Chronology of mercury enrichment factors in reef corals from western Venezuela

Ruth Ramos, Roberto Cipriani, Hector M. Guzman, Elia Garcia

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; Garcia-Rico et al., 2006; Shi et al., 2006). The inorganic ion \( \text{Hg}^{2+} \) is the predominant form of Hg associated with sediment particles (Lorey and Driscoll, 1999) whereas the elemental \( \text{Hg}^0 \) 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 \( \text{Ca}^{2+} \) ion (Amitel et al., 1973) or when they are adsorbed to particulate material that is incorporated into the growing crystalline network (Howard and Brown, 1994). 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.
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 Cara-bobo 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 Penchasadeh, 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 m³ s⁻¹ in
the Yaracuy River and 3.1 m² s⁻¹ in the Aroa River) are approximately one order of magnitude larger than those of the Borburata River, the largest in San Esteban Basin (0.4 m² s⁻¹). The 5-year-long moving average of the mean rainfall data from all the meteorological stations was normalized and compared to metal concentrations over time.

2.4. Samples

Between 1996 and 1999, three cores (1 m long x 9 cm in diameter) were collected in coral colonies growing in San Esteban National Park. One core was obtained from a colony of *S. siderea* found in the coral reef patch located south of Isla Larga (C0-SS-ISL). This island is located 2.3 km from the coast (Lat 10°29'22" N, Lon 67°58'26" W) and is surrounded by reefs and by coralline sandy beaches and reef patches on its south side. The other two cores were obtained from two separate colonies of *M. faveolata*. The first was sampled at the entrance of the internal lagoon of Alcatraz (C1-MF-ALC). Alcatraz Island is located 2 km from the coast (Lat 10°30'25" N, Lon 67°58'44" W) and its central lagoon has ca. 60,000 m² of surface area and a maximum depth of 7.5 m. The lagoon is connected to the sea by a 50-m long, 1-m deep channel. The other *M. faveolata* colony (C2-MF-ISL) was located in the same coral reef patch in which the colony of *S. siderea* was growing. All colonies were growing on substrates between 5 and 12 m deep (Fig. 1). Cores were extracted using a hydraulic-powered underwater drill (Guzman and Jarvis, 1996).

All cores were sliced longitudinally, yielding two laterals and one medial slab per core. All slabs were X-rayed and their bands were dated using published procedures (Guzman and Jarvis, 1996). Coral growth bands are produced by changes in carbonate density associated with water temperature. Alternating bands (i.e., high and low density bands) were used to infer the colony’s chronology (e.g., Guzman and Jarvis, 1996; Runnalls and Coleman 2003). One high density band plus one low density band represented one full growth band produced after 1 year of coral growth (2003). One high density band plus one low density band represented one full growth band produced after 0.5 year of coral growth (1996). The material corresponding to each growth band (i.e., a sample) was then dried at 60 °C.

To measure the concentrations of Al, Fe, and Ca, we obtained two new sub-samples (replicates) of 0.5 g from each sample of dried material. Each sub-sample was dissolved in an acid solution (5 ml of 30% HNO₃ in 5 ml of Milli-q water) and heated to 80 °C for 1 h. The resulting solution was filtered through a 0.45 µm mesh and diluted to 50 ml with Milli-q water. Analyses were performed using an inductively coupled plasma atomic emission spectrometer (ICP-AE, GBC Integra XL, Dandenong, Victoria, Australia) with a detection limit of 0.005 ppm. We used reagent blanks and certificated standards (SDWA 00-5, AccuStandard Inc., New Haven, CT, USA) for calibration and determination of each metal.

To measure the concentration of Hg, we obtained three new sub-samples of 1.0 g (replicates) from each sample of dried material. These sub-samples were digested with *aqua regia* for 2 min in a water bath at 95 °C, and then with potassium permanganate (5%), hydroxylamine (1.5%) and stannous chloride (10%) for 30 min at 95 °C (Bastidas et al., 1999). The resulting solutions were filtered through a <8 µm mesh and diluted to 100 ml with Milli-q water. Hg was measured by atomic fluorescence spectroscopy (PSA P.S.
3A. Rainfall and metal markers for runoff

2.6. Statistical analysis

Metal concentrations were expressed in µg/g and µmol metal/mol Ca and log-transformed (base 10). Because the precision of dates assigned using coral growth bands is approximately ± 2 years, metal concentrations were smoothed using a 5-year moving average. We used Spearman’s correlation coefficients (rS) and time series cross-correlations to assess the relationships among metals (Hg, Fe, and Al) and between Hg and rainfall. These statistics were calculated using Statistica 6.0 program (2002, StatSoft Inc., Tulsa, OK, USA).

