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Baseline

# Metal concentrations in the beach sediments of Bahia Solano and Nuquí along the Pacific coast of Chocó, Colombia: A baseline study



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### ABSTRACT

Thirty sediment samples from four different beaches along Bahia Solano and Nuquí (Department of Chocó) of eastern Colombia, with tourism and gold mining activities, were analysed to estimate the concentrations of fourteen different acid leachable metals. **Metal distribution patterns showed elevated concentrations of Co, Cr, Cu**, Pb and Zn compared with the upper continental crust values. Calculation of geochemical indices confirmed that the enrichment is due to periodic gold mining activities (severe to extremely severe enrichment of Cu, Zn, V, **Co, Cr and Pb)** along with natural (geological) contributions (minor and moderate enrichment of Ca, Mg, Fe, Ti, **Mn and Li)**. Potential ecological risk index revealed that Pb posed the highest risk. Our results together with a global comparison suggest that the observed metal enrichments are mainly caused by mining and to a lesser extent by tourism in this region, thus instigating continuous monitoring of metal concentrations in this region.

Tourism is considered as one of the biggest global industries with beaches hosting free plays and people as potential revenue partners. Beach tourism results in large economic benefits, thereby increasing the demand for new construction of high rise buildings, resorts, cottages and recreation parks at beaches (Propin-Frejomil and Sánchez Crispín, 2007; Faggi and Dadon, 2011; Pérez-Maqueo et al., 2017). The impact of tourism invasion has often led to the disposal of various contaminants, thereby causing serious concerns to coastal ecosystem (Vikas and Dwarakish, 2015; Wang et al., 2016). Metals are one among the most toxic contaminants that have received considerable attention on global scale owing to their close relationship with human health (Chopra and Pathak, 2015; Ye et al., 2015; Ramachandra et al., 2018). They enter the coastal waters through various natural (weathering and erosion) and anthropogenic (mining, waste disposal, agricultural and industrial activities) sources, wherein they do not remain in soluble form for a long time and have a tendency to deposit in sediments (Xu et al., 2016; El Nemr et al., 2016). Therefore, sediments, being the potential storehouse of metals, are the best tools to assess the contamination status of a given aquatic ecosystem.

In the recent years, our research group has been exploring this storehouse with the vision of generating baseline data for

understanding metal enrichments in various beaches located worldwide. We succeeded in generating a database for popular tourist destinations such as Mexico (Acapulco, Huatulco and Santa Rosalía), India (Chennai), South Africa (Richards Bay, South Durban, Sodwana Bay and St Lucia) and Malaysia (Miri), which have different geological characteristics. Acid leachable technique was effectively adopted as the fundamental method to determine metal concentrations for evaluating the potential environmental and ecotoxicological impacts in beach regions.

In this context, our vision now focuses on Columbia, where beach tourism symbolises one of the most important revenue income. During the period of 2009–2011, nearly 974,721 international (mostly from the U.S.A., Canada and the European Union) and 3,411,523 domestic tourists visited the coastal areas of Colombia (PROEXPORT - Ministerio de Comercio, Industria y Turismo, 2011). The capacity of rapid growth of this sector in the coming decades will bring economic strength to this region. Among diverse coastal regions, Chocó in Colombia is characterised with a unique ecosystem and unexploited natural resources. The richness of Chocó's landscape and its enormous biodiversity make this region quite overwhelming. It is the only region of Colombia that is lapped by the waves of two oceans: the Pacific and the Caribbean. In

