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RESEARCH ARTICLE

Assessment of trace element pollution and ecological risks in a river basin impacted by mining in Colombia

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Abstract

Trace element pollution in rivers by anthropogenic activities is an increasing problem worldwide. In this study, the contamination and ecological risk by several trace elements were evaluated along a 100-km stretch of the San Jorge River in Colombia, impacted by different mining activities. The increase of average concentration levels and range of trace elements in sediments (in μg/g) was as follows: Cu 6656 (454–69,702) > Cd 1159 (0.061–16,227) > Zn 1064 (102–13,483) > Ni 105 (31–686) > Pb 7.2 (5.1–11.7) > As 1.8 (1.0–3.2) > Hg 0.31 (0.12–1.37). Results showed that surface sediments could be classified as very high ecological risk index (RI > 600), associated with high contamination of Hg, Cd, and Cu, in stations close mining activities. Values for pollution load index indicate an environmental deterioration (PLI > 1), and sediment quality guidelines (SQGs) suggested that Cu, Ni, Zn, and Hg caused adverse biological effects. We further used pollution indices such as contamination factor (CF), enrichment factor (EF), and geoaccumulation index (Igeo) to assess the extent of contamination. According to these indices, discharges of hazardous chemicals over many years have resulted in a high degree of pollution for Cu, Pb, and Cd, with critical values in stations receiving wastes from mining activities. Multivariate statistical analysis suggested that Hg, Cd, Cu, and Zn derived from gold and coal mining, Ni and As were related from the mining of ferronickel and coal, respectively, whereas the high Pb load was attributed to diffuse source of pollution. In sum, our study provided the first detailed database on metal concentration and ecological risks to organisms in sediments of the San Jorge River Basin, and the current results also suggested future research for public health action.

Keywords Metal · Sediment quality · Ecological risk assessment · Pollution load index

Introduction

Colombia is one of the countries with the highest ferronickel production in the world, the largest natural reserves of coal in Latin America, and the sixth largest producer of gold worldwide (Ingeominas 2004). This may suggest that some areas could be potentially impacted by trace elements from anthropogenic origin. In this sense, the most important mining basin of Colombia is found in the San Jorge River Basin, where coal and ferronickel are exploited by mining companies with large infrastructures, and gold by artisanal and small-scale mining. The effluents (i.e., mine tailings) generated in these activities are being discharged into the aquatic ecosystems, sometimes without any treatment, which converges in the San Jorge River Basin and potentially contaminating different environmental matrices (Marrugo and Lans 2006). Metal pollution assessment in fluvial sediments and the orientation of their potential sources is of great importance to propose effective strategies to protect watershed ecosystems. Sediments usually provide useful information about environmental pollution (Uluturhan et al. 2011; Tamim et al. 2016) because they are the main reservoir of trace elements from the water column (Tam and Wong 2000). Different studies in the San Jorge River Basin have reported higher metal pollution levels than

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international standards, such as Hg levels in carnivorous fish and hair (Marrugo et al. 2007; Gracia et al. 2010), and DNA damage by metals in inhabitants of the region (Madrid et al. 2011). Likewise, atmospheric deposition of metals in this area has been reported (Marrugo-Negrete et al. 2014). Despite these scarce findings, contamination indexes and the ecological risk in the aquatic ecosystem associated with trace elements pollution has never been studied in this impacted mining area.

The main objectives of this work were to evaluate the contamination degree and spatial distribution of trace elements in the surficial sediments of the San Jorge River middle basin in the department of Córdoba, Colombia. To this end, several pollution indices, (i.e., enrichment factor, contamination factor, and geoaccumulation index) were calculated to evaluate the pollution levels of trace elements. In addition, we assessed the potential ecological risk in the surrounding areas using sediment quality guidelines (SQGs) and statistical approaches to identify potential sources of anthropogenic contamination.

Materials and methods

Study area

The San Jorge River Basin includes areas of the Colombian departments of Antioquia, Córdoba, Sucre, and Bolívar. This basin is part of the Momposina depression, which is a sedimentary hydrographic basin mainly constituted by unconsolidated sediments, originating from fluvial and fluvial-lacustrine environments associated with large permanent water bodies and overflow sediments on a large floodplain. This study in the San Jorge River Basin was performed in sampling sites (S1 to S14) located in the department of Córdoba (Fig. 1). The study area can be divided into two zones: San Jorge upper basin, and the San Jorge middle basin. The first corresponds to the mountainous slope located in the south of the department, between Serranía de San Jerónimo and Serranía de Ayapel. The San Jorge middle basin is a relatively flat area that coincides in large part with the alluvial valley of the San Jorge River extending from the mouth of the San Pedro River to Bocas de Sehebe close to the department of Sucre. The river flow in a south-northeast direction from the Paramillo node to its mouth at the Loba branch of the Magdalena River in the department of Bolívar. It has a length of 368 km of which two-thirds run through the department of Córdoba, where their most important tributaries are the San Pedro River and the Uré stream (see Fig. 1). The basin is affected by frequent overflows in times of high rainfalls (CVS 2005). Coal, ferronickel, and auriferous mining are the main economic activity that takes place in the basin. The open coal deposits exploited in the basin are located between the San Pedro and San Jorge rivers near the Puerto Libertador municipality. The extraction of ferronickel is located close to the Montelíbano municipality in the middle part of the sub-basin of the Uré stream. The auriferous holdings in the basin date from the time of the colony are established in the Uré stream (artisanal mining, especially alluvial mining) middle and upper part, and in the San Pedro River (quartz reef mining) upper part (higher production) using the amalgamation process with Hg for the recovery of the precious metal. Furthermore, there was a gold exploitation around Ayapel marsh between 1980 and 1992 (Ingeominas 2005; UPME-MME-UC 2014a).

