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# Impact of terrestrial mining and intensive agriculture in pollution of estuarine surface sediments: Spatial distribution of trace metals in the Gulf of Urabá, Colombia

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ABSTRACT

The Gulf of Urabá (northwestern Colombia) is a geostrategic region, rich in biodiversity and natural resources. Its economy is mainly based on agribusinesses and mining activities. In this research is determined the impact of these activities in bottom surface sediments of the estuary. Thus, grain size, total organic carbon, total nitrogen, carbonates, Ag, Al, Ca, Cr, Cu, Fe, Hg, Mg, Mn, Ni, Pb and Zn concentrations from 17 surface sediment samples were obtained and enrichment factors (EF) as well as geo-accumulation indices (Igeo) were calculated to determine the contamination level in the gulf. EF and Igeo values revealed that the estuary is extremely contaminated with Ag and moderately contaminated with Zn. Therefore, the observed enrichment of Ag may be explained as a residue of the extraction of gold and platinum-group metals and the enrichment with Zn associated mainly to pesticides used in banana plantations.



## 1. Introduction

Heavy metals are of particular concern worldwide due to their environmental persistence, biogeochemical recycling and ecological risks (Gonzalez-Macias et al., 2006; Nobi et al., 2010). Marine sediments are the ultimate reservoir for heavy metals in the coastal environments (Santos et al., 2005; Sin et al., 2001). Thus, contamination of estuarine sediments by trace elements is a worldwide problem, acting as sinks and sources of contaminants (Houda et al., 2011; Nasrabadi et al., 2010; Uba et al., 2009).

The spatial distribution of heavy metals in marine sediments is usually the result of both natural (i.e., parental rock weathering and climate) and anthropogenic factors (i.e., industrial wastewater, transportation, agriculture) (Morillo et al., 2004). As metal concentrations in marine sediments increase, more heavy metals will return to water bodies via chemical and biological processes (Sin et al., 2001). It is therefore essential to distinguish between natural and human sources on the accumulation of heavy metals in marine sediments.

In Colombia, most of the studies regarding mercury pollution have been focused on the gold mining (Alvarez et al., 2012a, 2012b; Cordy et al., 2011; Marrugo-Negrete et al., 2008; Olivero et al., 2002; Olivero and Solano, 1998), Mercury amalgamation process is widely used in the Urabá region (NW of Colombia) in the gold and silver mining because of the convenience, simplicity, fast results and low operating costs. Mining activities happen in the region since the Spanish colonization (Leyva, 1993) and they were intensively increased in the last century. In fact, Colombia was the largest supplier of platinum in the world market from 1916 to 1926, when its price was exceptionally high, mostly mined by the *Chocó Pacífico Mining Company* in the Condoto River, Department of Chocó located in the left side of the Gulf of Urabá (Leal León, 2009). Currently, mining continue to be the main economic activity of this Department.

Mining is responsible for soil degradation and forest clearing at a rate of approximately 3–4 ha yr-1. Artisanal mining processes (locally known as "*entables*") significantly alter the landscape and cause air, soil and water pollution. On average, each *entable* remove between 2000 and 3000 tons $yr^{-1}$ of sediments, employs approximately 35 kg $yr^{-1}$ of mercury, generates 1249 l $yr^{-1}$ of waste oil, and modifies the morphology of river beds. *Entables* are also associated with forced migration and loss of biodiversity, destruction of fragile ecosystems and the development of endemic diseases (Cújar-Couttín, 2005; Ponce Muriel, 2005). Additionally, during ore processing is produced inputs of mercury, cooper and silver to the rivers and coastal environments.

The semi-closed coastal area of the Gulf of Urabá (Fig. 1) is an estuary rich in natural resources, with a wide diversity of ecosystems (such

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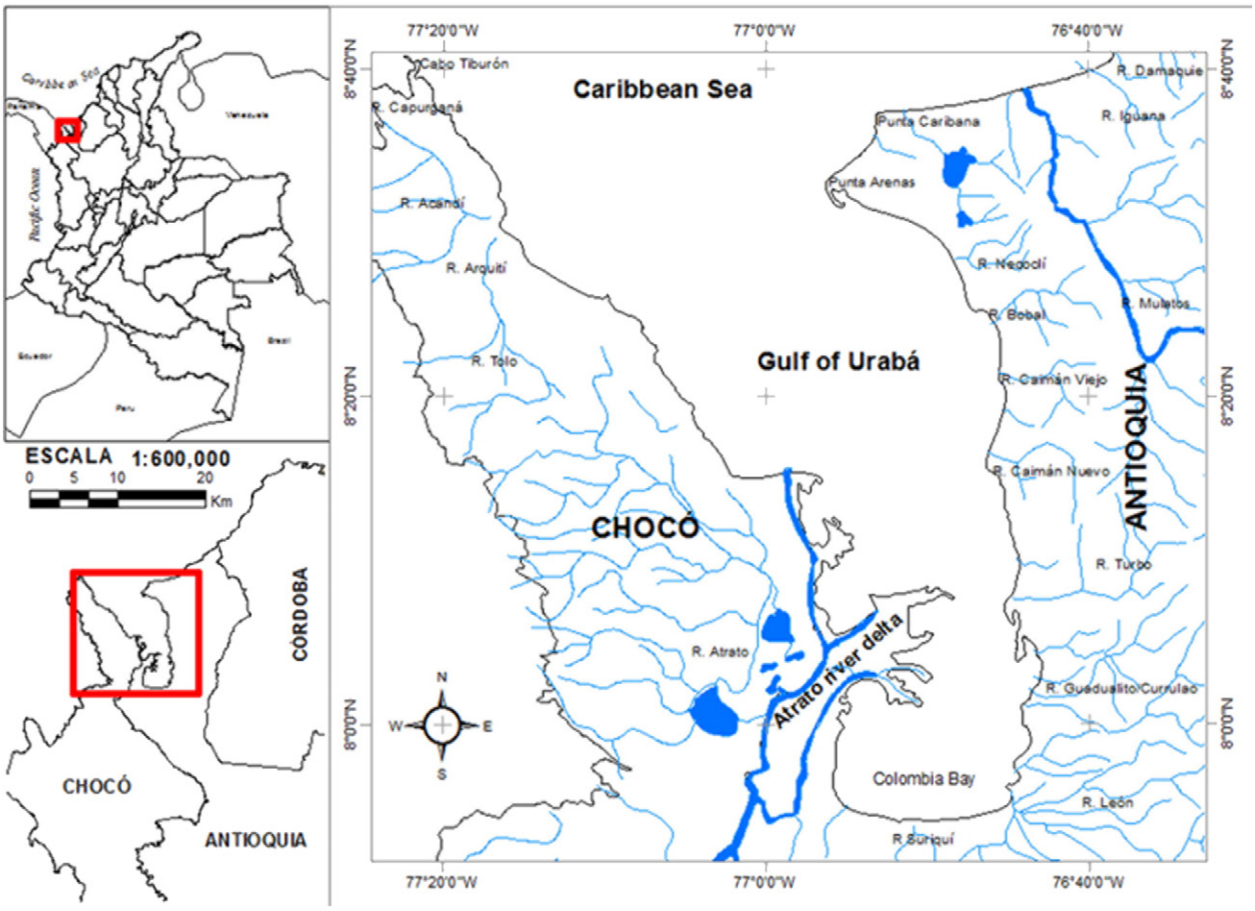


**Fig. 1.** Study area.

as mangroves and coastal lagoons) that are highly productive, breeding many aquatic resources that are the subject of artisanal and industrial fishery (Zamora and García Valencia, 2007).

In the western side of the gulf flows the Atrato River, which crosses the Chocó region that is one of the main areas devoted to gold mining in Colombia (Díaz and Gómez, 2000) carrying with all the pollutants derived from this process.

Moreover, in the eastern side of the gulf flow several small rivers: León River receiving the input of pollutants coming from the banana plantations, which play a very important role in the economy of the region; Turbo River supplying contamination due to both urban sewage and banana plantations too; and Caiman River, carrying the contaminants associated to extensive cattle raising activities (Garay et al., 2001; Zamora and García Valencia, 2007). The input of sediments and pollutants coming from these rivers are later modulated by the estuarine circulation in the gulf.

This study assesses the impact of mining and intensive agriculture activities in the Gulf of Urabá, by the analysis of trace metals concentration in their bottom surface sediments, considering not only the relationship with this activities, but also the locations of the inputs of pollutants, the circulation patterns and the grain size distribution of sediments. This approach will help to evaluate the impact of human activities and the potential ecological risks of trace metals on coastal areas as the result of to combine anthropogenic forcing and oceanographic processes.

## 2. Study area

The Gulf of Urabá is located on the southern Caribbean Sea, between latitudes 7°54′N–8°40′N and longitudes 76°53′W–77°23′W, with a total length of 80 km (Fig. 1). It has a maximum width of 48.5 km and an average depth of 25 m (Garcia Valencia and Sierra Correa, 2007). The Gulf of Urabá is characterized by a muddy bottom due to the strong sediment loads supplied by rivers (Chevillot et al., 1993).

In its southwestern flank flows out the Atrato River, which is considered one of the greatest in the world according to its ratio between water discharge and basin area, with a length of 650 km, and discharges in average 81.08 $km^3\ year^{-1}$ of water and $11.3 \times 10^6$ t $year^{-1}$ of sediments, being the second one with more sediments supply into the Caribbean Sea (Restrepo and Kjerfve, 2000).