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particular, the coast of Bahia Solano and Nuquí forms the economic and touristic corridor of Chocó. It offers plethora of activities such as scuba diving and sport fishing. This tourist capital of the Pacific coast of Colombia attracts a large number of visitors to explore the marine life, beaches and deep jungles with all the natural biodiversity that is different from other local destinations. Its additional economy relies on artisanal fisheries, agriculture and timber extraction (Matallana, 1999; Avila et al., 2008). Mining has precedented this region since the Spanish colonisation (Leyva, 1993). Numerous studies have focused on massive and uncontrolled gold mining activities in Chocó (Vallejo Toro et al., 2016; Gutiérrez-Mosquera et al., 2017; Salazar-Camacho et al., 2017; Palacios-Torres et al., 2018) and in adjacent regions (Olivero et al., 2002: Marrugo-Negrete et al., 2008: Cordy et al., 2011: Alvarez et al., 2012a, 2012b). Given this scenario, we ask whether the intense economic development associated with tourism, urban sprawl and mining are driving any geochemical changes to the beaches of Bahia Solano and Nuquí. On this background, the framework of this study involves the evaluation of metal concentrations in beach sediments along Bahia Solano and Nuquí to comprehend the natural and external (humen induced) impacts on the marine ecosystem.

vestigation was carried out on a ~200-km-long coastal strip of Bahia Solano and Nuquí in Chocó department of eastern Colombia (6°19'9.40"N/77°22'41.20"W and 5°36'28.20"N/77°26'28.40"W). A total of thirty sediment samples were collected from different beaches during May 2016. Based on sample collection, the coastal stretch was categorised into four different regions, wherein 1 and 2 belong to the municipality of Bahia Solano, and 3 and 4 belong to Nuquí municipality: 1) Mutis beaches (S. Nos. 1-13), 2) El Valle beaches (S. Nos. 14-21), 3) Nuquí beaches (S. Nos. 22-26) and 4) Coqui beaches (S. Nos. 27-30) (Fig. 1). Region 1 hosts a port for cargo boats and passenger transportation services and stores trading provisions (materials and timber). Region 2 has a "fishing village" at the mouth of the Rio Valle, where fertile breeding ground results in abundant fishing activities. Region 3 is characterised with mosaic ecosystems such as hot springs, rivers and beaches. It also contains a protective coastal marine environment (i.e. Utría National Natural Park) with humpback whales and sea turtle nests. Region 4 hosts the best-preserved mangroves of Colombia and offers excellent ecotourism. The geology of all the four regions comprises tholeiitic basalt, dolerite, basic tuff and volcanic breccia of the late cretaceous, limestone, sandstone and calcareous mudstone of the Oligocene-Miocene, alluvial deposits of the Quaternary and gravel, and sand and mud rich in organic materials of the Holocene (Gómez Tapias and Almanza Meléndez, 2015).

Sediment samples were collected from the intertidal zone using a

plastic spatula and placed in clean polythene bags. The collected samples were then transported to the laboratory and oven dried below 40 °C. Coning and quartering methods were applied to obtain a homogenous part of the sample, and the sample was powdered using an agate mortar for further analyses. Approximately 1 g of the sample was digested according to the modified EPA 3051A method (2007) and as described by Navarrete-López et al. (2012) using 2.5 ml of HNO<sub>3</sub>, 0.8 ml of HCl and 1 ml of H<sub>2</sub>O<sub>2</sub> acids (all analytical grade) in a closed vessel, which was made of a resistant material Poly(tetrafluoroethylene) (PFA) at 119  $\pm$  1.5 °C for 40 min. The final solution was made up to 10 ml after filtration and analysed for concentrations of fourteen metals (Al, Fe, Mg, Ca, Ti, Co, Cr, Cu, Mn, Pb, Zn, V, Sr and Li) using an inductively coupled plasma optical emission spectrometer (ICP-OES 8300 PerkinElmer). Standard reference materials namely SRM No. 691029, Loam soil B and Marine Reference Standard (SRM 2702 - Inorganics in marine sediment) were run along with the samples. The recoveries were as follows: Al 97.89% (  $\pm 1.62 \,\mu g \, g^{-1}$ ), Fe 98.82% (  $\pm 1.72 \,\mu g \, g^{-1}$ ), Mg 110.88% (  $\pm$  1.30 µg g<sup>-1</sup>), Ca 98.01% (  $\pm$  1.65 µg g<sup>-1</sup>), Ti 97.39%  $(\pm 2.50 \,\mu g \, g^{-1})$ , Co 101.39%  $(\pm 3.10 \,\mu g \, g^{-1})$ , Cr 102.35%  $(\pm 2.10 \,\mu g \,g^{-1})$ , Cu 101.66%  $(\pm 3.20 \,\mu g \,g^{-1})$ , Mn 92.70%  $(\pm 0.08 \,\mu g \, g^{-1}), Pb$ 111.07% (  $\pm 2.81 \, \mu g \, g^{-1}$ ), Zn 95.93%  $(\pm 1.10 \,\mu g \, g^{-1}), V 106.01\% (\pm 1.55 \,\mu g \, g^{-1}),$ Sr 105.46%  $(\pm 2.10 \,\mu g \, g^{-1})$  and Li 110.42%  $(\pm 1.05 \,\mu g \, g^{-1})$ . The detection limits for the analysed metals were Al 0.01%, Fe 0.01%, Mg 0.01%, Ca 0.01%, Ti 0.01%, Co 1 ppm, Cr 2 ppm, Cu 1 ppm, Mn 1 ppm, Pb 2 ppm, Zn 1 ppm, V 1 ppm, Sr 1 ppm and Li 0.0001-1%.

