



Mercury levels in coral reefs along the Caribbean coast of Central America

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Abstract

Sediment and coral skeleton samples from 23 coral reefs along the Caribbean coast of Costa Rica and Panama (1497 km) were evaluated for total mercury (Hg). High levels of pollution were found in the entire region with averages of 18.9 and 71.3 ppb in coral skeletons and sediments respectively. Significantly higher contamination was found in Panamanian corals (21.4 ppb) while compared to Costa Rican reef sediments (85.9 ppb). Hg from several processes and non-point sources (e.g., erosion, runoff, flooding, mining, overuse of agrochemicals, industrial waste, ports, and refineries) may have affected the entire region. The widespread observed distribution suggests that Hg is being carried along long distances within the region due to its high concentrations found in “pristine” reefs. Forest burning and colonial mining residues may be considered as possible contamination factors.

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1. Introduction

Many human activities have a negative impact on several biological processes and there is no doubt that these will continue to affect the functioning of highly productive coastal ecosystems. Contamination caused by trace metals affects both ocean waters and those of the continental shelf and the coastal zone where, besides having a longer residence time, metal concentrations are higher due to the input and transport by river runoff and the proximity to industrial and urban zones (Nriagu, 1990; Rainbow and Furness, 1990).

Mercury—globally distributed and considered as one of the most toxic metals is introduced into the environment from natural and anthropogenic sources—is known to be already incorporated in the marine ecosystem at various trophic levels, including, plants, invertebrates, fish, and humans (Fitzgerald, 1995; Renzoni, 1995; Morel et al., 1998; Rasmussen et al., 1998; Schroeder and Munthe, 1998). It is estimated that a large portion of the mercury (~60%) associated with

human activities is dispersed into the atmosphere, suggesting global emissions of ≈ 2000 t/year, of which around 73 t/year correspond to Central and South America (Mason et al., 1994; Pirrone et al., 1996), while another ≈ 1000 t/year is released from terrestrial sources (Mason et al., 1994).

Widespread mercury contamination on the coasts grows alarmingly with time and is already affecting most marine ecosystems in the Caribbean region (review in Rawlins et al., 1998). Many studies on the biota, sediments, and water have reported concentrations far above the levels tolerated by humans (Knight et al., 1997; Moreira and Piveta, 1997; Kannam et al., 1998; Olivero and Solano, 1998; Bastidas et al., 1999). The Central American Caribbean coast is continually contaminated by hydrocarbons originating from activities associated with refineries, ports, and ship traffic. In addition, the region is affected by trace metals released into the environment from extensive deforestation, agricultural practices, topsoil erosion, and runoff with excesses of fertilizers and agrochemicals (Guzmán and Jiménez, 1992; Bastidas and García, 1999).

Although Hg enters the trophic chain mainly as methylated Hg and other organic Hg complexes, in aquatic environments only 1% of total Hg is found in

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these forms (Stein et al., 1996). High sulfate concentrations convert all available metal to mercury sulfide (HgS), making Hg unavailable for methylation in most marine sediments (King et al., 1999). On the other hand, high sulfate concentrations in coastal sediments interfere with bacterial sulfate reduction processes, responsible for Hg methylation (Chen et al., 1997; reviewed in Morel et al., 1998). This study was not intended to deal with Hg speciation processes or Hg bioavailability. The prime goal was to develop a baseline database for levels of total mercury in Central America using reef sediments and coral skeletons as environmental indicators. The distribution of total Hg along the coasts of Panama and Costa Rica has never been previously assessed.

2. Methods

The sampling was done throughout 1497 km of coast between Costa Rica and Panama (Fig. 1). Large areas of

beaches, mangroves, and coral reefs characterize the coastal zone in this region. Few areas along this coast have not been disturbed by human activities, where most were considered as potential non-point sources of Hg into the environment. In this study we considered only the San Blas region, on the east of Panama (Fig. 1F), as a pristine area due to the absence of industrial or extensive agricultural activities and lower deforestation.