The Atrato River has formed a delta of approximately 400 $km^2$ that currently isolates the southern part of the gulf known as Colombia Bay, which maintains communication with the rest of the Gulf through a 5.9 km passage at its narrow-gauge (Velásquez, 2005).

Besides Atrato River, there are others important rivers in the eastern margin, such as León River in the inner southeastern, flowing into Colombia Bay and discharging in average 2.01 $km^3\ year^{-1}$ of water and $7.7 \times 10^5$ t $year^{-1}$ of sediments (Restrepo and Kjerfve, 2000), Caimán Viejo, Caimán Nuevo and Turbo River which have a lesser water flow, but may have a local influence especially in coastal geomorphology (Álvarez Láinez, 2008; Alvarez Laínez and Bernal Franco, 2007; Bernal Franco et al., 2005a; Correa, 1992).

The dynamics of the gulf is mainly influenced by solid and liquid discharges from tributaries, winds, waves, tides, and density gradients (Escobar, 2011; Lonin and Vasquez, 2005; Montoya, 2010). These factors are different during the dry (December to April) and rainy (May to November) seasons, which occur in the area as a response of the latitudinal migration of the Intertropical Convergence Zone (Hastenrath, 1990).

Marine circulation in the Gulf of Urabá follows a complex circulation pattern, comprising simultaneously typical estuarine circulation, one- to three-layer flows, and even inverse circulation. (Escobar et al., 2015) (Fig. 2).

## 3. Materials and methods

### 3.1. Sampling

A total of 17 surface sediment samples were collected on board R/V ARC-Quindío in December 2009, with an Ekman-type box corer (Fig. 3). The whole recollected samples were stored and freeze-dried following the procedures established by Loring and Rantala (1992).

### 3.2. Laboratory analysis

Standard sieve and pipette methods were employed to the sediment grain size analysis (Galehouse, 1971). The samples were classified according to the percentage of clay, silt and sand after the textural diagram of Folk (1974).

For the successive analysis, a portion of each sediment sample was ground to powder with a porcelain mortar and stored in polyethylene bags. Therefore, results of all analyses are referred to dry sediment weights in grams.

For the analysis of TOC, the sediment sample was oxidized with a mixture of $K_2Cr_2O_7 + Ag_2SO_4 + H_2SO_4$ and the excess was back-titrated with $Fe(NH_4)_2(SO_4)_2$ (Loring and Rantala, 1992). Total Nitrogen (TN) was determined using the Kjeldahl modified method according to NTC 370 (ICONTEC, 1997). Carbonates were determined using a Bernard's calcimeter, adding concentrated HCl and measuring the amount of $CO_2$ generated during the reaction (Guitián and Carballas, 1976; Ospina-Hoyos et al., 2014).

Metal analyses (Ag, Al, Ca, Cr, Cu, Fe, Mg, Mn, Ni, Pb and Zn) were performed by atomic absorption spectrophotometry in 0.5 g of dry sediment samples after digestion in closed Teflon PFA containers on a hot plate (~120 °C overnight) using a mixture of 5:4:1 $HNO_3$:HCl:HF (Loring and Rantala, 1992). Hg was analyzed after reduction with SnCl2 in a Cold Vapor Atomic Absorption Mercury Analyzer (Buck Scientific™). Accuracy and analytical precision of metal analyses were evaluated through six replicates of the certified reference material PACS-2, of the National Research Council of Canada.

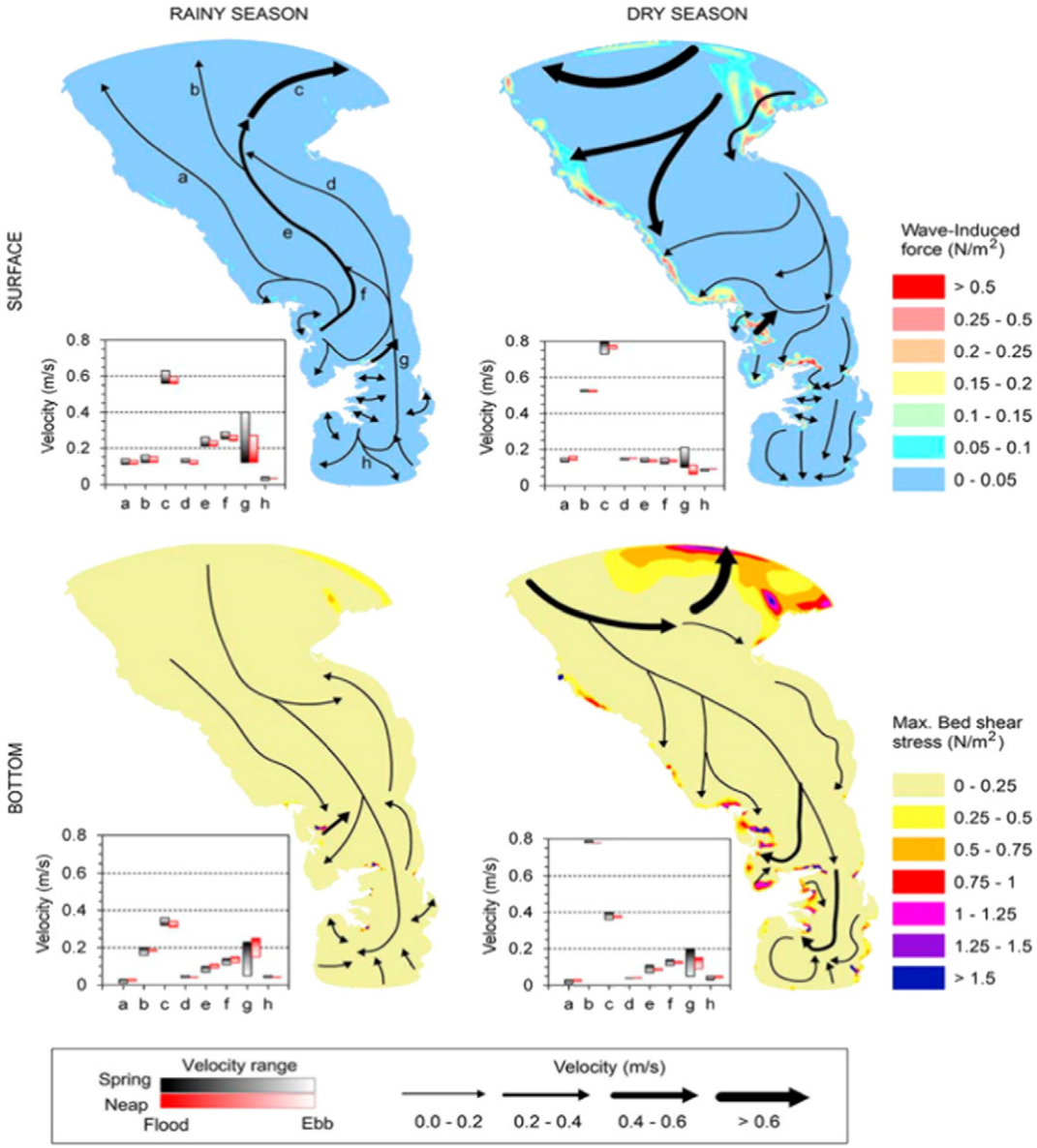


**Fig. 2.** Circulation pattern after Escobar et al. (2015).

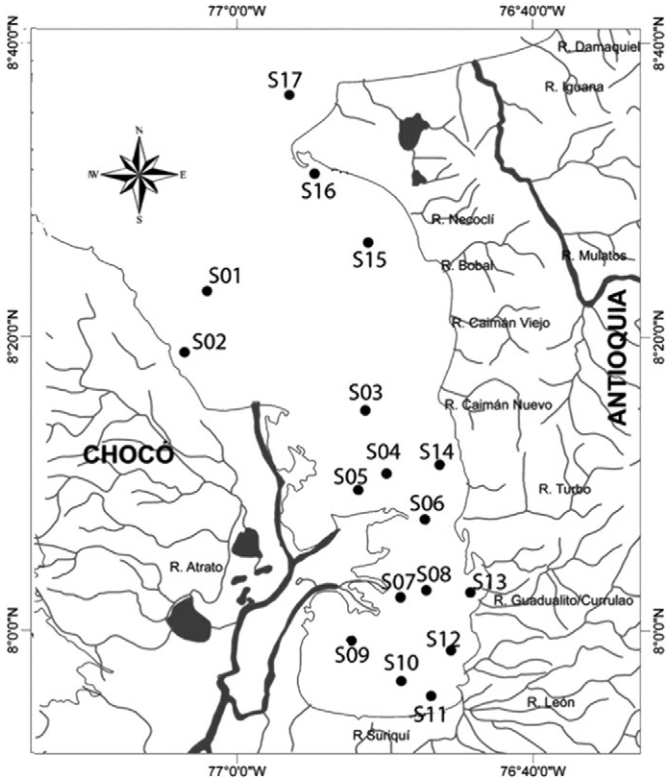


**Fig. 3.** Location of the sampling sites.

### 3.3. Data processing

#### 3.3.1. Sediments and organic matter origin

The C/N and N/C ratios were calculated to identify the source of organic matter in the sediments as well as the fraction of terrestrial organic carbon (Fter) (Biscara et al., 2011; Perdue and Koprivnjak, 2007; Tyson, 1995).

$$F_{ter} = \frac{X_s - X_m}{X_t - X_m} \times 100 \quad (1)$$

Where Xs is the calculated N/C ratio for each sample; Xm and Xt correspond respectively to the marine and terrestrial values for the N/C ratio taken from the available literature. According to Perdue and Koprivnjak (2007), terrestrial OM is relatively depleted in nitrogen, and the fraction of terrestrially derived organic carbon is underestimated by the C/N ratio. Thus results that were interpreted as the fraction of terrestrial derived carbon should be re-interpreted as the fraction of terrestrially derived nitrogen. Therefore, the N/C ratio was preferentially used.