The distribution pattern of analysed metals is presented in Fig. 2 a-n. The descending order of metal concentrations (all values in µg g<sup>-</sup> 1) in all the four regions is as follows: 1) Mutis beach: Fe (34,111) > Ca(9871) > Al (8846) > Mg (6494) > Ti (1699) > Pb (391) > Mn(372) > Cr (239) > V (176) > Zn (125) > Co (108) > Sr(49) > Cu (44) > Li (15); 2) El Valle beach: Fe (34,581) > Al (16,839) > Mg(15,070) > Ca(6152) > Ti(801) > Mn(556) > Pb(399) > Cr (279) > V (143) > Zn (127) > Co (111) > Cu(85) > Sr (51) > Li (30); 3) Nuquí beach: Fe (25,067) > Mg (10,684) > Ca(9388) > Ti (15,788) > Al(1099) > Pb(430) > Mn (416) > Cr (302) > Zn (124) > Co (109) > V(104) > Cu (36) > Sr (28) > Li (17) and 4) Coqui beach: Fe (20,875) > Mg (9661) > Ca (8068) > Al (7735) > Ti (963) > Pb (467) > Cr (309) > Mn (284) > Zn (130) > Co (110) > V(83) > Cu (45) > Sr (30) > Li (16). The above-mentioned array displayed no significant variations in metal concentrations in all the four regions. For a better understanding of the enrichment pattern, metal concentrations were compared with the upper continental crust



Fig. 1. Locations from which sediments were collected in four different beaches along Bahia Solano and Nuquí, Department of Chocó, Colombia.



(UCC; Wedepohl, 1995) background values. Extreme enrichment levels (all values in  $\mu g g^{-1}$ ) for Co (108; 111; 109; 110), Cr (239; 279; 302; 309), Cu (44; 85; 36; 45), Pb (391; 399; 430; 467), Zn (125; 127; 124; 130) and V (176; 143; 104; 83) in all the four regions were witnessed when compared with the UCC background values (Table 1).