2.1. Field procedures

Samples were collected from the same reefs where 12 heavy metals were previously assessed, following similar sampling protocols for comparative purposes (see Guzmán and Jiménez, 1992). Five replicate samples of the coral *Siderastrea siderea* (Ellis & Solander) and five reef surface sediment samples were collected at each of the 23 reefs, analyzing 230 samples for both indicators. Sampling was conducted at six sites in Costa Rica and 17 sites in Panama (Fig. 1). The samples—around 150 g of coral and sediments—were collected within an area of $\approx 1500 \text{ m}^2$ of reef habitat, with depths ranging between 1.5–3 m and 2.5–5 m for corals and reef sediments respectively. Coral skeleton samples representing around the last three years of growth, were combined for the analysis. The samples were first dried out and put in plastic bags for their transportation to the laboratory, where they were later oven dried at 60 °C for 48 h.

2.2. Laboratory procedures

Coral and sediment samples were pulverized in an acid-cleaned agate mortar and pestle, and $\approx 5 \text{ g}$ of each one were precleaned several times with distilled-deionized water and a low concentration solution of HNO_3 in a sonic bath (Guzmán and Jiménez, 1992). Between 2 and 3 g of the sample were analyzed in duplicate, with three readings per replicate. All laboratory work was done inside a clean room equipped with a laminar-flow bench hood. All reagents were of analytical-graded and certified purity. Solutions were prepared with grade II, doubly distilled and deionized water, following standard protocols (see Beaty, 1978; APHA, 1992). An inorganic mercury stock certified solution (1000 mg/l) was used (Perkin-Elmer # 303-0833). Polyethylene bottles for Hg samples were cleaned rigorously before use. Bottles were heated at 95 °C in concentrated HNO_3 for 48 h then cooled and rinsed with distilled-deionized water.

Sediment samples were digested with a solution of 3 ml of HNO_3 , 3 ml of H_2SO_4 , and 3 ml of HF in a water bath for 5 h at 58 °C while coral samples were digested with 5 ml HNO_3 1:1 and 2 ml HCl kept in a water bath at 59 °C for 6 h. Then solutions were filtered (using Whatman 51) and distilled-deionized water was added up to a final volume of 50 ml the samples. Total Hg was oxidized and reduced by six drops of KMNO_4 5%, 5 ml

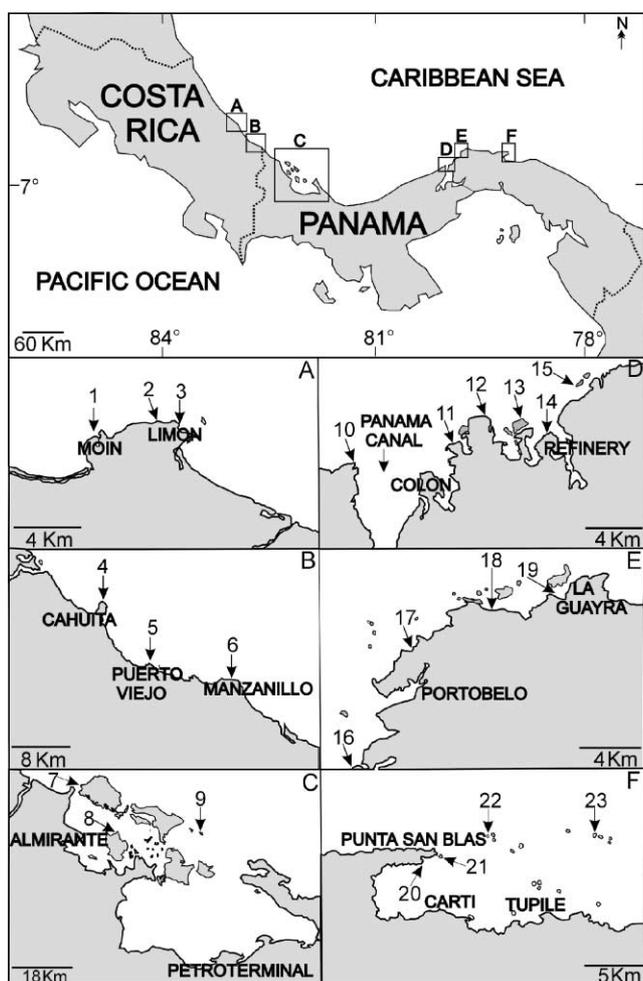


Fig. 1. Map of Costa Rica and Panama showing the location of the 23 reef sites along the Caribbean coastal zone grouped into six subregions (A–F).