For this estimation, the value used for terrestrial N/C = 1/30 has been reported for equatorial forests (Hedges et al., 1986). Therefore, it is considered representative of the gulf of Urabá main tributaries watersheds, while the value used for marine N/C = 1/6 has been reported for phytoplankton and zooplankton (Meyers, 1994). Additionally, the Fe/Ca ratio was determined to evaluate the input of terrigenous versus marine material (Govin et al., 2012).

#### 3.3.2. Geochemical indices of sediment pollution

Metal enrichment factors (EF) are commonly used to identify metal concentrations that are of environmental concern (GIPME, 1999) and to understand whether certain heavy metals are present in high concentrations relative to the concentrations in the Earth's crust (Salomons and Förstner, 1984; Szefer et al., 1996). This approach is based on the assumption that certain elements may represent proxies for the clay mineral concentration, considering both, aluminum and iron as conservative elements (Kersten and Smedes, 2002). EF was calculated by using the ratio between the metal concentration of the sample and the average background metal concentration of the Earth's crust (Salomons and Förstner, 1984; Szefer et al., 1996), considering for the last ones the values proposed by Taylor (1964). The normalization of elemental concentrations was done as follows (Szefer et al., 1998):

$$EF_N^M = \frac{M_s/N_s}{M_b/N_b} \quad (2)$$

where $M_s$ and $M_b$ are the examined metal contents in the sample and the reference background respectively; $N_s$ and $N_b$ are the concentration of the normalizer metal in the sample and the background reference respectively. The five-category pollution index (Sutherland, 2000) was used for the pollution assessment: EF < 2 minimal pollution; 2 < *EF* < 5 , moderate pollution; 5 < *EF* < 20, significant pollution; 20 < *EF* < 40, high pollution and *EF* > 40, extreme pollution.

An additional method to quantify metal pollution in aquatic sediments is the geo-accumulation index (Igeo) (e.g. Abrahim and Parker, 2008; Çevik et al., 2009). The Igeo is calculated using the equation (Eq.(3)) (Müller, 1979):

$$I_{geo} = log_2 \frac{M_s}{1.5\, M_b} \quad (3)$$

Where $M_s$ and $M_b$ were described above. Because Igeo is susceptible to grain size variability, values of Ms. were normalized by the clay content before Igeo index determination. The obtained values for the geo-accumulation index were classified according to Förstner et al. (1990) criteria: <0 practically unpolluted; 0–1 unpolluted to moderately polluted; 1–2 moderately polluted; 2–3 moderately to strongly polluted; 3–4 strongly polluted; 4–5 strong to very strongly polluted; and >5 very strongly polluted.

Due to the lack of local reference values for metal concentration, the Earth's crust background values were used, despite the advantages and disadvantages of its use (Abrahim and Parker, 2008), Thus, since the study area deals with mining, the local background could have naturally high concentrations of specific metals (Szefer et al., 1998). Therefore, the EF and Igeo values are assumed as the maximum values for the local context.

#### 3.3.3. Statistical analysis

A correlation analysis was applied on the entire set of data (metal concentrations, carbonates, TOC, TN and grain size fractions). The use of raw or normalized metal concentration values is selected after the correlation degree between Al (or Fe) and the clay content. Finally, a principal components analysis (PCA) was carried out, analyzing the correlation matrix to compensate the differences in the scale of the values between variables. Using R-Core-Team (2015) and the package R commander (Fox, 2005).

## 4. Results

### 4.1. General properties of sediments

The bottom surface sediments are mainly composed of silt and clay, with the sand fraction ranging from 0.02 to 15.38%, silt 28.08 to 73.34% and clay 17.07 to 71.41%, and average values of 1.84%, 45.55% and 52.61% respectively (Fig. 4). Therefore, according to their textural classification, most of the samples correspond to mud, while only three samples correspond to clay (S07, S11 and S14), one to silt (S02) and one to sandy silt (S17).

The total organic carbon (TOC) varies between 1.04 and 2.99%, total nitrogen (TN) between 0.0752 and 0.1700% and the calculated ratio C/N between 6.95 and 22.14, with average values for each determination of

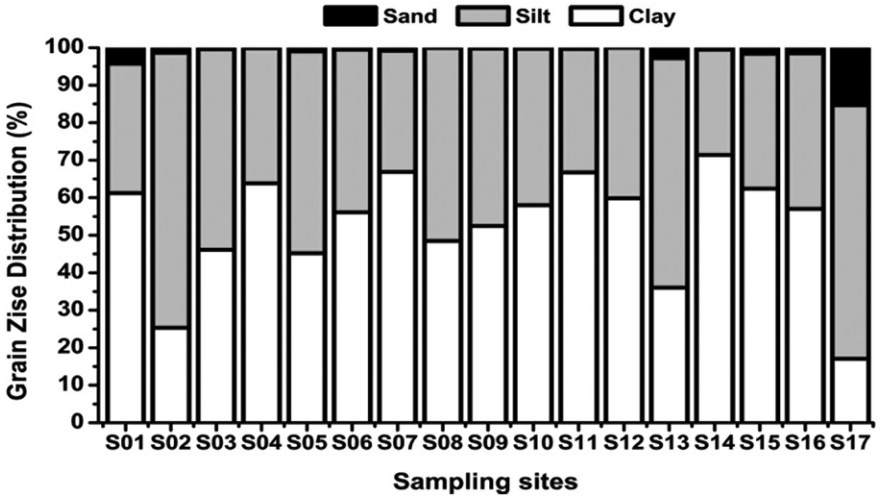


**Fig. 4.** Grain size distribution of surface sediments.

2.10%, 0.15% and 14.6 respectively (Fig. 5). Therefore, it can be deduced that most of the organic matter has a terrestrial origin, which is confirmed by the fraction of terrestrial organic carbon ($F_{ter}$), ranging from 17% to 92% with an average value of 68%.

The sediments are also characterized by low carbonates contents, ranging from 0.68 to 9.38%, with an average value of 2.12%, and by Fe/Ca ratios between 2.01 and 27.68, with an average value of 13.18 (Fig. 5), showing that most of the sediment has also a terrestrial or siliciclastic origin.

### 4.2. Sediment pollution by heavy metals

Enrichment factors calculated using Al and Fe as normalizer elements show slight differences among them, obtaining in general $EF_{Al}^{M} > EF_{Fe}^{M}$ (Table 1), Both, $EF_{Fe}^{M}$ and $EF_{Al}^{M}$ evidence that sediment samples are highly enriched with Ag ($EF_{N}^{Ag} \ll 5$), $EF_{Fe}^{M}$ show no enrichment for Zn, Cr, Cu and Hg in the entire sediment samples, while $EF_{Al}^{M}$ show a moderate enrichment for all these metals for sample S08, as well as slightly enrichment with Zn (samples S04, S12, S14 and S16) and Cr (sample S14). By the other hand, Igeo-Ag values range between 4.2 and 5.5, indicating that sediments are strongly to very strongly contaminated with silver; moderately to strongly polluted with Zn ($1 < Igeo < 3$) and moderately polluted with Cr, Cu and Hg (Table 1 and Fig. 6).

### 4.3. Statistical analyses

The correlation matrix reveals low correlation values among metals. Nevertheless, the highest positive correlations are obtained among Ag, Cr, Ni and Zn; as well as among Mn, Mg and Pb. Moreover, all metals, except Ca, show a positive correlation with clay, but a negative correlation with both sand and silt. Finally, all metals show low correlation with TOC and TN.

In particular, attending to normalizer metals, Al shows low correlation with all metals and clay content, while Fe has a slightly higher positive correlation with Cr, Cu, Zn an clay. In fact, due to this low correlation between both Al or Fe and the clay fraction ($r^2$ of 0.017 and 0.461 respectively), normalization procedure was considered not adequate, since it does not represent the changes due to grain size of sediments.

