0.3103	−0.3417	−0.3639	−0.0889
		0.0016	0.4401	**0.0375**	0.3695	0.3530	0.3037	0.2713	0.7950
Log Cd	**−0.8294**		−0.3192	0.4298	−0.4230	0.4223	**0.7123**	**0.6190**	0.2667
	0.0016		0.3387	0.1870	0.1949	0.1957	**0.0139**	**0.0423**	0.4279
Log CE	0.2600	−0.3192		0.4669	0.4492	0.3920	−0.2263	−0.3676	0.4898
	0.4401	0.3387		0.1477	0.1658	0.2332	0.5034	0.2661	0.1262
Log Co	**−0.6305**	0.4298	0.4669		0.2252	**0.6150**	0.1737	0.1587	0.3687
	0.0375	0.1870	0.1477		0.5055	**0.0440**	0.6096	0.6411	0.2644
Log Fe	0.3003	−0.4230	0.4492	0.2252		0.0618	−0.0933	−0.0223	0.4487
	0.3695	0.1949	0.1658	0.5055		0.8568	0.7849	0.9481	0.1662
Log Mn	−0.3103	0.4223	0.3920	**0.6150**	0.0618		0.2929	0.5932	0.5265
	0.3530	0.1957	0.2332	**0.0440**	0.8568		0.3821	0.0544	0.0962
Log Mo	−0.3417	**0.7123**	−0.2263	0.1737	−0.0933	0.2929		**0.6860**	0.4772
	0.3037	**0.0139**	0.5034	0.6096	0.7849	0.3821		**0.0198**	0.1378
Log Pb	−0.3639	**0.6190**	−0.3676	0.1587	−0.0223	0.5932	**0.6860**		0.4068
	0.2713	**0.0423**	0.2661	0.6411	0.9481	0.0544	**0.0198**		0.2143
Log Zn	−0.0889	0.2667	0.4898	0.3687	0.4487	0.5265	0.4772	0.4068	
	0.7950	0.4279	0.1262	0.2644	0.1662	0.0962	0.1378	0.2143	

Values in bold indicates significant correlation. For each parameter, the value in the upper file is the correlation coefficient and the value in the lower file evidence the statistical significance of the correlations

Table 9 Pearson correlation coefficients

	Log Pb (w)	Log Pb (s)	Log Cd (s)	Log Cd (w)	Log Mn (s)	Log Mn (w)
Log Pb (w)		0.7254 (correlation)				
		0.0115 (*P* value)				
Log Pb (s)	0.7254					
	0.0115					
Log Cd (s)				0.8776		
				0.0055		
Log Cd (w)			0.8776			
			0.0055			
Log Mn (s)						0.7863
						0.0041
Log Mn (w)					0.7863	
					0.0041	

$n = 11$, *s* sediment sample, *w* water sample

with a 95.0% of confidence were detected (Table 7; Fig. 6). The remaining parameters do not present statistically significant differences between groups (Table 6).

The differences for Pb and Cd between the group DI and the groups C and MI are attributed to the influence of mining in the first group. The superposition of the concentrations of Pb in the ID and C groups occur because the Pb concentration in the Lagunilla stream (station L) belongs to group C.

In the results of Pearson correlation analysis (correlation coefficient and probability) for dry season's water samples (Table 8), Cd, Mo and Pb show positive correlation, thus suggesting a common source. The same is observed between Co and Mn. In contrast, negative correlations are observed between Cd and Al, and Co and Al. These opposing dynamics are surely controlled by changing pH (i.e., increasing or decreasing), as the solubility, dependence of Al on pH is well known.

Water samples of CG1, CG2 and Y1 stations were grouped as directly influenced by mining activities. Pb and Cd correlation was statistically significant, identifying this group of samples as influenced by mining. In water samples in dry season, Cd, Mo and Pb; Co and Mn have positive correlation, whereas Cd, Al and Co have negative correlation. Dry season sediment and water samples have positive correlation between Pb, Cd and Mn (Table 9).

Conclusions

The Yacoraite River basin is naturally anomalous in metal concentrations due to the geochemical composition of a mineralized area. The composition of the Vizcarra stream allows to establish that it is not directly influenced by mining; the metal concentration of this stream is considered as a local background.

Nevertheless, the highest enrichment factors for Ba, Mo, Pb, Zn and Cd found in CG1 station indicate the influence of the Aguilar Mine in Casa Grande stream and then, in the Yacoraite River. The highest anomalies found in Cd, Pb and Zn are basically determined by the ore minerals in Aguilar Mine such as sphalerite and galene. The I_{geo} for the CG1 station indicates that it is very highly polluted; Y1 and Y2 are moderately polluted; Y3 and Y4 are moderately polluted to unpolluted; and Y5 has the geochemical background concentration.

High level of As is observed in water and sediments from the main tributaries, especially in Lagunilla stream. The As concentration is higher than the WHO and TEC guideline levels in all the water and sediments samples of the Yacoraite drainage basin; these values are representative of regional geochemical background.

Water data indicate that the concentrations of Al, Co, Mo and Pb are higher in the wet season than in the dry season; moreover, the values are higher than the WHO limits. Zn, Cd, Mn and Fe concentrations in both seasons are relatively low and their concentrations are lower than WHO reference limits.

Pearson correlation analysis for the dry season water samples shows positive correlation for Cd, Mo and Pb; the same is observed between Co and Mn. Negative correlation is observed between Cd, Al and Co. Pb and Cd correlation was statistically significant, allowing the identification of this group of samples as being influenced by mining activity. In the water samples collected during the dry season Cd–Mo–Pb and Co–Mn have positive correlation, whereas Cd–Al–Co has negative correlation. Dry season sediments and water samples exhibit positive correlations between Pb–Cd–Mn.

The decrease of EF and I_{geo} indexes in sediments from CG1 to Y5 stations indicates precipitation/adsorption processes in the river to restore the equilibrium composition. The concentration of As, Pb, Ba, Zn, Cd above PEC Security Quality Guidelines in Casa Grande stream and Yacoraite River sediments indicate toxicity to sediment-dwelling organisms.

Strict environmental controls in Aguilar Mine are mandatory to avoid the undesirable input of metals and the subsequent negative impact on Casa Grande stream and Yacoraite River.

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