Sediments sampling and chemical analysis

Sampling was conducted at 14 sampling stations along San Jorge River Basin (Fig. 1) during June 2018, covering both the rainy and dry seasons. At each station, four subsamples were collected at all cardinal points, within a radius of 3 m from a reference point, and a representative composite sample per station was generated by mixing the samples. Sediment samples were taken in the first 5 cm of surface layer with a Van Veen dredge launched from a boat, and only the central part of the sediment sample was collected, to avoid sample adulteration with the walls of the dredge. Samples were placed in plastic bags, labeled, packed in ice, transported to the laboratory, homogenized and sieved (60 μm), and dried in an oven at 40 °C for 48 h (Canário et al. 2007).

The analytical method used to determine the total Hg concentration in the sediments (30 mg dw) was based on thermal decomposition detected by atomic absorption spectrometry using a direct mercury analyzer (DMA-80, Milestone Srl, Italy) (USEPA 2007a). For As, Cu, Zn, Ni, Cd, and Pb analysis, the sediments samples (0.5 g) were digested with HNO_3/HCl 8:2 *v*/v in a microwave oven (in triplicate) using Method 3051 A (USEPA 2007b). Analyses were performed using a spectrometer Thermo Elemental Solaar S4 coupled hydride generation (As), flame (Cu, Zn, Ni), and graphite furnace (Cd, Pb). The method for trace element estimation was validated with the certified reference material IAEA 405. The percentage of recovery average for trace elements was 96.8% ($n = 3$). The concentration baseline or background values for trace elements was taken at 40 cm depth from station S14 (Table 1).

Assessment of pollution and ecological risk

The degree of contamination was calculated using geochemical indices such as the index of geoaccumulation (Igeo), enrichment factor (EF), contamination factor (CF), sediment quality guidelines (SQG), Mean ERM Quotient (M-ERM-Q), potential ecological risk factor (E_r^i), potential ecological risk index (RI), and pollution load index (PLI) as previously described elsewhere (Islam et al. 2017). Description for the