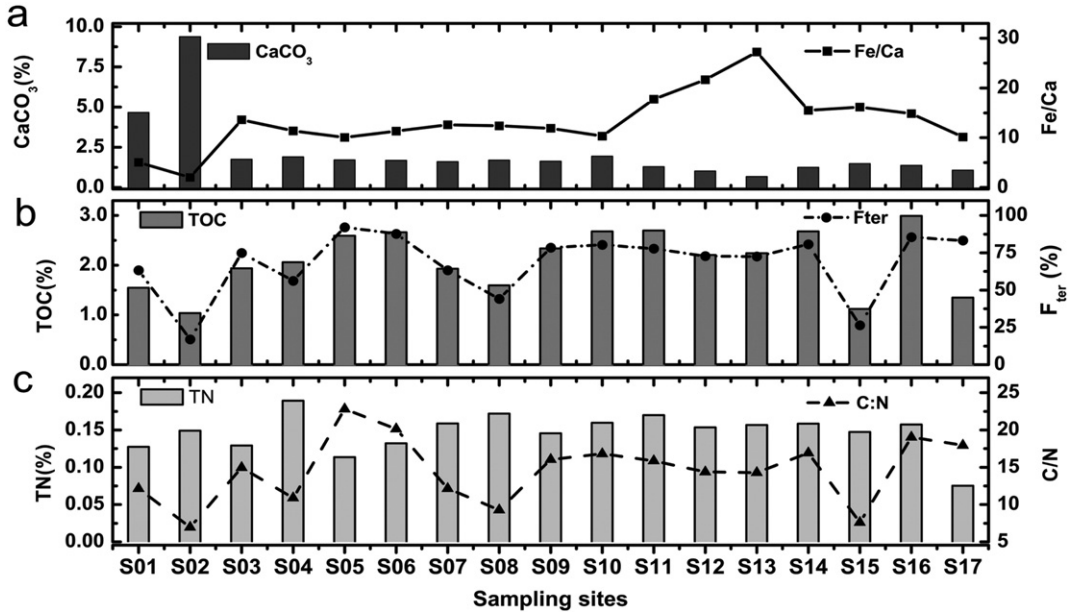


**Fig. 5.** Composition of sediments. a) Carbonates percentage and Fe/Ca ratio b) Total organic carbon and terrestrial fraction c) total nitrogen percentage and C/N ratio.

**Table 1**
Metal concentration (μg $g^{-1}$, *%), enrichment factor (EF) and geo-accumulation index (Igeo) for the surface sediments of the Gulf of Urabá.

| Metal concentration | | | | Geochemical index | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Background | | Sediment samples | | Enrichment factor | | | | Geoaccumulation index | |
| | | Range | Mean ± SD | $EF_{Al}$ | Mean ± SD | $EF_{Fe}$ | Mean ± SD | $I_{Geo}$ | Mean ± SD |
| Ag | 0.07 | 0.59–2.18 | 1.61 ± 0.42 | 8.43–39.20 | 20.9 ± 7.64 | 10.19–24.11 | 16.18 ± 4.32 | 4.21–5.53 | 4.81 ± 0.81 |
| *Al | 8.23 | 6.18–13.42 | 9.47 ± 1.81 | N.A. | N.A. | 0.51–1.28 | 0.82 ± 0.20 | N.A | N.A |
| *Ca | 4.15 | 0.27–3.75 | 0.85 ± 0.81 | 0.05–0.98 | 0.19 ± 0.22 | 0.08–0.68 | 0.14 ± 0.14 | N.A | N.A |
| Cr | 100 | 109.61–212-45 | 181.45 ± 29.16 | 1.05–2.64 | 1.63 ± 0.43 | 0.88–1.52 | 1.28 ± 0.20 | 0.50–2.10 | 1.26 ± 0.46 |
| Cu | 55 | 25.08–102.94 | 97.17 ± 18.10 | 0.46–2.05 | 1.28 ± 0.37 | 0.59–1.36 | 1.00 ± 0.19 | 0.49–1.81 | 0.89 ± 0.35 |
| *Fe | 5.63 | 4.37–9.58 | 8.06 ± 1.23 | 0.78–1.98 | 1.28 ± 0.30 | N.A | N.A | N.A | N.A |
| Hg | 0.08 | 0.001–0.136 | 0.10 ± 0.03 | 0.01–2.26 | 1.14 ± 0.48 | 0.01–1.15 | 0.88 ± 0.28 | −5.44–1.48 | 0.41 ± 1.55 |
| *Mg | 2.33 | 0.60–1.55 | 1.11 ± 0.26 | 0.22–0.76 | 0.43 ± 0.14 | 0.22–0.47 | 0.34 ± 0.07 | N.A | N.A |
| Mn | 950 | 361.92–905.47 | 647.60 ± 165.60 | 0.32–1.19 | 0.65 ± 0.24 | 0.31–0.67 | 0.50 ± 0.10 | N.A | N.A |
| Ni | 75 | 28.52–72.94 | 55.81 ± 10.77 | 0.38–1.05 | 0.67 ± 0.18 | 0.32–0.69 | 0.52 ± 0.09 | −0.76–0.57 | <0 |
| Pb | 12.5 | 0.17–6.93 | 3.81 ± 1.62 | 0.01–0.45 | 0.28 ± 0.12 | 0.01–0.40 | 0.22 ± 0.10 | −5.32–0.28 | <0 |
| Zn | 70 | 75.15–161.53 | 142.21 ± 19.72 | 1.07–2.69 | 1.82 ± 0.43 | 1.20–1.74 | 1.43 ± 0.14 | 1.02–2.15 | 1.43 ± 0.34 |

On the other hand, $CaCO_3$ and Ca show a perfect correlation, i.e. both variables represent the same information. For this reason, only $CaCO_3$ content is included as variable in the further PCA (Table 2).

Principal Components Analysis reveals two main components that explain most of the variations. Thus, the first principal component (PC.1) accounts 41.72% of the variation; when taken together with the second principal component (PC.2), this value increases to 60.52%. PC.1 indicates that Hg, Ag, Cr, Cu, Mg, Mn, Ni, Zn concentrations are directly related to the presence of clay and inversely related whit sand and silt. In the other hand, PC.2 summarizes the relative variability to Mg, Mn and Pb concentrations in the sediments, being more related with the presence of $CaCO_3$ and inversely related to the C/N and Fe/Ca ratios.

Moreover, PCA allows distinguishing among samples with a low concentration of metals (S02, S13 and S17), and the rest of samples, where samples S17 and S13 are associated with a higher content of sand, while sample S02 is associated with a higher content of silt and carbonates, as well as the lowest values of the C/N and Fe/Ca ratios (Fig. 7).

## 5. Discussion

### 5.1. Spatial distribution of metals

Bottom surface sediments of the Gulf of Urabá show the presence of heavy metals, due to both a lithogenic and anthropogenic origin. Thus, the concentrations of Pb and Ni are in accordance with background levels in the crust, which means that there is not a contamination in the area by these metals. In contrast, values of Ag, Zn, Cr, Cu and Hg show evidences of pollution due to human activities.

The Geology of the study area is complex (Chevillot et al., 1993), and consequently source areas of sediments to the gulf present different lithology, which favors different ratios among metal concentrations for different samples or sectors. This fact, combined with the diverse anthropic activities in the region, determines that distribution of pollutants is not homogeneous along the study area, and consequently explains the low values of the correlation matrix among them when the whole study area is considered (Table 2).

The northwestern sector of the gulf is characterized by sediments with high content of carbonates. Thus, samples S01 and S02 are characterized by high PC.2 and low PC.1 values, with high negative loadings of $CaCO_3$, Mg, Mn and Pb. These metals are known to have high affinity for the carbonates and possibly they have been incorporated into biogenic calcareous components, due to the structure of $CaCO_3$ (calcite or aragonite) can easily replace cations $Ca^{2+}$ by cations $Mg^{2+}$, $Mn^{2+}$, and $Pb^{2+}$ (Boyle, 1994; Mottl et al., 1998). The local source that has probably contributed to the supply of carbonates are the coral reefs fringing and patch, which cover an area of 3.5 $km^2$ along the coast of the northwestern margin of the gulf, near the Panama border (Díaz and Gómez, 2000). This sector is not influenced close to the coast (sample S02) by the main rivers of the region, but by water masses coming from the Panama crosscurrent (Chevillot et al., 1993).

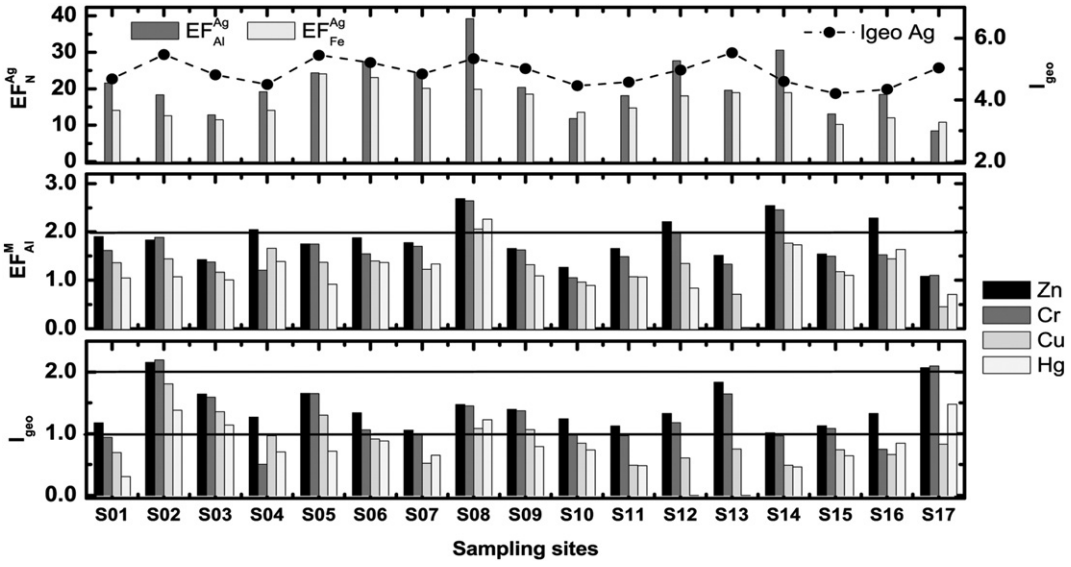


**Fig. 6.** Enrichment factors and geo-accumulation index for Ag, Zn, Cr, Cu, and Hg for surface sediments from Gulf of Urabá.