HNO₃ 5.6 N, 5 ml of H₂SO₄ 18 N, 5 ml of hydroxylamine 1.5% and 5 ml of SnCl₂ 10% (Beaty, 1978; Bastidas et al., 1999).

A Perkin–Elmer cold vapor atomic absorption spectrophotometer (Model 2380) equipped with a quartz cell and flow-injection system was used. A mercury hollow-cathode lamp operated at 6 mA was used as a radiation source. Mercury was read with the resonance line at 253.7 nm and a slit width of 0.7 nm. An instrumental standard calibration curve was achieved twice daily. Mercury standards, laboratory procedural replicates and standard reference materials of known total Hg concentrations were analyzed. Data accuracy was monitored by analyzing known standards every 20 readings. Detection limit for Hg was 0.02 mg/l (ppm), based on three standard deviations of the blank measurements. All samples were archived in the laboratory in Caracas, Venezuela (EMG).

3. Results

The regional concentration (Costa Rica and Panama) of Hg in reef sediments (71.4 ppb) was significantly higher than the average 18.95 ppb recorded in the biota (Mann–Whitney rank test, $T = 5413.5$, $P < 0.001$).

Out of the 23 reefs assessed, the higher concentrations of Hg in sediments were found in the reefs near the port and industrial area of Moín-Limón in Costa Rica, with averages higher than 130 ppb (Figs. 1A and 2). Likewise, higher values were recorded in coral skeletons from Panamanian reefs close to the ports of Colon and the refinery of Bahía Las Minas, with concentrations above 30 ppb (Figs. 1D and 2). It is important to notice the high level of mercury recorded in the pristine areas of Panama (San Blas, Fig. 1F), with average concentrations above 40 ppb and higher than 120 ppb in some samples (Fig. 2). When comparing the concentrations

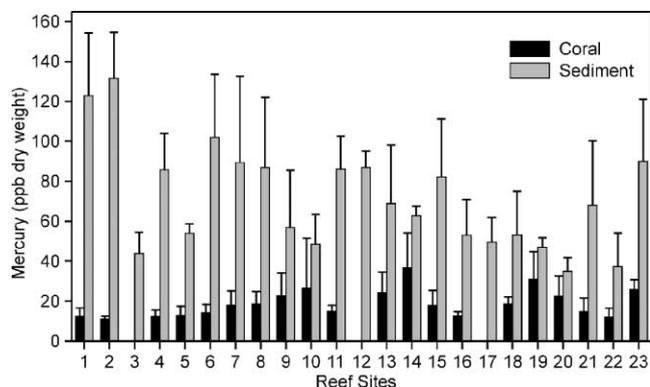


Fig. 2. Mercury concentrations (ppb dry weight) in the skeleton of *Siderastrea siderea* and reef sediments, at each of the 23 study sites from Costa Rica and Panama. Standard error bars are shown except for very small values.

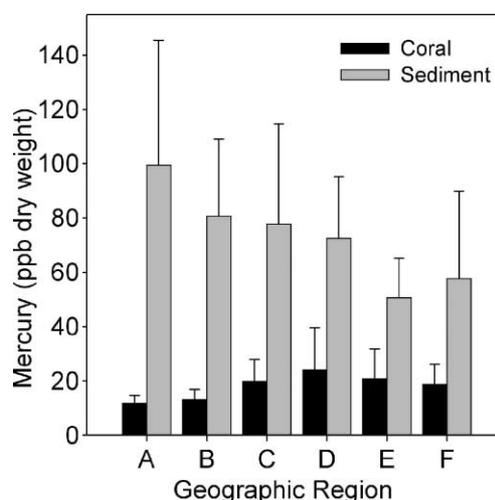


Fig. 3. Overall mean mercury concentrations (ppb dry weight) in reef sediments and in the skeleton of *Siderastrea siderea* grouped by six subregions along the Caribbean coast of Costa Rica and Panama.

per site, no direct relationship was found between sediments and coral skeletons (Spearman rank correlation; $r = -0.152$, $P > 0.05$).