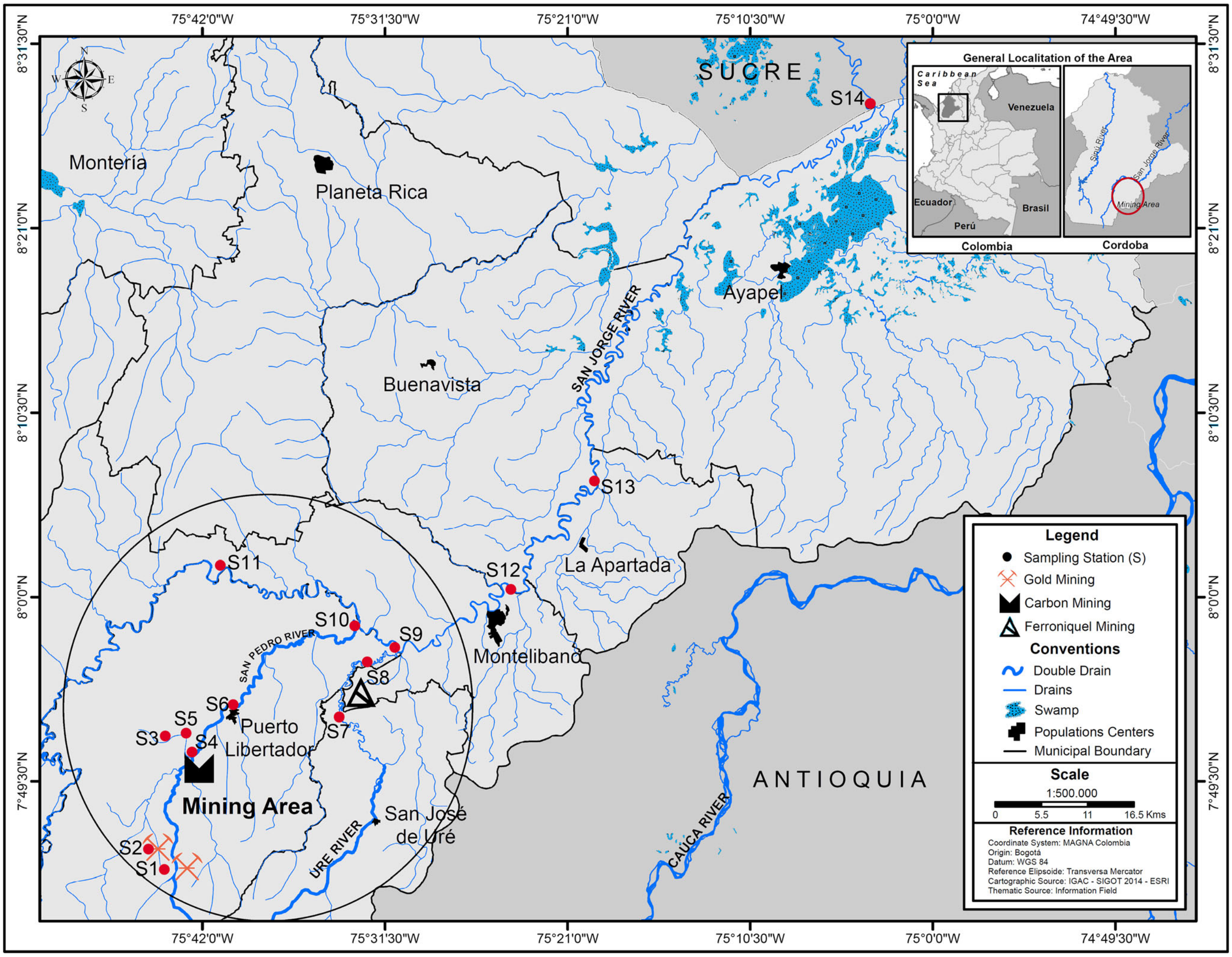

Fig. 1 Location of sampling sites in the San Jorge River basin. Sampling stations: S1. El Alacrán goldmine (Valdez stream); S2. Valdez stream; S3. Guacamaya stream before coal mining; S4. before Puerto Libertador municipality; S5. Guacamaya after coal mining; S6. after Puerto Libertador municipality; S7. Uré stream before ferronickel mining; S8. Uré stream after ferronickel mining; S9. San Jorge River - Bocas de Uré; S10. San Jorge river - Torno rojo; S11. San Jorge river – *Pica pica*; S12. San Jorge River after Montelibano municipality; S13. San Jorge River after La Apartada municipality; S14. San Jorge River - Bocas Sehebe

contamination factor, enrichment factor and geoaccumulation index and the categories of Er and RI could be found in Supplementary Table S1.

Statistical analysis

The results for each sample were expressed as the mean and standard deviation of triplicate set of data in dry weight (dw). Principal component analysis (PCA) was employed with the aim of identifying associations and common origin among trace elements. The PCA was used with Varimax rotation to minimize the number of variables with a high loading on each component. The results from the PCA were interpreted according to the hypothetical sources of chemical elements. Statistical analysis was performed with SPSS v26.0.0.0.

Results and discussion

Concentrations of trace elements

The concentrations of trace elements in sediments are shown in Table 1. Mean concentrations in sediments followed the order: Cu > Cd > Zn > Ni > Pb > As > Hg. The highest concentrations of Hg and Cu were presented at stations S1 and S2, highly impacted by gold mining (Fig. 1). Discharges without any treatment in these aquatic ecosystems containing Hg and Cu has been reported (e.g., mining area of Alacrán) (UPME-MME-UC 2014a, 2016). Despite station S13 that was far away from the gold mining area, the relatively high Hg is probably due to the downstream transport of Hg from small-scale mining that takes place upstream in the middle basin and discharge from the San Jorge River (UPME-MME-UC 2014b, 2016). The highest Ni concentrations are shown

