## Environmental Implications of Heavy Metals in Surface Sediments near Isla de Sacrificios, Mexico

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Modification to the global flux of sediments causes one of the largest environmental impacts on coastal zones. Sediments are an important sink and source for heavy metals, and play an important role in the remobilization of metals to the aquatic environment. The transfer of metals from sediments to organisms has been reported as an important metal source for many species (Zoumis et al. 2001).

"Isla de Sacrificios" is a coral island located offshore of Veracruz City, one of the most important Mexican ports in the Gulf of Mexico (Fig. 1). This area is characterized by a growing urban population and an increasing industrial development. Additionally, several rivers discharge very close to the reef ecosystem.

Coral reef ecosystems are characterized by great diversity and abundance of marine organisms. The quality of the water and sediments where these species are present is very important for healthy growth. The adverse effects of sediments with high amounts of heavy metals may produce reduced biodiversity, diminished production and even the death of certain corals (Ramos et al. 2004).

In the present study, metal concentration in surface sediments of the area surrounding Isla de Sacrificios were measured at three different seasons in order to see the spatial and temporal distribution of metals in the area, and to evaluate their potential source. The environmental risk of metals in the sediments were studied.

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## **Materials and Methods**

Isla de Sacrificios is located at 19° 10'27" north latitude and 96° 05'31" west longitude (Fig. 1), 1.56 km from the coast. Around 25 sediment samples were collected in June (dry season), October (rainy season) and February (stormy season). Samples were taken with a Van Veen dredge: sediment samples were removed from the middle part in such a way that sediments had no contact with the metallic parts of the dredge. Sediments were transferred to plastic bags and were kept at 4°C until analysis. The grain size distribution of the samples was determined using Coulter LS230 laser diffraction analyzer. Sediment samples for chemical analysis were dried at 55°C for 48 hours and homogenized in a SPEX 8000 mixer mill. Organic matter was measured by oxidation with potassium dichromate (Gaudette et al. 1974), the coefficient of variation was 2.64%. Major elements were analyzed with a Siemens XRF SRS 3000 spectrophotometer. Accuracy of the analyses was measured by the use of reference material with recovery percentages of ±2%. Trace metals were measured by flame in a Spectra AA-10 Plus Varian spectrophotometer; accuracy was determined using the MESS-3 standard and the percentages of recovery were Cu 102.5%, Cr 102%, Ni 102.4%, V 102% and Zn 98.2%. Pb was measured by GF-AAS; accuracy was measured using an HISS-1 certified standard, the percentage of recovery for Pb was 102.82%.

## **Results and Discussion**

The study area is a zone where terrigenous and carbonated sediments are mixed. Carbonate concentrations showed a



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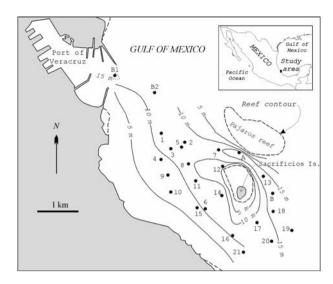


Fig. 1 Geographical location of the study area

high variation, ranging between 10.6% (station 4 in October) and 75.15% (station B in June). The particle size analysis of the studied sediments is illustrated in Fig. 2. Sediment types were defined according to Shepard's (1954) classification.

Gravel components were found at three locations in June and October and at six locations during February, apparently associated with the high winds present in the area at that time. Gravel samples were incorporated in the sand sector in Fig. 2. Sediment samples were mainly formed by sands, only five samples correspond to silty-sand sediments; in October, sample 19, located close to the river discharge area, had the highest silt concentration.

