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Chronology of mercury enrichment factors in reef corals from western Venezuela

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ABSTRACT

Mining and deforestation in the early 20th century, the development of petrochemical industries during the 1950s, and the constant weathering of natural deposits of cinabrium (HgS) have made Golfo Triste, Venezuela, a region impacted by mercury (Hg). We studied the chronology of Hg in coral skeletons of *Siderastrea siderea* (1 colony, 1900–1996) and *Montastraea faveolata* (2 colonies, 1930–1999) from Parque Nacional San Esteban. Maximum values of Hg/Ca ratios and standard deviations of Hg enrichment factors occurred in the 1940s, 1960s, and 1980s, and matched maxima of decadal rainfall. Values from the 1950s and 1970s matched periods of abundant but constantly decreasing rainfall and hence were best explained by the combination of runoff and the sudden bioavailability of Hg in the region. This sudden availability likely was associated with activities of the chlorine-caustic soda and fertilizer plants of Morón petrochemical complex, industries that started producing large amounts of Hg in 1958.

1. Introduction

Mercury (Hg) is one of the most toxic elements in fresh water and marine ecosystems due to its persistence and tendency to accumulate in organisms of all trophic levels (Weiss-Penzias et al., 2003; García-Rico et al., 2006; Shi et al., 2006). The inorganic ion (Hg^{2+}) is the predominant form of Hg associated with sediment particles (Lorey and Driscoll, 1999) whereas the elemental (Hg^0) and organic (HgMe) forms tend to accumulate in living tissues (Sunderland et al., 2006).

Approximately 80% of global Hg emissions are caused by man-made processes: today's rates of deposition are 2–20 times greater than those recorded in pre-industrial times (Schuster et al., 2002). Petrochemical plants, which usually are built on the coast for immediate access to ships, are one of the most important sources of Hg (Wilhelm, 2001). Consequently, coastal marine environments near heavily industrialized regions and petrochemical plants are polluted with this metal (Hornberger et al., 1999; Garcia-Rico et al., 2006). Mining, use of pesticides, incineration, and production of cement and chlorine also contribute to the dispersal and deposition of Hg in the oceans (Lin and Pehkonen, 1999; Guentzel, 2001; Wilhelm, 2001; Ram et al., 2003; Weiss-Penzias et al., 2003).

Hg also accumulates in the marine environment via natural processes. Cinabrium (HgS), a mineral commonly present in the Earth's cortex, is carried to the oceans by runoff and rivers (Schuster et al., 2002). Winds and rain contribute to the dispersion and accumulation of Hg in lands and oceans by transporting and bringing down particulate material released into the atmosphere by volcanic emissions and natural fires.

Because traces of heavy metals are incorporated into the skeletons of scleractinian corals during growth, chemical analyses of their growth bands provide historical records of the deposition of Hg and other elements in marine environments (Shen and Boyle, 1987, 1988; Guzman and Jarvis, 1996; David, 2003; Al-Rousan et al., 2007). The association between metals and carbonate skeletons occurs when metals directly replace the Ca^{2+} ion (Amiel et al., 1973) or when they are adsorbed to particulate material that is incorporated into the growing crystalline network (Howard and Brown, 1984). The amount of Hg in skeletons of living organisms usually is reported as concentration ratios to Ca (in order to account for variable rates of skeletal growth) or as enrichment factors (EFs) (e.g., Luoma, 1989). Traditionally, EFs have been widely used in pollution studies of marine sediments because they allow discrimination between the natural input of elements and that produced by human activities (Kehrig et al., 2003; Mil-Homes et al., 2006).

Golfo Triste, located on the western coast of Venezuela, is one of the most productive artisanal and industrial fishing grounds of the country, particularly because of its shrimp and snapper trawling industry (Molinet et al., 1991). The region provides food to the city of Puerto Cabello (with an estimated urban population of 213,167 in 2005, http://iies.faces.ula.ve/), to many other cities in the country, and to a number of towns and villages located along the gulf

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coast. It also harbors a variety of coastal marine communities (Bone et al., 2005), two national parks (Morrocoy and San Esteban), one faunal refuge, sandy and rocky beaches, bays, and coastal lagoons that are popular tourist destinations. However, the area is dangerously polluted, the concentration of Hg as high as 325 ppb have been measured in sediments from different locations within the Gulf (Pequiven, 1980; Pérez, 1991, 1999; Bastidas et al., 1999). Since the early 1950s, Golfo Triste has experienced a sustained development, especially in the petrochemical, military, and paper industries (Ministerio Energía y Minas, 1994). Moreover, some of the important rivers that discharge waters into the gulf (e.g., the Aroa River) transport leached Hg into the gulf from the only known formations of cinabrium (HgS) in the country, extending from the Yaracuy to Lara states (Rodriguez, 1986).

In this paper, we studied the historical relevance of the natural and anthropogenic processes that introduce Hg into the marine ecosystems of Golfo Triste by constructing three chronologies of Hg (37–97-years-long) from skeletons of *Siderastrea siderea* and *Montastraea faveolata* growing in San Esteban National Park. We used them to compare the patterns of EFs with historical events related to the development and operation of the Morón petrochemical complex and to the operation of other polluting industries along the gulf's coast since the 1950s. Finally, we identified massive discharges of Hg by comparing EFs, standardized to Fe and Al, with records of rainfall.