Table 1 Metal concentrations (µg/g) in surface sediments the sampling sites

Station	Hg	Cd	Ni	Pb	As	Cu	Zn
S1	1.374 ± 0.213	16,227 ± 143	34.1 ± 1.1	8.1 ± 2.1	1.4 ± 0.3	69,702 ± 543	13,483 ± 323
S2	0.801 ± 0.124	0.076 ± 0.010	31.1 ± 3.8	6.2 ± 1.0	1.1 ± 0.3	15,248 ± 356	102 ± 75
S3	0.138 ± 0.092	0.076 ± 0.023	44.2 ± 2.9	7.3 ± 1.2	1.3 ± 0.4	749 ± 24	107 ± 33
S4	0.216 ± 0.091	0.091 ± 0.018	33.8 ± 1.5	5.7 ± 1.1	1.0 ± 0.2	829 ± 77	105 ± 34
S5	0.201 ± 0.074	0.083 ± 0.014	104 ± 2	8.3 ± 1.4	3.2 ± 0.5	789 ± 65	112 ± 22
S6	0.172 ± 0.065	0.062 ± 0.022	60.9 ± 2.4	7.5 ± 2.5	1.8 ± 0.3	805 ± 99	110 ± 55
S7	0.131 ± 0.061	0.064 ± 0.011	62.9 ± 3.4	5.9 ± 1.2	1.1 ± 0.1	860 ± 110	103 ± 29
S8	0.135 ± 0.048	0.069 ± 0.009	686 ± 13	5.1 ± 0.9	2.3 ± 0.6	837 ± 97	104 ± 65
S9	0.118 ± 0.066	0.061 ± 0.012	87.1 ± 3.7	6.1 ± 2.8	1.9 ± 0.4	833 ± 125	106 ± 44
S10	0.140 ± 0.073	0.084 ± 0.027	44.1 ± 1.3	11.7 ± 2.7	1.5 ± 0.2	545 ± 78	124 ± 26
S11	0.135 ± 0.059	0.068 ± 0.017	47.0 ± 1.1	10.1 ± 3.8	1.4 ± 0.4	454 ± 65	103 ± 35
S12	0.162 ± 0.089	0.067 ± 0.028	110 ± 5	6.5 ± 1.2	2.8 ± 0.6	476 ± 78	107 ± 78
S13	0.330 ± 0.104	0.066 ± 0.016	59.4 ± 1.5	6.4 ± 1.6	3.0 ± 0.8	513 ± 66	117 ± 89
S14	0.231 ± 0.082	0.072 ± 0.011	65.2 ± 1.3	6.3 ± 1.4	1.9 ± 0.2	544 ± 86	118 ± 31
Mean	0.306	1159	105	7.2	1.8	6656	1064
Min	0.118	0.061	31.1	5.1	1.0	454	102
Max	1.374	16,227	686	11.7	3.2	69,702	13,483
Background	0.056	0.016	20.80	1.07	0.43	51.85	79.95

Table 2 Comparison of metal concentrations (µg/g) in surface sediments from different rivers around the world

Location	Hg	Cd	Ni	Pb	As	Cu	Zn	Reference
This study	0.306	1159	105	7.2	1.8	6656	1064	
Cauca River, Colombia	0.562	-	-	-	-	-	-	Marrugo et al. (2007)
Vaigai River, India	-	1.0	41.5	69.3	-	47.7	164.2	Paramasivam et al. (2015)
Cauca River, Colombia	0.883	-	-	-	-	-	-	Pinedo-Hernández et al. (2015)
Yangtze River, China	-	0.19	31.9	23.8	9.1	24.7	82.9	Wang et al. (2015)
Luanhe River, China	-	0.020–0.240	3.5–35.8	22.6–43.7	3.5–13.6	9.6–35.6	12.9–94.7	Liu et al. (2016)
Sundarban River, Bangladesh	0.021–0.046	0.35–0.82	18–38	-	3.4–9.0	13–30	46–89	Islam et al. (2017)
Mekong River, China	-	1.48	26.81	25.05	-	15.88	31.93	Strady et al. (2017)
Sürmene River, Turkey	-	0.50	28.70	70.45	7.55	59	79	Alkan et al. (2018)
Sinú River, Colombia	0.10–0.31	0.010–0.039	3.6–69.2	0.01–0.028	-	10.5–112	24.7–118	Feria et al. (2010)
Atrato River, Colombia	0.03–0.14	-	-	-	-	-	-	Palacios-Torres et al. (2018)
Zio Stream, Togo	-	0.3	78.05	17.4	2.06	39.55	39.55	Avumadi and Probst 2019)
Ganga River, China	-	1.6	25	13.84	-	35.57	41.97	Siddiqui and Pandey (2019)
Santurbán paramo, Colombia	-	-	-	-	484	-	-	Alonso et al. (2020)
Ganges-Brahmaputra-Meghna river system, Bangladesh	-	0.13 ± 0.02	46.32 ± 10.43	23.28 ± 2.20	-	30.88 ± 10.32	-	Khan et al. (2020)
Koshi River, India	-	0.22	22.8	22.5	-	21.2	51.2	Li et al. (2020)
Huaihe River, Anhui, China	0.031 ± 0.010	0.2 ± 0.1		32.3 ± 11.1	9.0 ± 3.0	23.1 ± 6.4	76.8 ± 14.2	Ting et al. (2020)
Rivers at Giresun, Northeast Turkey	-	0.68	14.8	50.4	11.8	72.6	115.1	Ustaoğlu and Saiful Islam (2020)