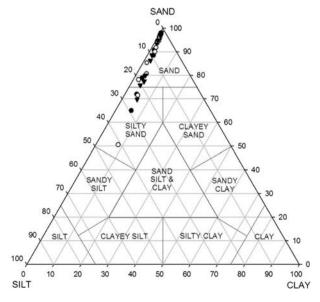


Fig. 2 Sediment classification

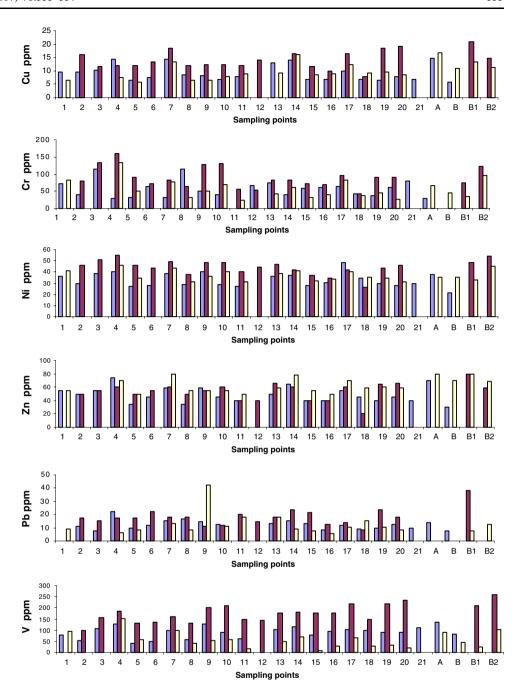


The average values of metals in sediments decreased in the order Fe > V > Cr > Zn > Ni > Pb > Cu. The highest average concentration for all metals, with the exception of Zn, was found during October (Fig. 3) and were associated with the rainy season in the basin, when the amount of sediment introduced to the area is higher. The distribution patterns of the metals in the area were different at the three different periods studied. In October, sampling point 4 showed the highest or among the highest concentrations for Cr, Ni, Zn and V; sampling points 19 and 20, located close to the Jamapa River discharge area, showed the highest concentration of Cu and V, suggesting a river source for these metals; sampling points B1 and B2 showed high values of Cu, Cr, Ni, V, Zn and Pb, apparently associated with the port activities. During February, metal concentrations were lower than those in June or October. Only Zn was observed at its highest concentrations at that time. Metal concentration maxima for different sampling points were observed at this time; apparently, a highly dynamic state caused by strong February winds produces the mixture of carbonates and terrigenous sediments, and a dilution of the metal concentration. Pb distribution pattern throughout the study is different compared to the other metals studied, suggesting that the introduction of this metal to the system occurs through a different mechanism.

Jamapa River sediments, located around 7 km to the south of Isla de Sacrificios, were analyzed at the three different periods. Under petrographic microscope, these samples showed the presence of intermediate volcanic rock fragments that may be responsible of some trace metals. Cu, Cr, Ni and Pb did not show significant changes in concentration; the average concentration throughout the year was Cu, 14.23 mg/kg; Cr, 63.78 mg/kg; Ni, 41.49 mg/ kg; and Pb, 10.97 mg/kg. V had different concentrations throughout the year: 161.17 mg/kg in June, 245.42 mg/kg in October, and 83.3 mg/kg in February. Burning of fossil fuel increases the amount of V in the air (Merian 1991); this may explain the higher concentration of V during the rainy season in the basin. Zn concentration was similar in June and October with an average concentration of 58.24 mg/kg. In February, Zn concentration in the river was 103.5 mg/kg. Using metal concentration in the river sediments as a reference, the enrichment factor (EF = [Mm]/[Alm] / [Mr]/[Alr]) was calculated for the different studied metals. The highest enrichment factors were found at sampling point 4 in October for Cr (EF = 4.42) and Ni (EF = 2.34); in June, for Pb (EF = 3.53); and in February, for V (EF = 3.4). Pb showed a high EF (7.69) at sampling point 9 during February. The EF observed in the coastal area suggests an introduction mechanism other than a river

A correlation analysis of the metals studied with different parameters shows a statistically significant correlation

Fig. 3 Mean metal concentration (mg/kg) in reef sediments in June (shaded bars), October (darker bar) and February (clear bar)



with grain size (Mz versus Cu, 0.559; Zn, 0.526; Ni, 0.48; Cr, 0.472; and V, 0.425). Fine sediments are associated with a higher concentration of metals. Only Pb has no correlation with the grain size; this again supports the idea that there is a different introduction mechanism to the area. Al shows a strong correlation throughout the study with Cu and Zn, supporting the association of these metals to natural plagioclases. However, the fact that Zn concentration is higher in February suggests the presence of an additional supply of Zn in the area. Organic matter has a significant correlation with Cu in June (0.68) and October (0.60). In

February (0.39) there is no significant correlation; apparently, the strong winds that affect the area produce a mixture of sediments and dilute the metal concentration of the surface sediments.