**Table 2**
Pearson correlation matrix for the sedimentary variables from Gulf of Urabá.

| | Al | Ag | Ca | Cr | Cu | Fe | Hg | Mg | Mn | Ni | Pb | Zn | TOC | TN | CaCO3 | Sand | Silt | Clay |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Al | 1.000 | | | | | | | | | | | | | | | | | |
| Ag | −0.109 | 1.000 | | | | | | | | | | | | | | | | |
| Ca | −0.218 | −0.217 | 1.000 | | | | | | | | | | | | | | | |
| Cr | 0.164 | 0.653 | −0.055 | 1.000 | | | | | | | | | | | | | | |
| Cu | 0.245 | 0.484 | 0.056 | 0.543 | 1.000 | | | | | | | | | | | | | |
| Fe | 0.269 | 0.297 | 0.048 | 0.506 | 0.697 | 1.000 | | | | | | | | | | | | |
| Hg | 0.002 | 0.181 | −0.056 | 0.251 | 0.704 | 0.430 | 1.000 | | | | | | | | | | | |
| Mg | 0.131 | 0.171 | 0.413 | 0.151 | 0.619 | 0.486 | 0.644 | 1.000 | | | | | | | | | | |
| Mn | −0.232 | 0.260 | 0.335 | 0.463 | 0.407 | 0.540 | 0.504 | 0.662 | 1.000 | | | | | | | | | |
| Ni | 0.199 | 0.725 | −0.281 | 0.431 | 0.778 | 0.464 | 0.455 | 0.336 | 0.077 | 1.000 | | | | | | | | |
| Pb | −0.058 | 0.001 | −0.013 | 0.136 | 0.163 | 0.095 | 0.457 | 0.424 | 0.611 | −0.124 | 1.000 | | | | | | | |
| Zn | 0.204 | 0.656 | −0.221 | 0.561 | 0.825 | 0.778 | 0.462 | 0.364 | 0.350 | 0.834 | 0.039 | 1.000 | | | | | | |
| TOC | 0.191 | 0.407 | −0.509 | 0.128 | 0.241 | 0.022 | 0.172 | −0.143 | −0.218 | 0.552 | −0.198 | 0.525 | 1.000 | | | | | |
| TN | −0.031 | 0.367 | −0.022 | 0.221 | 0.508 | 0.601 | 0.343 | 0.393 | 0.237 | 0.520 | −0.105 | 0.675 | 0.251 | 1.000 | | | | |
| CaCO3 | −0.218 | −0.217 | 1.000 | −0.055 | 0.056 | 0.048 | −0.056 | 0.413 | 0.335 | −0.281 | −0.013 | −0.221 | −0.509 | −0.022 | 1.000 | | | |
| Sand | −0.169 | −0.647 | −0.033 | −0.659 | −0.824 | −0.707 | −0.458 | −0.473 | −0.415 | −0.721 | −0.045 | −0.887 | −0.396 | −0.757 | −0.033 | 1.000 | | |
| Silt | −0.104 | −0.387 | 0.401 | −0.310 | −0.498 | −0.583 | −0.553 | −0.324 | −0.366 | −0.541 | −0.323 | −0.696 | −0.410 | −0.478 | 0.401 | 0.441 | 1.000 | |
| Clay | 0.132 | 0.494 | −0.339 | 0.430 | 0.635 | 0.679 | 0.592 | 0.397 | 0.419 | 0.646 | 0.291 | 0.821 | 0.453 | 0.600 | −0.340 | −0.628 | −0.975 | 1.000 |

The rest of the gulf is characterized by sediments with significant high concentration of Ag, Cr, Cu, Hg and Zn, associated with the clay content according to the PCA. In fact, higher concentration values are located in zones of maximum fluvial influence (samples S08, S12 and S14) characterized by clayey facies enriched with organic matter. This is in accordance with Thomas et al. (2007), who reported that clay distribution is well represented in the eastern sector of the gulf, reaching up 90%, and Colombia Bay, with values until 60%.

Inside this sector, sample S13 presents a particular behavior. Thus, it has a high sand content, due to it was collected in a very shallow environment (4 m depth). This is in agreement with the presence of sand close to the shoreline in both the eastern and western margin of the gulf (Thomas et al., 2007) Moreover, it presents the highest Fe/Ca ratios and the lowest carbonate content, which indicate that both, its sediments and organic matter have a continental origin. Furthermore, the PCA shows that sample S13 is associated with sand and silt by the PC.1, and associated with C/N and Fe/Ca by the PC.2. Therefore, it confirms that concentration of pollutants is lower close to the shoreline of the gulf, where the percentage of the sandy fraction increases.

The northeastern margin of the gulf (sample S17), located between Punta Arenas and Punta Caribaná, is characterized by the coarsest sediments (highest percentages of sand) and the lowest metal concentrations, with negative PC.1 and low PC.2 values. High sand concentrations is due to this area presents high coastal erosion and low influence of the rivers (Bernal Franco et al., 2005b; Correa-Arango et al., 2005). This sample is not correlated with pollutants in the PCA. However, it shows evidence of enrichment by silver after the EF, as well as by Ag, Zn, Cr and Hg after the Igeo. Take into account its location, it evidences that a proportion of the polluted sediments can leave the estuary. Consequently, the coral reef recently identified in front of Punta Caribaná (Barranco et al., 2015; Correa et al., 2015) could be affected by pollutants coming from the gulf of Urabá, similarly to the drastic impact in Rosario Island reefs (Colombian Caribbean) due to continental Canal del Dique outputs (Restrepo et al., 2016). Moreover, in accordance with Mahiques et al. (2016), it could represent a neglected output of pollutants off the estuary.

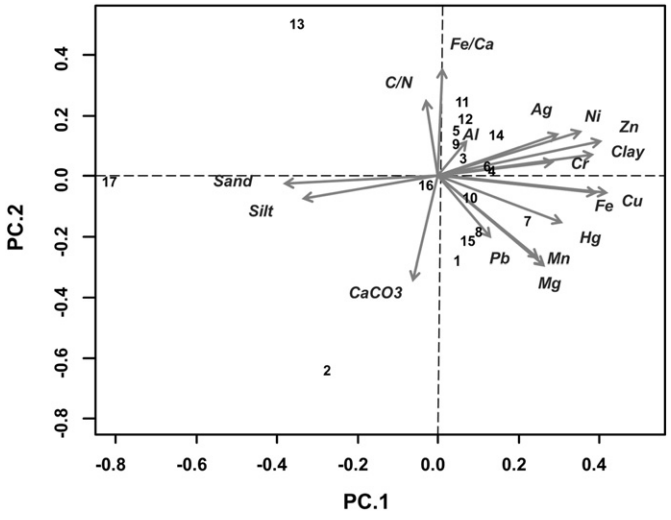


**Fig. 7.** Results of PCA applied to 17 sedimentary variables.

This heterogeneous distribution of pollutants in the gulf is influenced by factors such as the rivers mouths location, due to they work as a point source of the contaminants, and the circulation patterns, which are complex and show different behaviors across the entire gulf, being the estuarine circulation predominant (Escobar et al., 2015).

### 5.2. Lithogenic versus anthropogenic sources of metals

All the sediment samples from the Gulf of Urabá contain terrigenous particles that are originated from weathering of crustal continental rocks and transported by rivers as suspended load (Velásquez, 2005). Chlorite is one of the most abundant clay phyllosilicate and corresponds to sediments from the Mandé and Santa Cecilia La X batholith complex, coming either via the Atrato and León rivers or carried along the gulf's west coast (Téllez-Arjona, 2006). Chlorite displays a wide composition range that can be described in terms of its major cations Si and Al. Other components that commonly occur in minor amounts in the tetrahedron representation of chlorite are Fe (Chamosite), Mg (Clinochlore), Ni (Nimite) and Mn (Pennantite) (De and Walshe, 1993; Vidal et al., 2001). The relative strong correlation shown in the PC.1 among the metals described above (Fe, Mg, Mn and Ni) may be indicative of the presence of these minor cations in the silicate lattice of the Chlorite.

Mg, Mn, Ni and Pb, with the EF < 1, are metals that can be commonly attributed to lithogenic components of the gulf, but the separation observed for these elements in PCA may indicate a retention of metals controlled by the mechanisms of co-precipitation or incorporation of metals into the crystalline mesh of carbonates (Mucci and Edenborn, 1992; Tessier et al., 1979).

Usually Ag, Cr, Cu, Hg and Zn concentrations for the surface sediments range between several-fold greater than and one-third of the global mean values for the Earth' crust (Gast, 1960; Nockolds and Allen, 1956; Rader et al., 1963; Turekian, 1963; Turekian and Wedepohl, 1961; Vinogradov, 1962). Some studies have explained that their sources are closely related to industrial activities (e.g. Pekey, 2006; Garcia et al., 2008). However, likely this is not the case for the

Gulf of Urabá; due to metals concentrations are relatively high in surface sediments around the mouths of the Atrato River (Fig. 3). Moreover, these high concentrations of metals are highly related to clays, according to the PCA (Fig. 6). These relationships indicate that these metals come mainly from the drainage area of the main rivers.