The coastal area was divided arbitrarily into six geographic areas with the goal of facilitating comparisons between the 23 reefs (Fig. 1). When comparing the six areas, significant differences were observed in average Hg in coral *Siderastrea siderea* (Kruskal–Wallis one-way ANOVA, $H = 19.483$, $P = 0.002$) and in reef sediments ($H = 21.151$, $P < 0.001$) (Fig. 3). These differences for sediments occurred between the highest average (area A in Costa Rica, 99.4 ppb) versus the lowest in areas E and F on the east coast of Panama (≈ 50 –57 ppb), and in area B (80.6 ppb) versus the relatively pristine area F. In coral skeletons, only area D, the most heavily polluted area in Panama (18 ppb), was different from areas A and B in Costa Rica (Dunn's pairwise multiple comparisons). When comparing the concentrations per area, no direct relationship between sediments and corals was found (Spearman rank correlation; $r = 0.308$, $P > 0.05$).

Mean levels of mercury recorded among the countries were 21.4 ppb (SD ± 12.5) and 15.2 ppb (± 6.6) in the corals of Panama and Costa Rica respectively. While in sediments, 62.0 ppb (± 25.5) and 85.9 ppb (± 38.3) were found, respectively. By comparing the average concentrations mentioned above, significantly higher values were found in Costa Rican sediments and in corals from Panama ($T = 3155.5$, $P = 0.002$ and $T = 1594.0$, $P = 0.003$, respectively).

4. Discussion

It is widely accepted, both in the scientific community and among politicians, that mercury incorporated into

the food chain is potentially hazardous for the environment and human health (Pilgrim et al., 2000). In addition, we know of the apparent increase in the concentrations of mercury worldwide (Slemr and Langer, 1992; Fitzgerald, 1995) and the capacity of mercury for long-range atmospheric transport or through marine currents by thousands of kilometers in only a few months (Rasmussen, 1998). However, there is no overall consensus on the origin or source—natural or anthropogenic—of this metal, which has been recorded abundantly in industrialized, rural, and remote areas (Nriagu, 1990; Rasmussen, 1998; Fitzgerald et al., 1998).

This study shows relatively high levels of Hg in sediments and biota associated with coral reefs in Caribbean Central America, and suggests a steady accumulation has been taking place over a long period in the region. Averages of above 71 ppb of Hg in sediments are high and comparable to other contaminated regions of the Caribbean (Table 1). This preliminary baseline information might contribute to the development of improved Hg budgets for this tropical region, where the risk mercury poses on the environment is appreciated and underestimated at present (*sensu* Burger, 1997).

Efforts on a regional and global level have been made to obtain a realistic budget for Hg emissions, particularly those that are atmospheric and those caused by erosion/runoff (Pirrone et al., 1996; Rasmussen et al., 1998; Gustin et al., 2000; Woo-Jun et al., 2000; Kang et al., 2000). Pirrone et al. (1996) point out that Hg emissions have changed considerably in past years and indicate that there has been an annual reduction of 1.3% of the anthropogenic contribution on a global level, when compared to the values of the 1980s. However, the authors indicate that these emissions have remained constant in developed countries while they have gone up in non-developed countries. In addition, the historical contamination of mercury since colonial times (1587–1820) in the American continent appears to be partially responsible for the high concentrations that have been reported for the region, the Antarctic, and the southern hemisphere (see reviews in Nriagu, 1994; Lacerda, 1997a; but see Fitzgerald et al., 1998). These authors

have estimated that silver–gold mining during that time was a dominant source of atmospheric mercury, with averages of 612 t/year between 1589 and 1900, estimating a cumulative loss in the environment of 196,000 t, dispersed across Central and South America. It is thought that in tropical conditions with abundant heat and moisture, part of the mercury deposited is methylated and later dispersed into the atmosphere (Lindberg, 1986; Nriagu, 1994).