Guzman and Jimenez (1992) conducted a survey of heavy metals in the skeletons of corals and reef sediments in 23 reefs along the Caribbean coast of Coast Rica and Panama (1497 km). They consider the San Blas region in Panama as a relatively pristine area, as it is far away from major human disturbances. Table 1 shows the range of concentration in reef sediments reported by these authors



**Table 1** Trace metal concentration (ppm) in reef sediments

	Costa Rica	Panama	Panama (San Blas)	This study
	n = 6	n = 14	n = 4	n = 25
$Al^a$	0.05-1.35	0.1-1.24	0.04-0.12	2.04-3.76
Fe <sup>a</sup>	0.023-1.14	0.06-0.36	0.024-0.64	0.065-2.03
Mn	17.1–525.0	126.6-294.0	17.1–29.1	420.0-800.0
Cr	10.8-29.6	4.1-13.7	5.6-8.2	28.2-159.7
Cu	2.2-16.9	2.9-6.0	2.2-2.4	5.9-20.9
Zn	11.3–37.5	10.9–27.4	7.6–39.6	19.9–79.7
Pb	20.8-36.8	17.9–45.3	30.3-36.8	5.3-42.4
V	83.2-265.4	43.4–125.4	41–55.6	9.9-257.0
Ni	89.0-122.0	74–109.8	88.4–100.2	21.0-54.9

<sup>&</sup>lt;sup>a</sup> Concentration expressed in %

**Table 2** ERL and ERM (mg/kg) for the incidence of biological adverse effects (%) (modified from Long et al. 1995)

	Guideline (mg/kg)		Adverse effects (%)		
	ERL	ERM	>ERL	ERL-ERM	>ERM
Cu	34	270	9.4	29.1	83.7
Ni	20.9	51.6	1.9	16.7	16.9
Pb	46.7	218	8	35.8	90.2
Cr	81	370	2.9	21.1	95
Zn	150	410	6.1	47	69.8

and the values obtained in the present study. Aluminum concentration is indicative of terrigenous sediments. Matson (1989) suggested that Al and Fe can be considered good tracers for terrigenous material in coastal areas. Higher Al and Fe in the present study support the presence of high terrestrial inputs to the area. Concentrations of Cr, Cu, and Zn are considerably higher in the Veracruz area than sediment samples from Costa Rica and Panama. Concentrations relative to the values reported in San Blas, Panama are 19.5 times the concentration of Cr, 8.7 times that of Cu, and twice that Zn; Pb values are similar to the values found in Costa Rica and Panama. V values are similar in Veracruz and Costa Rica, and Ni levels are lower in the Veracruz area.

Heavy metals are persistent pollutants that can remain in the environment unchanged for years. In order to asses the environmental risk of the metals found in marine sediments, Long et al (1995) reviewed and screened many publications for the assessment on the biological adverse effects of trace metals in sediments. Based on that work, two guideline values were suggested for nine trace metals: ERL (effects range-low) and ERM (effects range-median. The guideline values and percentage of biological adverse effects of five metals according to Long (1995) are given in Table 2.

Based on the data reported on Table 2, and the metal concentration found in this work, Zn presented 6.1%; Pb, 8.0%; Cu, 9.4%; and Ni, 16.7% incidence of biologically adverse effects throughout the area during the three

sampling periods studied. Cr presented 21.1% of the incidence of biologically adverse effects at sampling points 3, 4, 7, 9, and A during June, and at sampling points 3, 4, 5, 9, 10, 13, 14, 17, 19, 20, and B2 during October. In February, only sampling points 1, 4, 17, and B2 presented a 21.1% of biological adverse effects.

According to this data, Cr is the metal that presents greatest pollution risks in the area. The possible metal sources for the EF observed at sampling point 4 may be associated to non-point sources (domestic and industrial sewage). The distribution pattern of Pb in the area and the high EF at sampling point 9 during February also suggest the introduction mechanism of this metal is by air, given the painting activities that take place in the port dockyards.

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