Table 3 Sediments classification and comparison according to Er, RI and SQGs

Station	E_r^i							RI	Risk grade	M-ERM-Q
	Ni	Hg	Cd	Pb	As	Cu	Zn			
S1	8	981	$3\ 10^7$	38	33	6722	169	$3\ 10^7$	Very high	283.42
S2	7	572	143	29	26	1470	1	2249	High	8.36
S3	11	99	142	34	31	72	1	389	Considerable	0.59
S4	8	154	170	27	24	80	1	463	Considerable	0.62
S5	25	144	156	39	73	76	1	513	Considerable	0.80
S6	15	123	116	35	43	78	1	409	Considerable	0.68
S7	15	94	120	28	26	83	1	366	Considerable	0.70
S8	165	96	130	24	54	81	1	551	Considerable	2.41
S9	21	84	115	29	43	80	1	375	Considerable	0.75
S10	11	100	157	55	34	53	2	411	Considerable	0.49
S11	11	96	128	47	33	44	1	360	Considerable	0.44
S12	27	116	125	31	65	46	1	410	Considerable	0.64
S13	14	236	123	30	74	49	1	528	Considerable	0.55
S14	16	165	135	29	44	53	1	443	Considerable	0.56
Media	25	219	$2\ 10^6$	34	43	642	13	$2\ 10^6$	Very high	20.11
E_r^i grade	Low	High	Very high	Moderate	Moderate	Very high	Low			Probability toxicity (76%)

Sediment quality guidelines (SQGs)/(effect)	Metal concentrations (mg/kg)						
	Ni	Hg	Cd	Pb	As	Cu	Zn
TEL	15.9	0.13	0.68	30.24	7.24	18.7	124
PEL	42.8	0.70	4.20	112	41.6	108	271
ERL	20.9	0.15	1.20	46.7	8.2	34	150
ERM	51.6	0.71	9.60	218	70	270	410
Compared TEL and PEL	% SQGs						
< TEL	0	13.3	100	100	100	0	93
TEL-PEL	20	66.6	0	0	0	100	0
> PEL	80	13.3	7	0	0	100	7
Compared ERL and ERM	% SQGs						
> ERL	0	40	7	0	0	100	7
ERL-ERM	46.6	46.6	0	0	0	100	0

Er^i potential ecological risk factor; CCME 1999 (*TEL* threshold effects level; *PEL* probable effects level); NOAA 2012 (*ERL* effect range low; *ERM* effect range medium)

at stations S5, S8, S9, and S12, which are possibly influenced by the extraction of ferronickel and coal (DNP 2009; Ingeominas 2004; UPME 2009; UPME-MME-UC 2014b). The highest concentrations of Cd (16,227 μg/g), and Zn (13,483 μg/g) were found in station S1, which is directly impacted by the dumping of gold mining areas that release both metals from the parent material. Cd is characterized by its migration in aquatic systems where compounds such as CdS among others are soluble in water and easily entrapped by suspended solids and sediments. The highest concentrations of Pb occurred at stations S10 and S11, away from the hotspot area, probably as a consequence of diffuse pollution coming from the San Jorge River Basin. The higher concentration of As was found in station S5, influenced by coal mining. Previous studies close to this station show that coal mining is an anthropogenic source of TEs such as As, Zn, Cu, Ni, Cd, Pb, and Hg (World Coal Quality Inventory 2006). Furthermore, wet and dry atmospheric deposition of trace elements from ferronickel and coal mining, and artisanal gold mining (Marrugo et al. 2014) located in this area can contribute to pollute the sediments of the San Jorge River. Examples of point source of pollution include a nickel metallurgical complex (located on the banks of the Uré stream), the coal exploitations near Puerto Libertador municipality (located on the banks of La Guacamaya stream, affluent of the San Pedro River), and the gold mining operations (i.e., amalgamation process with Hg) located on the Valdez stream (close to station S1).