2. Materials and methods

2.1. Study area

Parque Nacional San Esteban was created in 1987, has a surface area of 44,050 ha and extends through the northern border of Carabobo state. The park covers most of the altitudinal forest environments in the mountains of Cordillera de la Costa, and it extends to the coasts and islands of Golfo Triste: Isla Larga, Santo Domingo, Isla Ratón, Alcatraz, and Isla del Rey. Coral communities, rocky coasts, sandy beaches, muddy bottoms, seagrass beds, and coastal lagoons are the most common tropical marine ecosystems in the park (Villaroel, 2001).

The Aroa, Borburata, Morón, and Yaracuy Rivers discharge large amounts of sediments and fresh water to the park and to the gulf (Fig. 1), and sedimentation notably increases when rainfalls peak in June–July and December. Water temperature oscillates between 26 and 29 °C throughout the year round (Pérez, 1991).

2.2. History

We reviewed key scientific contributions and technical reports (some rather obscure) describing the development and operation of industries in the coastal areas of Golfo Triste (Grau, 1972, 1995; Iglesias and Penchaszadeh, 1983; Ministerio Energía y Minas, 1994; Jaffe et al., 1998; Roulet et al., 2000; Wilhelm, 2001; Wright and Welbourn, 2002; Ram et al., 2003).

2.3. Rainfall

To approximate river runoff, we used yearly rainfall data from 10 meteorological stations located in the San Esteban, Aroa, and Yaracuy River Basins spanning from 1938 to 1996 (Table 1). Data were transcribed from printouts of a meteorological database from the Ministerio de Recursos Naturales Renovables and transformed to anomalies by subtracting their overall mean. San Esteban is the meteorological station closest to our sampling area, but rainfall data from Yaracuy and Aroa were deemed very important as well, as the stream flows of the main rivers of these basins (8.7 $m^3\ s^{-1}$ in

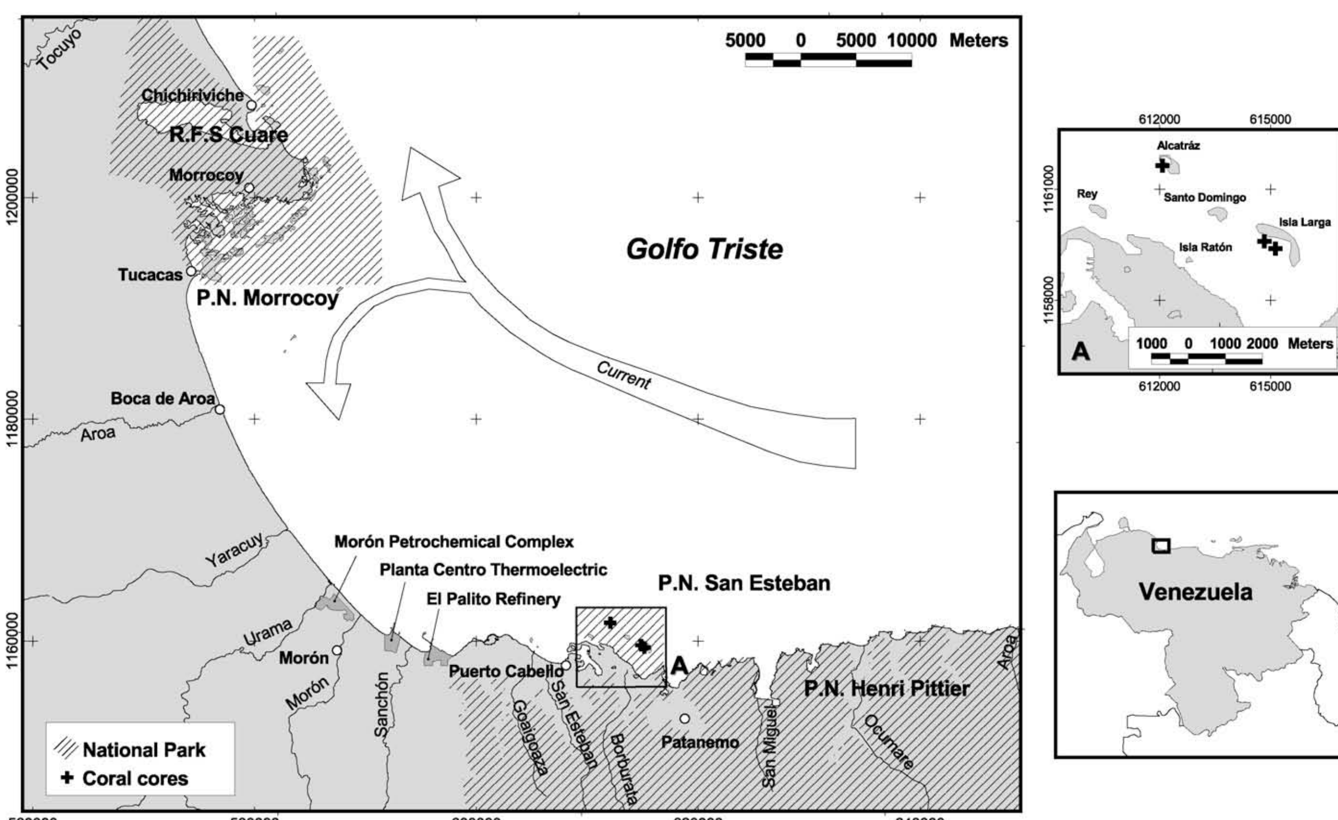

Fig. 1. Map of Golfo Triste, which lies on the central-western coast of Venezuela: petrochemical complex of Morón, sampling sites and predominant marine currents.