Zn comes from the aerial application of Zn-pesticide, as Mancozeb (-$SCSNHCH_2CH_2NHCSSMn$-) × (Zn), in the banana and plantain crops, which represent 35.000 ha in the Gulf of Urabá (AUGURA, 2011). Given that the dose of this product (concentration 80%, 2% w/w of Zn) varies between 2 and 2.5 kg $ha^{-1}$ per cycle, the annual input of Zn to the soils ranges between 1400 and 1750 kg $ha^{-1}$, which are potentially exposed to be transported by the river sediment loads to the estuary.

Mining activities are other important source of Zn. Currently there are two precipitation processes to retrieve the gold dissolved in the cyanide process: cementation with zinc powder and electro-deposition with cyanide solutions, using coal activated carbon, ion exchange resins or organic solvent extraction (Rees and Van Deventer, 2000; Stanley, 1987). Many metals extracted in this process such as Zn, Cu, Fe, are released into the environment in their elemental forms, which subsequently will join the organic matter. Gold extractive practices, which include amalgamation, percolation cyanidation and precipitation with zinc wood, are still very informal in the area, with low levels of technology and few environmental controls.

Copper (Cu) is a common contaminant in coastal waters, particularly in industrialized bays, fjords and estuaries (Salomons and Förstner, 1984). Cu is also used in antifouling paints and for impregnation of nets used in fish farming. Because of its widespread use, Cu is one of the most common environmental pollutants (Sadiq, 1992). Copper ions readily form complexes with organic materials and also bind to particles of sediment. Therefore, much of the copper entering coastal environments will be incorporated into the sediments of those environments (Bryan and Langston, 1992). In areas where the input of Cu from anthropogenic sources is low or nonexistent, sediment generally contains <50 μg $g^{-1}$ of Cu, whereas the level can reach several thousand ppm in polluted areas (Harrison et al., 1984). Cu levels in sediment from 17 sites along the coastal area of Urabá ranged between 25.08 and 103 μg $g^{-1}$ with an average value of 79.17 ± 18.10 μg $g^{-1}$. These levels reflect the anthropogenic input as well as the mineral content of the regional bedrock. Given the development of small-scale mining of copper, gold, silver and platinum group metals in the zone, Cu could be an important source of pollution. However, the Cu concentrations found in sediments are not high enough to be toxic (200–2000 mg $kg^{-1}$ dry weight) to aquatic animals, including meio- and macrofauna (Austen and Somerfield, 1997; Morrisey et al., 1995).

### 5.3. Relationships with the mining activities

A complete discussion of the metals concentrations found in the sediments, their possible sources, their enrichment factors and geochemical indexes, and their relation to anthropogenic sources, cannot be fully understood without considering the regional context of the Colombian Darien, where for centuries, the gold and platinum mining tradition has been the primary form of sustenance in the Chocó region.

High levels of total Ag in the surface sediments found in our research, characterized by Igeo and EF ≫ 1 suggest a significant anthropogenic input for this metal, which has been primarily associated with the discharges of untreated urban wastewater (Bryan and Langston, 1992; Hornberger et al., 1999). No other source is clearly identified for this element. Although sediment quality criteria for Ag have not yet been promulgated in Colombia, the EF-Ag and Igeo values obtained in this study lead us to conclude that moderate to significant enrichment of Ag is occurring in the study area. The observed enrichment of Ag may be caused by the different clay mineral compositions in regional soils that have relatively high Ag background (Feng et al., 2011), which may indicate contaminants from the refining of the platinum group metals (Alguacil, 1995; Alguacil et al., 1997).

Previous research has demonstrated that heavy metals such as Cu, Pb, Zn, Cd, Ag, As, Hg, Sb, and Bi are released from mining and processing of gold-bearing sulphide minerals (Prieto, 1998). The main sources of these elements are acid mine drainage, tailings and erosion of waste rock deposits (Salomons, 1995).

The traditional refining processes of platinum group metals are based on their chemical properties, especially by the change in their oxidation states and coordination of their complexes in acid with chlorides (Alguacil, 1995; Lo et al., 1983). $HCl/Cl_2$ is used as leaching agent of these metals (Renner et al., 1992). These processes can extract all platinum group metals except Ag, which remains in the insoluble fraction and its discharged in the environment (Alguacil et al., 1997; Xue et al., 1984). Ag is discarded in this type of mining because of its low economic value compared with platinum group metals (palladium, rhodium, ruthenium, iridium and osmium) and gold. Also, the extraction from the insoluble phase involves additional steps, making the process more expensive.

In particular, the dominant adsorption processes cause a transfer of the dissolved metals to the suspended matter and deposited sediments. Thus, the fact that sediments from the Gulf of Urabá are enriched in Ag and particulate matter reflects the impact of mining activities and reveals the contribution of platinum group metals. Therefore, in this study we suggest the use of Ag as a proxy of pollution by platinum mining activities.

Alternatively, mercury (Hg) is used by small-scale gold miners in more than 50 locations in Antioquia and Chocó. These miners release Hg into the environment affecting human health and the ecosystem. The release of material contaminated with mercury into the rivers produces a local accumulation of this metal near the discharge site.

## 6. Conclusions

Bottom surface sediments of the Gulf of Urabá have shown the presence of heavy metals. The content of Mg, Mn, and Pb in the sediment of the Gulf of Urabá shows background levels, which indicate that they are not derived from anthropogenic sources. Their association with $CaCO_3$ content supports their common natural origin. In contrast, high concentration of silver, with moderate to significant EF and high $I_{geo}$ values is directly related to contamination from the refining of the platinum group metals, coming mainly by the Atrato River. In addition, there is a slight pollution with Cr and Zn (and also Cu and Hg in some areas of the Gulf), which are mainly attributed to anthropogenic activities and supplied mainly by the principal rivers (Atrato and León). Therefore, the main source of high concentrations of Ag and Zn are the mining activities, while a second source of Zn is due to intensive agricultural, being the rivers discharge the main input areas of pollutants to the Gulf of Urabá.

Distribution of pollutants in the gulf is influenced by three main factors: the location of the rivers mouths, which determines the inputs of pollutants to the gulf; the marine currents patterns that distribute them; and the grain size distribution, due to pollutants concentrations are mainly associated to the sedimentation of the clay fraction. Thus, the gulf acts as a sink for pollutants, because the clays are mainly deposited on its bottom surface. Nevertheless, there is also a minor output of contaminants through the northeastern margin of the gulf, due to the marine currents pattern.

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## References


Abrahim, G., Parker, R., 2008. Assessment of heavy metal enrichment factors and the degree of contamination in marine sediments from Tamaki Estuary, Auckland, New Zealand. Environ. Monit. Assess. 136 (1–3), 227–238.

Alguacil, F., 1995. El refino de los metales del grupo del platino. Rev. Metal. 31 (4), 246–255.

Alguacil, F.J., Cobo, A., Coedo, A., Dorado, M., Sastre, A., 1997. Extraction of platinum (IV) from hydrochloric acid solutions by amine alamine 304 in xylene. Estimation of the interaction coefficient between PtCl62-and H+. Hydrometallurgy 44 (1–2), 203–212.

Álvarez Láinez, A.M., 2008. Estudio del Transporte de Sedimentos Superficiales en El Piso Marino del Golfo de Urabá. Magíster en Ingeniería — Recursos Hidráulicos. Universidad Nacional de Colombia, sede Medellín.

Alvarez Laínez, A.M., Bernal Franco, G., 2007. Estimación del Campo de Transporte Neto de Sedimentos en El Fondo de Bahía Colombia Con Base en análisis de Tendencia del tamaño de Grano. Avances en Recursos Hidráulicos 16, pp. 41–50.

Alvarez, S., Jessick, A.M., Palacio, J.A., Kolok, A.S., 2012a. Methylmercury Concentrations in Six Fish Species from Two Colombian Rivers. Bull. Environ. Contam. Toxicol. 1–4.

Alvarez, S., Kolok, A.S., Jimenez, L.F., Granados, C., Palacio, J.A., 2012b. Mercury Concentrations in Muscle and Liver Tissue of Fish from Marshes Along the Magdalena River, Colombia. Bull. Rnviron. Contam. Toxicol. 1–5.

AUGURA, 2011. Experiencias en BPA Y protección del Medio Ambiente: Asociación de Bananeros de Colombia AUGURA: GEFREPCar.

Austen, M., Somerfield, P., 1997. A community level sediment bioassay applied to an estuarine heavy metal gradient. Mar. Environ. Res. 43 (4), 315–328.

Barranco, A., Díaz de Rada, J., Ospina, J.B., Sánchez, D., Rey, J., Correa, I.D., 2015. Identificación de Las Unidades Sismodeposicionales Cuaternarias en la Plataforma Interna del Litoral Oriental del Golfo de Urabá: El Rol de Los Factores morfológicos, Estructurales y Eustáticos. Proceedings XV Colombian Conference of Geology, Bucaramanga (Colombia), pp. 497–500.