Spatial variability in metal concentrations (all values in  $\mu g g^{-1}$ ) revealed that the majority of metals such as Al (16,839; 10,684), Fe (34,581; 25,067), Mg (15,070; 15,788), Co (111; 109), Cr (279; 302), Cu (85; 36), Mn (556; 416), Pb (399; 430), Zn (127; 124) and Li (30; 17) are elevated in El Valle and Nuquí beaches (Fig. 2 a–n). Elevated levels of aforementioned metals are geological, and they are attributed to the alluvial deposits of the Ouaternary and organic material-rich Holocene sed me ts (Gómez Tapias and Almanza Meléndez, 2015). Higher values of elements such as Ca (9871) and Sr (49) of the Mutis beach are derived from the carbonate-bearing sedimentary rocks (limestone and calcareous mudstone) of the Oligocene-Miocene (Gómez Tapias and Almanza Meléndez, 2015). Additional geological component of this region is the presence of volcanic deposits (tholeiitic basalt, basic tuff and volcanic breccia) (Gómez Tapias and Almanza Meléndez, 2015), which consequently contributed to higher concentrations of V (176) and Ti (1699). Compared to other regions, elevated concentrations of Cu (85) were observed in El Valle beaches. This can be explained by contributions from Cu in antifouling paints and impregnation of nets used in fish farming (Vallejo Toro et al., 2016). Gold production in this region accounts for 23.6% of Colombia's total production and represents 15% of Chocó's GDP (Goñi et al., 2014). A considerable number of tailings are inevitable during the retrieval of precious metals (gold, silver and platinum). These mine tailings are generally characterised with higher concentrations of Co, Cr, Cu, Pb, Zn and V (Ferreira da Silva et al., 2004; Bryan et al., 2006; Ahmadi et al., 2015; Fashola et al., 2016; Falagán et al., 2017). Apart from the natural geological inputs, the higher levels (avg. values in  $\mu g g^{-1}$ ) of Co (109), Cr (269), Cu (54), Pb (410), Zn (126) and V (143) along the entire coast are attributed to the mining activities related to platinum, gold and silver production in the Department of Chocó. San Juan and Dagua are important rivers that drain into the Pacific coast of Chocó further south to the study area and have been significantly affected by gold mining activities (Maria Fernanda and Collazos-Santos, 2014). The distribution of metals in sediments along the Pacific coast of Chocó is strongly influenced by the longshore sand drift. It has a dominant northeast component during rainy season (April-May) when southerly winds are dominant in some sectors and set up short, high-frequency waves (Correa and Morton, 2011; Rangel-Buitrago et al., 2017). In addition, the Humboldt Current system flowing in the direction of the equator transports the metal-contaminated sediments bought in by the rivers San Juan & Dagua) from the south to the north of the Chocó.

The inter-relationships among different metals were identified by correlation analysis. Statistica 8 software was used wherein the entire dataset was Varimax normalised and the Pearson correlation matrix was generated with p < 0.5, 0.01 and 0.001 (Table 2). The data analysis presented in this study represents only significantly correlated values, which have some direct relationship in the geochemical process. The significant correlation of Al and Fe vs Co ( $r^2 = 0.54$ ; 0.67), Cu  $(r^2 = 0.93; 0.47)$ , Mn  $(r^2 = 0.73; 0.67)$ , Zn  $(r^2 = -; 0.76)$  and Li  $(r^2 = 0.93; 0.48)$  suggested their detrital origin associated with aluminosilicates from the alluvial deposits and organic-rich sediments of the Quaternary. Ca and Sr presented ( $r^2 = 0.73$ ) a strong positive correlation, and the assemblage of Ca-Sr combination is believed to behave similarly with each other due to their similar ionic radii  $(r_{Sr} = 0.113 \text{ nm})$  $vs r_{Ca} = 0.099 \text{ nm}$ ) and charge. Sr is typically found in calcium-bearing minerals, and their strong inter-relationship reflects the presence of carbonate rocks such as limestone, sandstone and calcareous mudstone in the study region (Gómez Tapias and Almanza Meléndez, 2015). In addition, the strong inter-relationship among Co vs Cu ( $r^2 = 0.57$ ), Zn  $(r^2 = 0.61)$ , Cr  $(r^2 = 0.61)$  vs Pb  $(r^2 = 0.63)$  suggested their common origin. The correlation among Co, Cu, Zn, Cr and Pb indicates the