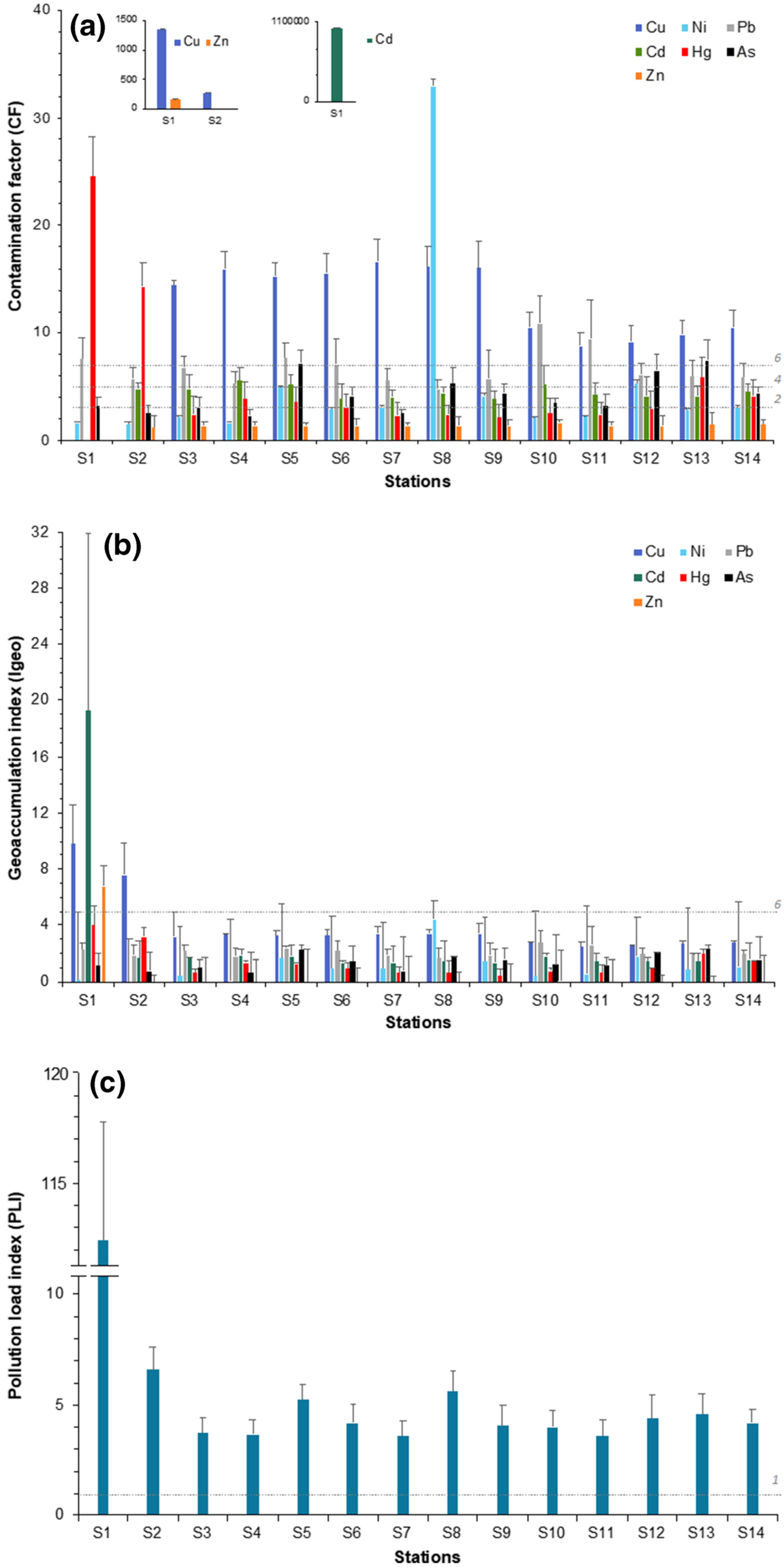
(a)
Contamination factor (CF)
Cu Ni Pb
Cd Hg As
Zn
Cu Zn
Cd
S1 S2 S3 S4 S5 S6 S7 S8 S9 S10 S11 S12 S13 S14
Stations
(b)
Geoaccumulation index (Igeo)
Cu Ni Pb
Cd Hg As
Zn
S1 S2 S3 S4 S5 S6 S7 S8 S9 S10 S11 S12 S13 S14
Stations
(c)
Pollution load index (PLI)
S1 S2 S3 S4 S5 S6 S7 S8 S9 S10 S11 S12 S13 S14
Stations

Fig. 2 Bar chart for different contamination indexes, horizontal lines indicate the threshold limits or classification: (**a**) contamination factor, 0 = none; 1 = none to medium; 2 = moderate; 3 = moderately to strong; 4 = strongly polluted; 5 = strong to very strong; 6 = very strong; (**b**) geoaccumulation index, class 0 (uncontaminated): Igeo ≤ 0; class 1 (uncontaminated to moderately contaminated): 0 < Igeo < 1; class 2 (moderately contaminated): 1 < Igeo < 2; Class 3 (moderately to heavily contaminated): 2 < Igeo < 3; Class 4 (heavily contaminated): 3 < Igeo < 4; Class 5 (heavily to extremely contaminated): 4 < Igeo < 5; Class 6 (extremely contaminated): 5 < Igeo. (**c**); and pollution load index, PLI >1

In general, the concentrations of Hg, Cd, Ni, Cu, and Zn in sediments of the San Jorge River Basin were notably higher than values in other areas worldwide, while the Pb and As showed lower values (Table 2). Compared with other rivers in Colombia, concentrations for all the trace elements were higher than in the Sinú River Basin (Feria et al. 2010). For Hg, values were higher than those reported in the Atrato River Basin (Palacios-Torres et al. 2018), and similar than those reported in sediments from the Cauca River Basin, which is one of the main rivers in the country, and it is strongly impacted by Hg due to gold mining (Marrugo et al. 2007; Pinedo-Hernández et al. 2015).