Bernal Franco, G., Montoya, L.J., Garizábal, C., Toro Botero, F.M., 2005a. La Complejidad de la dimensión física en la problemática costera del golfo de Urabá, Colombia. Gestión y ambiente 8, 123–135.

Bernal Franco, G., Toro Botero, M., Montoya Jaramillo, L.J., Garizábal, C., 2005b. Estudio de la dispersión de Sedimentos del Río Atrato y Sus Impactos Sobre la Problemática Ambiental Costera del Golfo de Urabá: Informe Final de investigación.

Biscara, L., Mulder, T., Martinez, P., Baudin, F., Etcheber, H., Jouanneau, J.-M., Garlan, T., 2011. Transport of terrestrial organic matter in the Ogooué deep sea turbidite system (Gabon). Mar. Pet. Geol. 28 (5), 1061–1072.

Boyle, E., 1994. Isotopic and elemental tracers in calcium carbonate fossils. Min. Mag. 58 A, 111–112.

Bryan, G., Langston, W., 1992. Bioavailability, accumulation and effects of heavy metals in sediments with special reference to United Kingdom estuaries: a review. Environ. Pollut. 76 (2), 89–131.

Çevik, F., Göksu, M.Z.L., Derici, O.B., Fındık, Ö., 2009. An assessment of metal pollution in surface sediments of Seyhan dam by using enrichment factor, geoaccumulation index and statistical analyses. Environ. Monit. Assess. 152 (1–4), 309–317.

Chevillot, P., Molina, A.L.G., Molina, C., 1993. Estudio geológico e hidrológico del golfo de Urabá. Bol. Cient. CIOH 14, 79–89.

Cordy, P., Veiga, M.M., Salih, I., Al-Saadi, S., Console, S., Garcia, O., Mesa, L.A., Velásquez-López, P.C., Roeser, M., 2011. Mercury contamination from artisanal gold mining in Antioquia, Colombia: the world's highest per capita mercury pollution. Sci. Total Environ.

Correa, I.D., 1992. Erosión Y sedimentación Litoral de la línea de Costa Entre Turbo Y Necoclí, Golfo de Urabá, Departamento de Antioquia. Universidad Escuela de Administración, Finanzas y Tecnología (EAFIT).

Correa, J.D., Parra, F.J., Quan, L.I., Chaverra, F., Guzmán, S., 2015. Caracterización de losfondos duros biogénicos de la Punta Caribana (Necoclí, Antioquia). Technical report 400-08-01-06-1511-2015. CORPOURABA-Universidad de Antioquia, Apartadó(Antioquia).

Correa-Arango, I.D., Alcántara-Carrió, J., González, D., 2005. Historical and recent shore erosion along the Colombian Caribbean coast. J. Coast. Res. (Coastal Erosion), SI 49, 52–57.

Cújar-Couttín, O., 2005. Geología económica, Municipio del río Iró.

De, C., Walshe, L., 1993. Chlorite geothermometry: a review. Clay Clay Miner. 41 (2), 219–239.

Díaz, J., Gómez, D., 2000. Programa nacional de investigación en biodiversidad marina y costera (PNIBM): INVEMAR. FONADE y MMA, Santa Marta.

Escobar, C.A., 2011. Relevancia de procesos costeros en la hidrodinámica del golfo de urabá (caribe colombiano). Bol. Invest. Mar. Cost 40, 2.

Escobar, C.A., Velásquez, L., Posada, F., 2015. Marine currents in the Gulf of Urabá, Colombian Caribbean Sea. J. Coast. Res. 31 (6), 1363–1374.

Feng, H., Jiang, H., Gao, W., Weinstein, M.P., Zhang, Q., Zhang, W., Yu, L., Yuan, D., Tao, J., 2011. Metal contamination in sediments of the western Bohai Bay and adjacent estuaries, China. J. Environ. Manag. 92 (4), 1185–1197.

Folk, R.L., 1974. Petrology of Sedimentary Rocks.

Förstner, U., Ahlf, W., Calmano, W., Kersten, M., 1990. Sediment Criteria Development. Springer.

Fox, J., 2005. The R commander: a basic statistics graphical user Interface to R. J. Stat. Softw. 14 (9), 1–42.

Galehouse, J., 1971. Sedimentation Analysis: Procedures in Sedimentary Petrology 10 pp. 69–94.

Garay, J., Marín, B., Calvano, N., Ramírez, G., Troncoso, W., Medina, O., 2001. Diagnóstico Y evaluación de la Calidad Ambiental Marina en El Caribe Y Pacífico Colombiano. Red de Vigilancia Para la protección Y conservación de la Calidad de Las Aguas Marinas Y Costeras. Tomo II. Informe Final. INVEMAR.

Garcia Valencia, C., Sierra Correa, P.C., 2007. Un Golfo en El Caribe Colombiano. In: García-Valencia, C. (Ed.), Atlas del Golfo de Urabá: Una Mirada Al Caribe de Antioquia Y Chocó. Instituto de Investigaciones Marinas y Costeras –Invemar– y Gobernación de Antioquia, Santa Marta - Colombia.

Garcia, E., Cruz-Motta, J., Farina, O., Bastidas, C., 2008. Anthropogenic influences on heavy metals across marine habitats in the western coast of Venezuela. Cont. Shelf Res. 28 (20), 2757–2766.

Gast, P.W., 1960. Limitations on the composition of the upper mantle. J. Geophys. Res. 65 (4), 1287–1297.

GIPME, 1999. Global investigation of pollution in the marine environment. Guid. Assess. Sediment. Qual. 23 (v. IOCeUNEPeIMO).

Gonzalez-Macias, C., Schifter, I., Lluch-Cota, D., Mendez-Rodriguez, L., Hernandez-Vazquez, S., 2006. Distribution, enrichment and accumulation of heavy metals in coastal sediments of Salina Cruz Bay, Mexico. Environ. Monit. Assess. 118 (1), 211–230.

Govin, A., Holzwarth, U., Heslop, D., Ford Keeling, L., Zabel, M., Mulitza, S., Collins, J.A., Chiessi, C.M., 2012. Distribution of major elements in Atlantic surface sediments (36 N–49 S): imprint of terrigenous input and continental weathering. Geochem. Geophys. Geosyst. 13 (1).

Guitián, F., Carballas, T., 1976. Técnicas De análisis de Suelos. Pico Sacro, Santiago de Compostela, Spain.

Harrison, F.L., Knezovich, J.P., Rice, D.W., 1984. The toxicity of copper to the adult and early life stages of the freshwater clam, Corbicula manilensis. Arch. Environ. Contam. Toxicol. 13 (1), 85–92.

Hastenrath, S., 1990. Diagnostics and prediction of anomalous river discharge in the northern South America. J. Clim. 3, 1080–1096.

Hedges, J.I., Clark, W.A., Quay, P.D., Richey, J.E., Devol, A.H., Santos, U.D.M., 1986. Compositions and fluxes of particulate organic material in the Amazon River. Limnol. Oceanogr. 31 (4), 717–738.

Hornberger, M.I., Luoma, S.N., van Geen, A., Fuller, C., Anima, R., 1999. Historical trends of metals in the sediments of San Francisco Bay, California. Mar. Chem. 64 (1–2), 39–55.

Houda, B., Dorra, G., Chafei, A., Emna, A., Khaled, M., 2011. Impact of a mixed" industrial and domestic" wastewater effluent on the southern coastal sediments of Sfax(Tunisia) in the Mediterranean Sea. Int. J. Environ. Res. 5 (3), 691–704.

ICONTEC, 1997. Ntc 370 Abonos O Fertilizantes determinación de nitrógeno Total.

Kersten, M., Smedes, F., 2002. Normalization procedures for sediment contaminants in spatial and temporal trend monitoring. J. Environ. Monit. 4 (1), 109–115.

Leal León, C., 2009. The Choco Pacifico Mining Company and the Platinum Boom in Colombia, 1897–1930. Historia Crítica 39, pp. 150–164.

Leyva, P., 1993. Colombia Pacifico. 2 Vols: Bogota, DE: Fondo Para la Proteccion del Medio Ambiente. Jose Celestino Mutis. Fondo FEN.

Lo, T.C., Baird, M.H.I., Hanson, C., 1983. Handbook of Solvent Extraction. John Wiley & Sons, p. 980 (1983).

Lonin, S., Vasquez, J.G., 2005. Hidrodinámica y distribución de coliformes en el golfo de Urabá. Bol. Cient. CIOH 23, 76–89.

Loring, D., Rantala, R., 1992. Manual for the geochemical analyses of marine sediments and suspended particulate matter. Earth Sci. Rev. 32 (4), 235–283.

Mahiques, M.M., Hanebuth, T.J., Martins, C.C., Montoya-Montes, I., Alcántara-Carrió, J., Figueira, R.C., Bícego, M.C., 2016. Mud depocentres on the continental shelf: a neglected sink for anthropogenic contaminants from the coastal zone. Environ. Earth Sci. 75 (1), 1–12.

Marrugo-Negrete, J., Verbel, J.O., Ceballos, E.L., Benitez, L.N., 2008. Total mercury and methylmercury concentrations in fish from the Mojana region of Colombia. Environ. Geochem. Health 30 (1), 21–30.