Comparison of concentrations of the	e studied metals in the s	ediments of Bahia Sc	olano and Nuquí with	those in other globa	l coastal environmen	ts.		
Locations	Extraction type	Metal concentratior	IS					
		AI	Fe	Mg	Ca	ΤΪ	Co	Cr
Worldwide								
Portugal coast	$HCI + HNO_3 + HF$	I	12,000–88,000	I	I	I	22–89	18–133
Rosetta coast, Egypt	HCI + HNO <sub>3</sub> + HF	I	109,560	I	I	I	69.78	0.18
Salaam coast, l'anzania	$HCI + HNO_3$	I	461-5352	I	I	I	6/.7-12.0	1-9.6
Huatulco beaches, Mexico	$HCI + HNO_3$	I	7492	I	I	I	4.63	89.26
Venezuela coast	I	I	1	I	I	I	1 7	10.27
Arabian Gulf, Saudi Arabia	I	I	3447	I	I	I	6.35	27.10
Chennai, India	$HCI + HNO_3$	I	442	I	I	I	I	14.10
Lutong beach, Malaysia	$HCI + HNO_3$	I	1888	I	I	I	12.64	85.33
Quintero Bay, Chile	1	I	I	I	I	I	9.6	45.7
Korea coast	$HCI + HNO_3 + HF$	67,000					10.2	58.3
Gulf of Urabá, Colombia	$HCI + HNO_3 + HF$	61,800–134,200	43,700–95,800	6000-15,500	2700–37,500	I	I	109.61–212.45
Stratoni_lerissos Gulf, Greece	XRF	I	I	I	I	I	I	I
Sulcis-Iglesiente, Sardinia Italy	$HCI + HNO_3$	I	I	I	I	I	I	5.59
Sodwana Bay, South Africa	$HCI + HNO_3$	I	7784	1008	I	I	6.90	426
Present study								
Bahia Solano Beaches, Colombia	$HCI + HNO_3$	11,136	30,964	10,752	8558	1261	109.08	269.17
Sediment quality guidelines								
TEC	I	I	I	I	I	I	ı	43.4
PEC	I	I	I	I	I	I	I	111
Ecotoxicological values								
LEL	I	I	20.000	ı	I	I	I	26
SEL	1	I	40,000	I	I	I	I	110
ERL	ı	I	, I	I	I	I	I	81
ERM	I	I	I	I	I	I	I	370
Locations	Metal concentrations							References
	Cu	Mn	Pb	ΠZ	v	Sr	Li	
Worldwide								
Portugal coast	117-884	200-4632	35.7-437	38.3-349.3	I	I	I	Vidinha et al., 2009
Rosetta coast, Egypt	24.57	553	384.68	183.23	374.78	114.06	I	El-Sorogy et al., 2016
Salaam coast, Tanzania	0.3-2.1	17-219	0.8-2.2	2.6–9.3	1.1-13.7	I	I	Rumisha et al., 2012
Huatulco beaches, Mexico	3.35	69.24	4.48	7.86	1	1	1	Retama et al., 2016
Venezuela coast	3.79	I	11.64	113.38	I	I	I	García et al., 2008
Arabian Gulf, Saudi Arabia	5.78	75.17	58.68	17.57	I	I	I	Youssef et al., 2015
Chennai, India	4.05	46.8	19.77	9.89	ļ	I	I	Santhiya et al., 2011
Lutong beach, Malaysia	28.81	12.83	12.88	17.93	I	62	I	Nagarajan et al., 2013
Quintero Bay, Chile	404 20 r	602	25.2	111	I	I	I	Parra et al., 2015
Korea coast Gulf of Hrahá Colomhia	30.5 25 08–102 94	361 92-905 47	35 0 17_6 93	122 75 15-161 53				Ka et al., 2013 Valleio Toro et al 2016
Stratoni lerissos Gulf. Greece	143	10.150	1146	1863	1	1	1	Panna et al., 2016
Sulcis-Iglesiente, Sardinia Italy	2.87	204.33	203	3272	I	I	I	Romano et al., 2017
Sodwana Bay, South Africa	4.53	72.16	1.27	2.81	I	I	I	Vetrimurugana et al., 2018
Present study								
Bahia Solano Beaches, Colombia	53.93	416.82	409.67	125.80	142.55	43.59	19.37	

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(continued on next page)

Locations	Metal concentrations							References
	Cu	Mn	Pb	Zn	Λ	Sr	ці	
Sediment quality guidelines								
TEC	31.6	I	35.8	121	I	I	I	MacDonald et al., 2000
PEC	149	I	128	459	I	I	I	
Ecotoxicological values								
LEL	16	460	31	120	1	1	1	USEPA, 2001
SEL	110	1100	250	820	I	I	I	
ERL	34	I	46.7	150	I	I	I	Long et al., 1995
ERM	270	I	218	410	I	I	I	
All values expressed in $(\mu g g^{-1})$ . UCC	= upper continental of	crust (Wedepohl, 1995	); TEC: threshold effe	ct concentration; PEC	: probable effect con	centration; LEL: lowee	st effect level; SEL: sev	ere effect level; ERL: effects
range low; ERM: effects range mediur	л.							