Assessing or identifying the likely sources responsible for mercury contamination in the Central American region is complex and although it is beyond the scope of the current study, the following brief discussion will hopefully lead to new investigations in the region. We have identified three historical periods that might partially explain mercury levels in this region. Firstly, from the 16th century until the mid-1700s, Panama was known as “Gold Castilla” due to the large quantities of gold found in different parts of the country (Castillero, 1967; Mena, 1984; Araúz and Pizzurno, 1997). Since 1520, different mining exploitation ventures were devoted to the extraction of this metal in “open skies or patios”, and were located in areas of high precipitation and evaporation (Veraguas, Colon, and Darien), potentially leading to high loss of Hg into the environment. Hence, if we use the conservative estimate of 1.3–1.7 kg Hg per kg of produced gold (Nriagu, 1994; Lacerda, 1997b) and the only value of gold production obtained for Panama (15 t) during 35 years of mining (1698–1727) (Araúz and Pizzurno, 1997), we can calculate that approximately 19.5–25.5 t of mercury was lost into the environment. This estimation suggests that part of the mercury lost during the colonial period might be present in the area (*sensu* Nriagu, 1994). Secondly, later in the mid-19th century, agriculture based on banana and coffee plantations began in the fertile alluvial valleys of the great rivers of Caribbean Central America, becoming extensive and intensive in the region early in the last century (Heckadon-Moreno, 1997). Consequently, the rate of deforestation increased dramatically as well as soil erosion and runoff, which is annually estimated in millions of tons (Heckadon-Moreno, 1997). By 1950, $\approx 75\%$ of the region was forested while at present, $\approx 30\%$

Table 1
Concentration of total mercury (ppb) in Caribbean coastal sediments

Country	Hg	Ref.
Morón, Venezuela	60–300	PEQUIVEN (1980)
Golfo Triste, Venezuela	91–218	Pérez (1991)
Santa Marta, Colombia	130–5000	Ramírez (1995)
South Florida, USA	1–219	Kannam et al. (1998)
Florida Bay, USA	3–100	Kannam et al. (1998)
Biscayne Bay, USA	3–66	Kannam et al. (1998)
Morrococoy, Venezuela	161–325	Bastidas et al. (1999)
Golfo Triste, Venezuela	12–41	Pérez (1999)
Florida Bay, USA	14–236	Woo-Jun et al. (2000)

remains relatively undisturbed (Heckadon-Moreno, 1997). Thus, we could estimate mercury emissions of 0.3 t/year for the region by assuming a total release of 7.8 g Hg per hectare of forest burning (Lacerda, 1997b) and a current deforestation rate of 376,000 ha/year (Heckadon-Moreno, 1997). Thirdly and finally, development in the coastal zone begun in the 1940s and might have contributed to current Hg levels, with the installation of refineries, energy plants, ports, and the increase of urban areas.

All those land-use changes have possibly contributed significant quantities of mercury into the environment, making it impossible to estimate natural sources with the available data. It has been suggested that Al and Fe are good tracers for terrigenous materials in coastal areas (Matson, 1989; Ruiz-Fernández et al., 2001). In addition, elevated concentrations of those metals were reported for Central America as an indication of high sedimentation associated with deforestation and runoff (Guzmán and Jimenéz, 1992). Here, we compare the mean concentration for Al and Fe in corals and reef sediments provided for each of our reef sites (see Table 1 in Guzmán and Jimenéz, 1992) with those Hg values from this study. Hg in corals and sediments showed no correlation with Al or Fe. These lacks of correlation suggest that the main source of Hg may not be runoff exclusively. Undoubtedly, colonial gold mining (Castillero, 1967), the overuse of agrochemicals (Guzmán and Jimenéz, 1992), deforestation and forest burning (see Veiga et al., 1994; Lacerda, 1997b), and hydrocarbon fossils combustion (see Nriagu, 1990) are an inexorable reflection of the state of development in this region during different periods of time, which could partly explain the contamination of mercury reported here.

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