Ecological risk potential assessment

All the samples exceed the reference values for Cu (Table 3), according to threshold effects level (TEL), probable effects level (PEL), effect range low (ERL), and effect range medium (ERM), suggesting that Cu had adverse biological effects on the sediments. On the other hand, Ni and Hg were within the TEL-PEL range for 20% and 67% of the samples, respectively, indicating an occasional association with adverse biological effects. In addition, 80% and 13% of the samples analyzed in Ni and Hg, respectively, had values above PEL, indicating that both metals probably cause the frequent appearance of harmful effects in organisms that inhabit these sediments (Long et al. 2000; Zhang et al. 2013). Moreover, Hg presented a 40% of the samples above ERL, while 47% of Ni and Hg were within the ERL-ERM range. Concentrations of Cd, Pb, As, and Zn had values lower than TEL, PEL, and ERL, except for Zn and Cd at station S1 where the results were higher than the reference values. In sum, results suggested that trace elements had adverse biological effects, because 3/4 of samples showed a probability of toxicity of 50% (0.51 ≤ M-ERM-Q < 1.5), and 1/5 of the samples a toxicity probability of 75% (M-ERM-Q > 1.5).

Based on Er^i, the sediments were classified with a potential ecological risk factor between low ($Er^i < 40$) and very high ($Er^i >= 320$) (Supplementary Table S1). Hg exhibited a considerable and high ecological risk in 73% and 13% of the samples, respectively, and a very high ecological risk in stations S1 and S2. Moreover, As, Pb, and Zn presented low ecological risk for 47%, 87%, and 100% of the sediments, respectively, whereas Cd indicated considerable risk for 87% of the sediments, except for station S1 that showed very high ecological risk. A moderate ecological risk for 60% of the sediments, considerable (27%), and very high (7%) was presented by Cu.

When the stations were examined according to potential ecological risk index (RI), the highest values were found in stations S1 and S2 (Table 3) with values that classified them as very high ecological risk index (RI > 600) (Table S1). Based on the results of RI for each sampling station, surface sediments showed considerable ecological risk in 86% of the sediments, while high to very high in a 7% of the sediments.

The results of sediment classification based on SQGs suggest that Cu, Ni, Zn, Cd, and Hg produced adverse biological effects, while Pb and As were not expected to cause adverse biological effects on biota, as concentrations were below TEL, PEL, and ERL reference values.

Assessment of sediments pollution

Results for CF and Igeo in sediments are shown in Fig. 2. The sediments were classified between moderate contamination (CF: 2–3) to very strong contamination (CF > 6) according to Muller (1979) (see Supplementary information). For example, all the sediments presented very strong contamination for Cu, 20% for As, 53% for Pb, 13% for Hg, and 7% for Ni, Cd, and Zn. Half of the sediments show strong contamination for As, 20% and 73% for Cd. A 53% of sediments show moderate contamination characteristics for Hg, 40% for Ni, and 27% for As. When comparing the results of CF, it is found that they are higher than those reported for Hg in the Atrato River (Palacios-Torres et al. 2018) and the Sinú River sediments (Feria et al. 2010) for Hg, Cu, and Ni, but lower for Cd and Pb.

Figure 2b shows the geoaccumulation index of trace elements in sediments. The order as a function of the mean of Igeo for trace elements was Cu (3.9) > Cd (2.77) > Pb (2.11) > As (1.40) > Hg (1.31) > Ni (1.07) > Zn (0.33). In the sediments, 80% (As), 53% (Pb), 93% (Ni, Cd, and Hg) presented class 2 (moderately contaminated grade, 0 < Igeo < 2). 40% (Pb), 33% (Cu), and 20% (As) presented class 3 (moderate to strongly contaminated, 2 < Igeo < 3). Cu presented 53% of the sediments in class 4 (heavily contaminated) 3 < Igeo < 4; Ni and Hg class 5 (from strongly to extremely contaminated, 4 < Igeo < 5) for 7% of the sediments and class 6 (extremely contaminated, Igeo > 5) for Cu (13%) and 7% (Zn and Cd).

Concentrations of trace elements showed significant enrichments (EF > 1) of As, Cu, Cd, and Pb in all the studied samples, a 73% of Hg and Ni, and a 13% of Zn (Supplementary Fig. S1). The average EF revealed the