Table 1 (continued)

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presence of chalcophile elements and the influence of external anthropogenic sources in the study area. (The long-term gold mining activities contribute to the source of Co, Cr, Cu, Pb and Zn metals in the beach sediments of Bahia Solano and Nuquí.)

To have a panoramic view, the metal concentration data from other tourist beaches worldwide along with that from Bahia Solano and Nuquí beach sediments are presented in Table 1. Vallejo Toro et al. (2016), Pappa et al. (2016) and Romano et al. (2017) reported significant impacts of gold mining activities on metal concentrations in the coastal sediments of the Gulf of Urabá (Colombia), Stratoni\_lerissos Gulf (Greece) and Sulcis-Iglesiente (Sardinia Italy), respectively. In the present study ( $\mu$ g g<sup>-1</sup>), Cr (269), Cu (54), Pb (410) and Zn (126) concentrations were within the range or even lower compared to those in other regions. From the results of the present study and a previous study on the Gulf of Urabá (Colombia), we report that both regions namely the Atlantic coast and Pacific coast of Colombia are greatly affected by extensive gold mining activities. Similarly, when compared with metal concentrations in other tourist beaches such as Huatulco (Mexico), Chennai (India) and Lutong (Malaysia), those obtained in the present study were approximately 10- to 15-fold higher. El-Sorogy et al. (2016), Rumisha et al. (2012), García et al. (2008), Youssef et al. (2015) and Ra et al. (2013) demonstrated that anthropogenic activities such as urbanisation, industrialisation and sewage disposals greatly influence the metal concentrations in the sediments of Rosetta coast (Egypt), Salaam coast (Tanzania), Venezuela coast, Arabian Gulf (Saudi Arabia) and Korea coast, respectively. Compared with these regions, Bahia Solano and Nuquí sediments had higher concentrations (avg.) of Co (109.08), Cr (269.17), Cu (53.93), Pb (409.67) and Zn (125.80). Globally, Bahia Solano and Nuquí beach sediments presented higher concentrations of metals than other tourist and human-influenced beaches. However, the results of the present study were found similar to those obtained in areas influenced by gold mining activities, thus confirming the substantial impact of gold mining activities on the metal concentrations of Bahia Solano and Nuquí sediments.

We compared the obtained metal concentrations with sediment quality guidelines (SQGs) (MacDonald et al., 2000) and ecotoxicological values (USEPA, 2001; Long et al., 1995) to evaluate the quality of sediments. SQGs and ecotoxicological values were developed to evaluate the degree to which the sediment-associated metal concentrations might adversely affect the aquatic biota and help in the interpretation of the sediment quality. They include the threshold effect concentration (TEC), probable effect concentration (PEC), lowest effect level (LEL), severe effect level (SEL), effect range low (ERL) and effect range medium (ERM). The values below TEC, LEL and ERL indicate no harmful effects while values above PEC, SEL and ERM suggest the frequent occurrence of adverse biological effects. In this study, Cr ( $269 \ \mu g \ g^{-1}$ ) and Pb ( $410 \ \mu g \ g^{-1}$ ) concentrations in Bahia Solano and Nuquí sediments pose severe threats to the aquatic biota because they exceed the PEC, SEL and ERM values (Table 1).

