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Anthropogenic influences on heavy metals across marine habitats in the western coast of Venezuela

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ABSTRACT

Concentrations of ten metals were measured in waters and sediments at 14 sites during four sampling periods (1996–1997). These sites include various marine ecosystems that are highly influenced by industry, tourism and river discharges, nine of which are within the Morrocoy National Park. Spatially, metal concentrations in water were homogenous, whereas in sediments their distributions were related to grain size. Maximum concentrations of cadmium (Cd) and mean concentrations of copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn) in water were above the guideline values proposed by NOAA, indicating the potential of these metals for producing chronic effects in marine biota. Sheltered sites showed the highest metal concentrations in sediments; with Cd and Zn above these guidelines. Enrichment factors and geo-accumulation indexes suggested that metals in sediments were largely of natural origin except for Pb, Cd and vanadium (V), which were apparently associated with industrial effluents. A disruption of the spatial distribution of metals after heavy rainfall, when exposed sites reached concentrations as high as those in sheltered sites, showed the influence of nearby rivers. The potential increase of such climatic events could represent additional stress for natural protected areas in the Caribbean.

1. Introduction

Metal accumulation in marine sediments may reflect a diversity of natural processes such as erosion, early diagenesis and anthropogenic influences. Distinguishing between these potential sources is, however, very difficult due to geochemical variability in grain size distribution, mineralogy and organic matter content (Mil-Homens et al., 2006). Given the toxicity, persistence and non-degradable nature of heavy metals in the environment, the contamination of sediments by these elements, represents one of the greatest ecological risks for coastal-marine ecosystems (Pekey, 2006).

Coastal ecosystems are particularly susceptible to the input of heavy metals because industrial wastes and urban effluents are usually disposed of in rivers and creeks; rapidly reaching coastal zones (Stoker and Seager, 1981). These heavy metals are mainly associated with particulate and colloidal matter, which precipitate and deposit once they reach the marine environments (Gibbs, 1983; Loring and Rantala, 1992). The input of natural or anthropogenic metals has consequences for their natural biochemical cycles, temporal and spatial distribution patterns; and ultimately, their bioavailability to organisms (Hutzinger and Veerkamp, 1981; Spacie and Hamelink, 1984; Brock and Madigan, 1993).

In our study, we investigated a stretch of coastline in north-western Venezuela with conflicting activities, i.e. industrial activities (oil refining and production of chemical reagents), tourist development, and management of natural protected areas. Additionally, this region is influenced by the discharge plumes of three rivers (Aroa, Yaracuy and Tocuyo), whose catchment areas are affected by human population growth (e.g. agricultural lands, construction of dams, logging), and which have been reported as important inputs of contaminants (e.g. Bastidas et al., 1999). The Morrocoy National Park (MNP) is located in the heart of this region, and the natural beauty of its different ecosystems has prompted the development of diverse economic activities related to tourism. Tourism, in its turn, has sped up urbanization and coastal development, becoming a potential threat for biodiversity and the resilience of the ecosystems in the MNP. Given this scenario, and in order to improve coastal management strategies that might help ameliorate the impact of these activities on this protected area, it is essential to determine existing levels of potential contaminants and their probable sources.

It is often difficult to distinguish between the fraction of these potential contaminants that is anthropogenic and the fraction corresponding to their natural concentrations. Ideally, to achieve

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this objective, sampling designs should consider gathering data before the start of human activities that might produce changes in the concentrations of potentially contaminating elements (e.g. Underwood, 1992, 1994). This condition (i.e. having data from "before") is unachievable in most situations and our particular study case is not an exception. There have been some studies done in this region, published mainly in the grey literature (mostly technical reports, but see Bastidas et al., 1999; Iglesias and Penchaszadeh, 1983, Caldera et al., 2005), showing the basal concentrations of some contaminants. These studies have not attempted, however, to distinguish between natural and anthropogenic sources of the concentrations of heavy metals. In this investigation, we propose to address the problem by using two approaches:

(1) Evaluating the quality of sediments using normalization indexes (factor of enrichment and index of geo-accumulation), that facilitate comparison with toxicity guidelines, and the identification of potential sources of contamination;
(2) Describing the patterns of spatial and temporal distribution of the concentrations of elements that might contaminate waters and sediments.

In particular, if there is an anthropogenic input of metals in our study area, we would expect that; (a) the values of the factor of enrichment and geo-accumulation index (I_{geo}) surpass the guidelines for enriched sites and non-contaminated, respectively; (b) the spatial distribution of metals will be correlated with the spatial distribution of sampling sites in relation to the potential sources of contaminants (i.e. rivers and industrial developments) and (c) the patterns described should be consistent through time.