Meyers, P.A., 1994. Preservation of elemental and isotopic source identification of sedimentary organic matter. Chem. Geol. 114 (3–4), 289–302.

Montoya, L.J., 2010. Dinámica oceanográfica del Golfo de Urabá Y Su relación Con Los Patrones de dispersión de Contaminantes Y Sedimentos. Magister en Aprovechamiento de Recursos hidráulicos. Universidad Nacional de Colombia – Sede Medellín (254 pp.).

Morillo, J., Usero, J., Gracia, I., 2004. Heavy metal distribution in marine sediments from the southwest coast of Spain. Chemosphere 55 (3), 431–442.

Morrisey, D., Underwood, A., Howitt, L., 1995. Development of sediment-quality criteria—a proposal from experimental field-studies of the effects of copper on benthic organisms. Mar. Pollut. Bull. 31 (4), 372–377.

Mottl, M., Wheat, G., Baker, E., Becker, N., Davis, E., Feely, R., Grehan, A., Kadko, D., Lilley, M., Massoth, G., 1998. Warm springs discovered on 3.5 Ma oceanic crust, eastern flank of the Juan de Fuca ridge. Geology 26 (1), 51–54.

Mucci, A., Edenborn, H.M., 1992. Influence of an organic-poor landslide deposit on the early diagenesis of iron and manganese in a coastal marine sediment. Geochim. Cosmochim. Acta 56 (11), 3909–3921.

Müller, G., 1979. Schwermetalle in den Sedimenten des Rheins-Veränderungen seit 1971. Umschau 79 (24), 778–783.

Nasrabadi, T., Nabi Bidhendi, G., Karbassi, A., Mehrdadi, N., 2010. Evaluating the efficiency of sediment metal pollution indices in interpreting the pollution of Haraz River sediments, southern Caspian Sea basin. Environ. Monit. Assess. 171 (1), 395–410.
Nobi, E., Dilipan, E., Thangaradjou, T., Sivakumar, K., Kannan, L., 2010. Geochemical and geo-statistical assessment of heavy metal concentration in the sediments of different coastal ecosystems of Andaman Islands, India. Estuar. Coast. Shelf Sci. 87 (2), 253–264.
Nockolds, S., Allen, R., 1956. The geochemistry of some igneous rock series–III. Geochim. Cosmochim. Acta 9 (1–2), 34–77.
Olivero, J., Solano, B., 1998. Mercury in environmental samples from a waterbody contaminated by gold mining in Colombia, South America. Sci. Total Environ. 217 (1–2), 83–89.
Olivero, J., Johnson, B., Arguello, E., 2002. Human exposure to mercury in san Jorge river basin, Colombia (South America). Sci. Total Environ. 289 (1–3), 41–47.
Ospina-Hoyos, J., Palacio-Baena, J., Vásquez-Bedoya, L., 2014. ¿ Responden los micromoluscos a los cambios ambientales durante el Holoceno tardío en el Sur del mar Caribe colombiano? Univ. Sci. 19 (3), 233–246.
Pekey, H., 2006. The distribution and sources of heavy metals in Izmit Bay surface sediments affected by a polluted stream. Mar. Pollut. Bull. 52 (10), 1197–1208.
Perdue, E.M., Koprivnjak, J.-F., 2007. Using the C/N ratio to estimate terrigenous inputs of organic matter to aquatic environments. Estuar. Coast. Shelf Sci. 73 (1), 65–72.
Ponce Muriel, A., 2005. La Minería Del Platino En Colombia, Unidad de Planeación Minero Energética – UPME.
Prieto, G., 1998. Geochemistry of heavy metals derived from gold-bearing sulphide minerals in the Marmato District (Colombia). J. Geochem. Explor. 64 (1), 215–222.
Rader, L., Swadley, W., Huffman, C., Lipp, H., 1963. New chemical determinations of zinc in basalts, and rocks of similar composition. Geochim. Cosmochim. Acta 27 (6), 695–714.
R-Core-Team, 2015. R: A Language and Environment for Statistical Computing. R Foundation for Statistical Computing, Vienna, Austria.
Rees, K., Van Deventer, J., 2000. The mechanism of enhanced gold extraction from ores in the presence of activated carbon. Hydrometallurgy 58 (2), 151–167.
Renner, H., Schlamp, G., Kleinwächter, I., Drost, E., Lüschow, H.M., Tews, P., Panster, P., Diehl, M., Lang, J., Kreuzer, T., 1992. Platinum Group Metals and Compounds: Ullmann's Encyclopedia of Industrial Chemistry.
Restrepo, J.D., Kjerfve, B., 2000. Water discharge and sediment load from the western slopes of the Colombian Andes with focus on Rio San Juan. J. Geol. 108 (1), 17–33.
Restrepo, J.D., Park, E., Aquino, S., Latrubesse, E.M., 2016. Coral reefs chronically exposed to river sediment plumes in the southwestern Caribbean: Rosario Islands, Colombia. Sci. Total Environ. 553, 316–329.
Sadiq, M., 1992. Toxic Metal Chemistry in Marine Environments.
Salomons, W., 1995. Environmental impact of metals derived from mining activities: processes, predictions, prevention. J. Geochem. Explor. 52 (1), 5–23.
Salomons, W., Förstner, U., 1984. Metals in the Hydrocycle. Springer-Verlag.
Santos, I.R., Silva-Filho, E.V., Schaefer, C.E.G.R., Albuquerque-Filho, M.R., Campos, L.S., 2005. Heavy metal contamination in coastal sediments and soils near the Brazilian Antarctic Station, king George Island. Mar. Pollut. Bull. 50 (2), 185–194.
Sin, S., Chua, H., Lo, W., Ng, L., 2001. Assessment of heavy metal cations in sediments of Shing Mun River, Hong Kong. Environ. Int. 26 (5), 297–301.
Stanley, G., 1987. The Extractive Metallurgy of Gold in South Africa. South African Institute of Mining and Metallurgy.
Sutherland, R., 2000. Bed sediment-associated trace metals in an urban stream, Oahu, Hawaii. Environ. Geol. 39 (6), 611–627.
Szefer, P., Szefer, K., Glasby, G., Pempkowiak, J., Kaliszan, R., 1996. Heavy-metal pollution in surficial sediments from the southern Baltic Sea off Poland. J. Environ. Sci. Health A 31 (10), 2723–2754.
Szefer, P., Glasby, G.P., Kusak, A., Szefer, K., Jankowska, H., Wolowicz, M., Ali, A.A., 1998. Evaluation of the anthropogenic influx of metallic pollutants into Puck Bay, southern Baltic. Appl. Geochem. 13 (3), 293–304.
Taylor, S., 1964. Abundance of chemical elements in the continental crust: a new table. Geochim. Cosmochim. Acta 28 (8), 1273–1285.
Téllez-Arjona, L., 2006. Provincias de Minerales Densos en Los Sedimentos del Fondo Marino del Golfo de Urabá [Master: Universidad Nacional de Colombia.
Tessier, A., Campbell, P.G.C., Bisson, M., 1979. Sequential extraction procedure for the speciation of particulate trace metals. Anal. Chem. 51 (7), 844–851.
Thomas, Y.F., Garcia Valencia, C., Cesaracci, M., Rojas, G.X., 2007. El Paisaje en El Golfo. In: García-Valencia, C. (Ed.), Atlas del Golfo de Urabá: Una Mirada Al Caribe de Antioquia Y Chocó. Instituto de Investigaciones Marinas y Costeras –Invemar– y Gobernación de Antioquia, Santa Marta - Colombia.
Turekian, K.K., 1963. The chromium and nickel distribution in basaltic rocks and eclogites. Geochim. Cosmochim. Acta 27 (7), 835–846.
Turekian, K.K., Wedepohl, K.H., 1961. Distribution of the elements in some major units of the earth's crust. Geol. Soc. Am. Bull. 72 (2), 175–192.
Tyson, R., 1995. Sedimentary Organic Matter. Springer, Netherlands (Organic facies and palynofacies).
Uba, S., Uzairu, A., Okunola, O., 2009. Content of heavy metals in Lumbricus Terrestris and associated soils in dump sites. Int. J. Environ. Res. 3 (3), 353–358.
Velásquez, A., 2005. Dirección de Transporte de Sedimentos Costeros en El Golfo de Urabá. Universidad Nacional, Caribe colombiano (77 pp.).
Vidal, O., Parra, T., Trotet, F., 2001. A thermodynamic model for Fe-Mg aluminous chlorite using data from phase equilibrium experiments and natural pelitic assemblages in the 100 to 600C, 1 to 25 kb range. Am. J. Sci. 301 (6), 557–592.
Vinogradov, A., 1962. Average contents of chemical elements in the principal types of igneous rocks of the earth's crust. Geochemistry 7 (1962), 641–664.
Xue, T., Osseo-Asare, K., Ciminelli, V., Kudryk, V., Corrigan, D., Liang, W., 1984. Precious Metals: Mining, Extraction and Processing: Precious Metals: Mining, Extraction and Processing.
Zamora, A.P., García Valencia, C., 2007. El Golfo: Un Espacio socioeconómico. In: García-Valencia, C. (Ed.), Atlas del Golfo de Urabá: Una Mirada Al Caribe de Antioquia Y Chocó. Instituto de Investigaciones Marinas y Costeras –Invemar– y Gobernación de Antioquia, Santa Marta - Colombia.