Further, the degree of metal contamination in sediments was assessed using geochemical indices such as the enrichment factor (EF) geoaccumulation index (Igeo) and potential ecological risk index (PERI). We used UCC (Wedepohl, 1995) values for calculating the geochemical index. The enrichment factor distinguishes between crustal and noncrustal sources, thereby estimating the anthropogenic sources of metals in sediments (Buat-Ménard and Chesselet, 1979; Ibrahim et al., 2014; Ashraf et al., 2016). It encompasses the normalisation of metal concentrations with uncontaminated background values: EF = (Me/ Al)\_{sample}/(Me/Al)\_{baseline}, where (Me/Al)\_{sample} and (Me/Al)\_{baseline} represent the ratio of metal to Al concentration in the studied samples and in the background sample, respectively. Al is highly abundant in earth's crust, and we used it as a normaliser in this study. Moreover, its close association with aluminosilicates makes it one of the dominant metalbearing phases in sediments (Windom et al., 1989; Schropp et al., 1990; Alexander et al., 1993; Vink et al., 1999; Gao and Chen, 2012). Different classes and their corresponding EF values calculated for the

#### Table 2

Correlation matrix analyses of sediments collected from different beaches along Bahia Solano and Nuquí, Department of Chocó, Colombia.

	Al	Fe	Mg	Ca	Ti	Со	Cr	Cu	Mn	Pb	Zn	V	Sr	Li
Al	1.00													
Fe	0.40*	1.00												
Mg	$0.82^{*^{\dagger \pm}}$	-	1.00											
Ca	-	-	-	1.00										
Ti	-0.41*	-	-	-	1.00									
Co	0.54* <sup>†</sup>	0.67* <sup>†‡</sup>	0.66* <sup>†‡</sup>	-	-	1.00								
Cr	0.39*	-	0.69* <sup>†‡</sup>	-	-	$0.61^{*^{\dagger \ddagger}}$	1.00							
Cu	0.93* <sup>†‡</sup>	0.47* <sup>†</sup>	$0.71^{*^{\dagger \ddagger}}$	-	$-0.38^{*}$	$0.57^{*^{\dagger}}$	-	1.00						
Mn	$0.73^{*^{\dagger \pm}}$	$0.67^{*^{\dagger \ddagger}}$	0.65* <sup>†‡</sup>	-	-	0.63* <sup>†‡</sup>	-	0.79* <sup>†‡</sup>	1.00					
Pb	-	-	-	-0.44*	-	-	0.63* <sup>†‡</sup>	-	-	1.00				
Zn	-	0.76* <sup>†‡</sup>	-	-	-	$0.61^{*^{\dagger \ddagger}}$	0.38*	-	$0.53^{*^{\dagger}}$	-	1.00			
V	-	$0.62^{*^{\dagger \ddagger}}$	-	-	0.73* <sup>†‡</sup>	-	-	-	-	-	$0.52^{*^{\dagger}}$	1.00		
Sr	$0.52^{*^{\dagger}}$	-	0.42*	0.73* <sup>†‡</sup>	-	-	-	0.49* <sup>†</sup>	$0.51^{*^{\dagger}}$	-0.45*	-	-	1.00	
Li	0.93* <sup>†‡</sup>	0.48* <sup>†</sup>	0.81* <sup>†‡</sup>	-	-0.41*	0.65* <sup>†‡</sup>	0.46* <sup>†</sup>	0.94* <sup>†‡</sup>	0.81* <sup>†‡</sup>	-	-	-	$0.51^{*\dagger}$	1.00

 $p < 0.05^*, 0.01^{\dagger}, 0.001^{\dagger}.$ 

#### Table 3

Calculated enrichment factor (EF) values for sediments collected from the beaches along Bahia Solano and Nuquí, Department of Chocó, Colombia.

Beaches	Enrichment fact	or values (EF)					
	No enrichment (< 1.5)	Minor enrichment ( < 3)	Moderate enrichment (3–5)	Moderately severe enrichment (5–10)	Severe enrichment (10–25)	Very severe enrichment (25–50)	Extremely severe enrichment (> 50)
Mutis El Valle Nuquí Coqui	Sr Ca, Sr Sr Sr	Ca Ti Ca, Ti, Ca	Mg Ti	Ti, Mn, Li Fe, Mg, Mn, Li Fe, Mg, Mn, Li Fe, Mg, Mn, Li	Fe Zn, V Cu, Zn, V V	Cu Cu Cu, Zn	Co, Cr, Pb, Zn, V Co, Cr, Pb Co, Cr, Pb Co, Cr, Pb