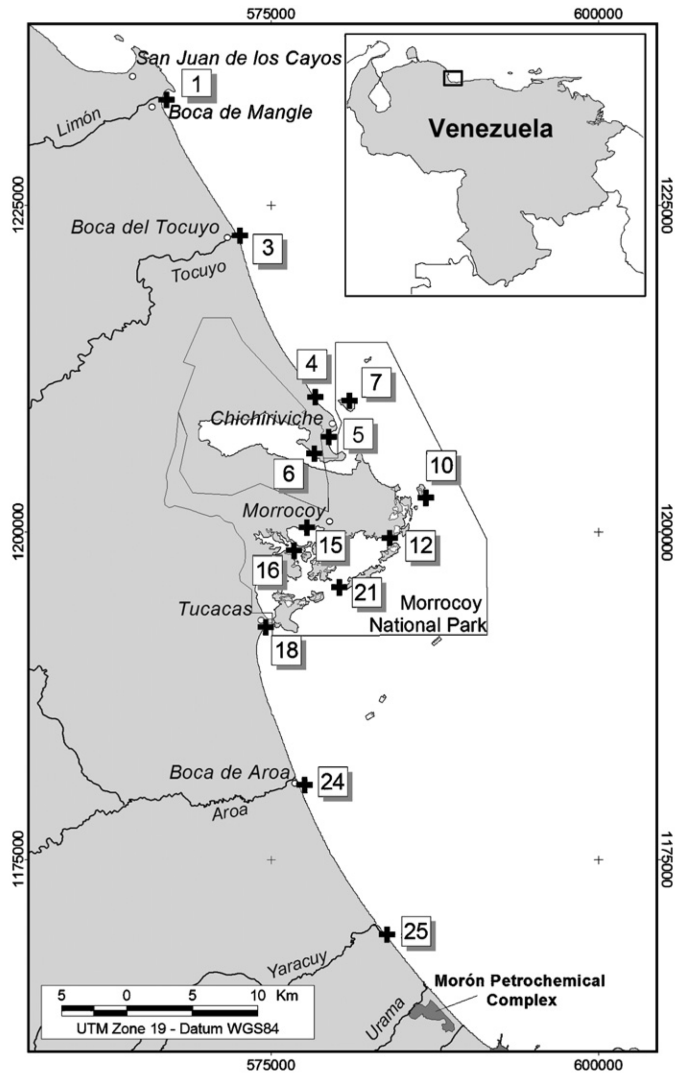

Fig. 1. Map of the study area showing the sampling sites.

2. Materials and methods

2.1. Area of study

This study was done in and around the MNP, on the western coast of Venezuela (Fig. 1). The study area not only included the MNP, but extended northwards and southwards in order to incorporate three important rivers (Yaracuy, Aroa and Tocuyo), which greatly influence the physical–chemical processes of this region. Over 80 km of coastline was covered by the study and was characterized by the presence of very diverse and heterogeneous ecosystems, including patches of coral reefs, mangroves, seagrass beds, sandy beaches and estuaries. These ecosystems receive a considerable amount of anthropogenic pressure from condominium developments and tourist businesses operating in the area as well as from industrial activities (mainly petrochemicals and production of fertilizers) located 40 km south of the boundaries of the MNP, and operating since 1956.

2.2. Collection of samples

Within the study area, 14 evenly spaced sites were selected between the mouth of the Tocuyo river (11°03′01″N–68°20′11″W) and the Mi Bohío beach, situated 500 m north of the mouth of the Yaracuy river (10°35′23″N–68°14′57″W) (Fig. 1). The selection of these sampling sites aimed to cover potential gradients occurring between the mouths of the rivers located north and south of the MNP, and the park itself. Furthermore, these sites represented all the ecosystems present within the study area, and were grouped in four types (Table 1): (1) Sheltered sites, characterized by the presence of seagrasses growing on muddy bottoms and typically surrounded by mangrove forests; (2) Exposed sites, characterized by the presence of extant patches of coral reefs and sandy bottoms; (3) Beach sites, which included typical sandy beaches located between the boundaries of the National Park and the river mouths; and 4) River sites, which included estuarine areas located in the river mouths. At each site, one sample of water and one sample of surface sediment (<10 cm deep) were collected using a Van Dorn bottle (4 L) and hand held PVC corer (12 cm ∅), respectively. Water samples were integrated over the water column with the exception of shallow sites (2 m deep), where samples were collected at 0.5 m. All 14 sites were sampled four times: (1) November 1995, (2) February 1996, (3) March 1997, and (4) November 1997.

2.3. Analytical procedures

Grain size distribution of sediments was determined by wet sieving. The following fractions were obtained by weight (Lewis 1984): silt-clay (<63 μm), sand (1 mm<χ<63 μm) and gravel (>1 mm).

The content of metals was determined after the total decomposition of samples by acid digestion during 6 h in a water bath (60 °C). Analyses were performed using a Varian SpectrAA-20 Plus Atomic Absorption Spectrometer. Aluminum (Al), arsenic (As),