We calculated EFs from the average concentrations of Hg measured in growth band replicates standardized with concentration values of Fe (EFs-Fe) and Al (EFs-Al) using the following equation:

\[
{\text{EFs metal}} = \left[ \left( \frac{\mu \text{mol Hg}_{(t_1)}}{\mu \text{mol metal}_{(t_1)}} \right) / \left( X \mu \text{mol Hg}_{(t_1-t_0)}/ \mu \text{mol metal}_{(t_1-t_0)} \right) \right]
\]

\[t_1 = \text{oldest growth band and } t_0 = \text{youngest growth band.}\]

Due to the nature of the chemical analyses and the formation of growth bands, most increments of EFs resulted from passive trends: they were characterized by a mixture of peaks of increasing height occurring during short periods (i.e., few years). As passive trends are best represented by increments of parameters describing their variability, we also calculated EFs from the standard deviations of the band replicates (sdEFs) and scaled them to 1 to describe mid- and long-term oscillations of Hg concentration (e.g., Runnalls and Coleman, 2003). Reference values of Hg, Fe, and Al used to estimate EFs and sdEFs were calculated from concentrations of total suspended solids from sites adjacent to ours (Bastidas et al., 1999).

Because EFs and sdEFs are functions of the runoff markers Fe and Al, we expected that these parameters would change according to rainfall as long as Hg is introduced into the marine environment by runoff and rivers. Massive dumping of Hg into the system in years without heavy runoff and river discharge should appear in these analyses as peaks of EFs or sdEFs that are uncorrelated with rainfall. In these comparisons we would not detect river and runoff discharges of Hg from natural deposits of cinabarium, from anthropogenic activities releasing large amounts of Hg in years of maximum rainfall or releasing Hg into rivers gradually, during long periods.

3. Results and discussion

3.1. Rainfall and metal markers for runoff

We dated the growing bands of our coral samples as follows: C0-SS-ISL from 1900 to 1996 (97 years); C1-MF-ALC from 1930 to 1996 (37 years); and C2-MF-ISL from 1934 to 1999 (65 years).

We used rainfall as a proxy of runoff. The overall rainfall recorded in the area between 1940 and 1996 exhibited a decreasing trend (extreme rainfall anomalies went from 1500 to -1067 mm), and in the early 1980s (1980, maximum standardized anomaly = 1.11). During the mid-1930s, the highest rainfall peaks occurred between the 1930s and 1940s (Fig. 3). Regional data on rainfall from the 1910s through the 1990s; and C2-MF-ISL from 1934 to 1999 (65 years).

Rainfall anomalies were calculated using Statistica 6.0 program (2002, StatSoft Inc., Tulsa, OK, USA). The next important rainfall peaks occurred in the late 1950s (1967, maximum standardized anomaly = 1.78). A relatively dry period followed (1959, minimum standardized anomaly = – 1.41). The next important rainfall peaks occurred in the late 1960s (1977, minimum standardized anomaly = 0.02), and were separated by a drier period (1977, minimum standardized anomaly = – 0.32) (Fig. 3). Fe and Al are regarded as markers of terrigenous materials because they are present in high concentrations in all continental sediments (Kennedy, 1986; Loring, 1991; Ravichandran et al., 1995). If we assume that corals do not incorporate Fe, Al, and Hg selectively and that the only source of inorganic Hg is that adsorbed onto sediment particles, then the ratios Hg/Fe and Hg/Al found in coral skeletons should be similar to those existing in the sediment particles carried to the sea by rivers and runoff. Hence, large peaks of the Hg/Fe or Hg/Al ratios in skeletons not positively correlated to rainfall would suggest that the Hg originated from sources other than the inorganic Hg contributed from freshwater sources. Fluctuations in these ratios have been described in diverse coral species by a number of authors (cited elsewhere in this paper) and have been explained either as the result of differences in the ability of the corals’ organic matrix to bind metals during the process of sclerogenesis or in the bioavailability of metals (Budd et al., 1993; Taylor et al., 1995; Allison, 1996; Esslemont et al., 2000; Ramos et al., 2004). However, little is known about the mechanism(s) of metal uptake into the calcareous matrix and its variability among coral species (David, 2003; Ramos et al., 2004).