Mutis beaches 🔛 El Valle beaches 🔛 Nuqui beaches 💹 Coqui beaches

Fig. 3. Igeo values for sediments collected from different beaches along Bahia Solano and Nuquí, Department of Chocó, Colombia.

sediments of Bahia Solano and Nuquí are presented in Table 3. Values of < 1.5 for Sr suggest its crustal origin along with Ca and T Fe, Mg, Mn and Li displayed EF values between 3 and 10, thus revealing a moderately severe enrichment of these metals. Severe and extremely severe enrichments of Co, Cr, Cu, Pb, Zn and V (EF > 50) reflect the extensive gold mining activities in Chocó (Yacoub et al., 2012; Wasiu et al., 2016).

As proposed by Muller (1979), another relative contamination assessment of sediments is the geoaccumulation index ( $I_{geo}$ ), which is calculated by  $I_{geo} = (log_2 C_n/1.5 B_n)$ , where  $C_n$  is the concentration of the element 'n',  $B_n$  is the background concentration for the element and 1.5 is a factor employed to compensate for the difference in metal concentrations due to lithogenic variations. On the basis of the respective ranges of Igeo values, seven classes (0–6) were obtained from uncontaminated to extremely contaminated sediments as shown in Fig. 3. Sediments were uncontaminated to moderately contaminated (Class 1) with Cu, Zn and V. In sediments from the El Valle beach, Cu alone presented moderate contamination (Class 2) and revealed the influence of substantial fishing activities (Nikolaou et al., 2014; Berillis et al., 2017). However, the heavy to extreme contamination of Co, Cr (Class 3) and Pb (Class 4) in the beach sediments was attributed to the extensive illegal mining activities in the Department of Chocó.



Fig. 4. Potential ecological risk index values calculated for all the sediments collected from the beaches along Bahia Solano and Nuquí, Department of Chocó, Colombia.

The PERI developed by Hakanson (1980) is one of the most widely applied methods to evaluate metal contamination and their associated ecological risk (Li et al., 2015; Maanan et al., 2015; Lin et al., 2016; Yang et al., 2016). It is calculated as follows:  $RI\Sigma_f^i ER_f^t$ ;  $ER_f^i = Tr^i \times C_f^i = Tr^i \times \left(\frac{C_s^i}{C_n^i}\right)$ , where  $ER_f^i$  is the potential ecological risk factor for a given element *i*;  $Tr^i$  is the biological toxicity factor for element *i*, which is defined as Mn = 1, Cr = 2, Cu = Pb = 5, Zn = 1and V = 2 (Hakanson, 1980); and  $C_f^i$ ,  $C_s^i$  and  $C_n^i$  are the contamination factor, the concentration in the sediment and the background reference value for element i, respectively. According to Hakanson (1980), four categories of PERI have been defined ranging from low ecological risk (PERI  $\leq$  150) to significantly high ecological risk (RI > 600). From the PERI results obtained in the present study, the ranking of metals was in the following order: Pb (723) > Cu (116) > Cr (92) > V (32) > Zn (14) > Mn (5) (Fig. 4). All the metals in Bahia Solano and Nuquí sediments displayed a low ecological risk, except for Pb with a PERI value 723; this indicates the high ecological risk caused by Pb. In majority, Pb accounted for 74% (Fig. 4) of the ecological threat in beach sediments resulting from the atmospheric deposition of dust released during the crushing and grinding of the ore to extract gold (Tirima et al., 2017).

In summary, this study accounted data on the current state of metal concentrations and enrichments along the Pacific coast of Bahia Solano and Nuquí beach sediments. Briefly, the key findings include the presence of Co, Cr, Cu, Pb, Zn and V at elevated levels, among which Pb exhibits significant ecological risks. The main sources of these metals are illegal gold mining and extraction processes in the Department of Chocó. However, the lack of previous studies over this region limits the comprehension and estimation of metal enrichments that occurred over the last several decades. The presented results serve as a baseline for further investigations, and this study portrays the impacts of long-term mining practices on the marine ecosystem in Colombia.

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