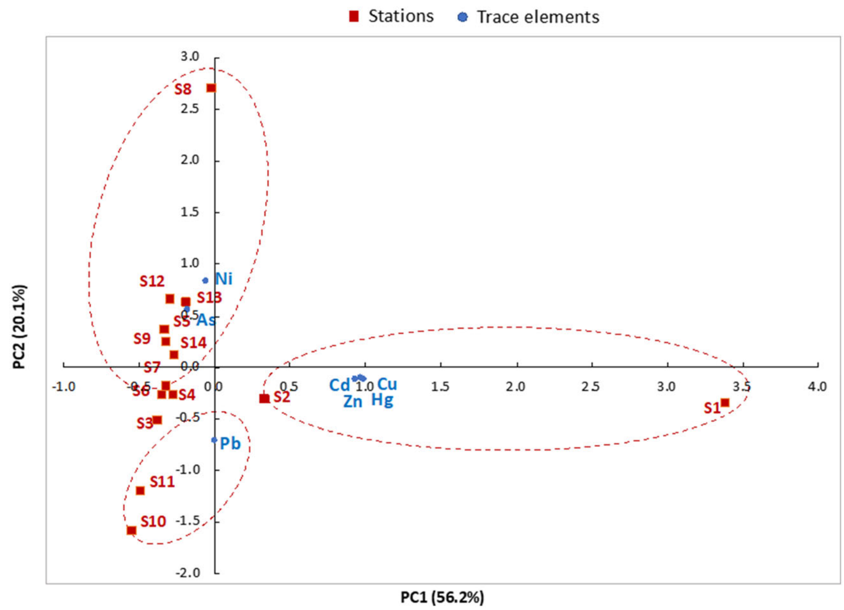

Fig. 3 PCA biplot showing the loading of selected trace elements (blue circles) and the scores of each sampling station (red squares) in the San Jorge River basin

following order: Cd (28449) > Cu (51.2) > Zn (5.3) > Pb (3.1) > Hg (2.3) > Ni (2.2) > As (2.0). The enrichment factor of Cu and Cd (EF > 50) classified them as extreme enrichment, minor enrichments for Hg, Ni, and As (EF = 1–3) and moderate enrichments Pb and Zn (EF = 3–5). The enrichment is possibly due to the different anthropogenic mining activities developed in the study area. In the case of Hg and Ni, they were clearly associated with gold and coal mining, and to ferronickel metallurgical processes, respectively. For the rest of trace elements, the EF values were related to different releases during extraction processes in the mining operations (e.g., coal mining). Artisanal gold mining could be also responsible for Cu, Cd, and Zn enrichment due to higher EF values (Supplementary Fig. S1) in sampling stations S1 and S2. In addition, the application of phosphate fertilizers in agriculture could be another diffuse source of Cd and Pb (Marrugo 2005).

Finally, according to PLI values (Fig. 2c), surface sediments in all the sampling sites of the San Jorge River Basin indicated an environmental deterioration (PLI > 1) with greater impact for stations located close to mining areas, such as station S1 (PLI = 113) with a large contribution of metals such as Cu, Zn, Hg, and Cd.

Distribution and relationship of trace elements

The relationship between the trace elements and stations were further analyzed by PCA, as shown in the biplot (Fig. 3). Two principal components explained 76.3% of data variation. The first principal component (PC1) showed high loads (> 0.93) of Hg, Cd, Cu, and Zn (Supplementary Table S2a). PC1 could be explained as a composite anthropogenic source (gold mining and coal), as it does not present Hg, Cd, Zn, and Cu significant correlation with respect to Ni. A strong significant correlation existed between Hg, Cu, Cd, and Zn (Table 4) indicating that these metals in the San Jorge River sediments were derived from similar sources, mostly from anthropogenic activities (i.e., gold mining and coal mining). Stations (S1–S6) were more related to these metals at sampling sites collected in the San Pedro River. PC2 accounted for 20.1% of the total data variability. Despite loads were not high (Supplementary Table S2a), it suggested some associations between Ni and As

Table 4 Pearson correlation matrix for trace elements in sediment samples

	Hg	Cd	Ni	Pb	As	Cu	Zn
Hg	1	0.868**	-0.202	0.015	-0.223	0.947**	0.868**
Cd		1	-0.121	0.137	-0.172	0.978**	1.000**
Ni			1	-0.355	0.294	-0.144	-0.121
Pb				1	-0.086	0.099	0.138
As					1	-0.233	-0.171
Cu						1	0.978**
Zn							1

**Significance at the 0.01 probability level in stations S5–S9 and S12–S14, located downstream ferronickel mining area (Figs. 1 and 3). Residues of As should be attributed to residues in coal mining. In fact, its highest concentration was found in station S5, very close to the coal mining area. Previous studies revealed concentrations of Pb in atmospheric deposition from ferronickel smelting plants (Marrugo-Negrete et al. 2014); however, Pb showed an atypical behavior with no correlation with any other trace element.

Conclusions

The concentration of trace elements in sediments along a 100 km stretch of the San Jorge River showed spatial variability, being higher in those areas that receive loads of pollutants from mining areas. Multivariate analysis showed that contamination by trace elements in the sediments comes mainly from anthropogenic mining activities. Ni concentrations were derived mainly from the ferronickel exploitation, whereas Cd, Zn, As, and Cu were related to coal mining and also to gold exploitation because the strong significant correlation with Hg (except for As). Contamination indices (Igeo, CF, EF, and RI) suggested a moderate to strong contamination with a high ecological potential risk and a great environmental deterioration (PLI > 1) in sediments of the San Jorge River Basin.

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