In our samples, log-transformed average concentrations of Fe/Ca in cores C0-SS-ISL and C1-MF-ALC increased in the mid 1950s, mid 1960s, the 1980s and later in the 1990s (Fig. 4A). Those in C2-MF-ISL increased during the 1940s, from the 1950s to the 1960s, and 1980s were common in all three cores.

Concentrations of Fe in S. siderea and M. faveolata (measured in ppm) (Table 2) were within values reported for other coral species growing in the same region but were higher than those reported for coral species growing in areas with less deposition of terrigenous materials. Concentrations from 1.32 to 369.31 ppm of Fe were found in Porites astreoides from Golfo Triste (Bastidas and Garcia, 1999) and values between 0.5 to 3.3 ppm in Porites sp. were reported from the Philippines (David, 2003).

Log-transformed concentrations of Al/Ca followed a highly variable pattern that is difficult to explain (Fig. 4B). Al/Ca and Fe/Ca ratios were neither correlated nor cross-correlated and were two orders of magnitude lower (Table 2) than values of the same metals in total suspended solids reported for the region in previous studies (Bastidas and Garcia, 1999). Average concentrations of Al (Table 2) were higher than values previously reported in P. astreoides from...
3.2. Chronology of Hg

In Venezuela, natural deposits of cinabrium occur between Aroa (Yaracuy state) and Carora (Lara state) in clastic rocks of the Matatere formation from the lower tertiary (Rodriguez, 1986). This region is drained by several rivers that discharge into Golfo Triste, including the Tocuyo, Aroa, and Yaracuy Rivers and their tributaries. Contrary to the overall temporal decrease in rainfall and the mixed signals of the runoff markers, our results suggest that the overall tendency of Hg peaks was to remain constant or to increase in height along chronologies. These results suggest that rivers and runoff likely were not the only sources of Hg for coral skeletons.

Qualitatively, the log-transformed concentrations of Hg/Ca in all samples were relatively high in the mid-1930s, late 1940s through the mid 1950s, and in the mid-1980s but chronologies were rather incongruent (Fig. 4C). Particularly in C2-MF-ISL, Hg/Ca ratios were one order of magnitude higher than those recorded in the other two cores (Table 2). This result is not entirely unexpected as these two cores, C2-MF-ISL and CO-SS-ISL, came from different species that could differ in their rate of metal incorporation. Metal concentrations fluctuations have been described in diverse coral species by other authors, and they have been ascribed mainly to the ability of the corals’ organic matrix to bind metals during the sclerosynthesis process, which in turn may differ between regions of the coral, among species, or by differential selectivity for metals (Allison, 1996; Budd et al., 1993; Esslemont et al., 2000; Taylor et al., 1995).

High concentrations of Hg were also reported in *P. astreoides* from Punta Brava (from none detected to 2.50 ppb between 1960 and 1995) (Bastidas and Garcia, 1999), but larger than those reported in *S. siderea* from Central America (from 18.9 to 71.0 ppb in 1996 to 1997) (Guzman and Garcia, 2002). High concentrations of Hg also were reported in sediments from different localities within Golfo Triste: in the beach opposite the Morón petrochemical complex (60–300 ppb) (Pequiven, 1980); in a number of open water localities within Golfo Triste (91–220 ppb in 1991 and 12–41 ppb in 1999) (Pérez, 1991, 1999); and in Morrocoy National Park (161–325 ppb) (Bastidas et al., 1999). Almost all of these values ranged within those reported for Hg-polluted marine-coastal ecosystems elsewhere (Coggins et al., 2006; Garcia-Rico et al., 2006).

Correlation between the concentrations of Hg/Ca and Fe/Ca in all three cores was significant (n = 157, Spearman, $r_{Hg,Fe} = 0.70$, p < 0.001) suggesting either that the mechanisms of uptake of these two elements into the calcareous matrix were similar or that their bioavailability was somehow coupled or both. However, the concentrations of Hg/Ca and Al/Ca were neither correlated nor cross-correlated. Despite of both Fe and Al being used as markers for terrigenous sediments, patterns of incorporation of these elements have differed in a number of previous studies. For example, in corals *Heliofungia actiniformis* and *Galaxea fascicularis* from the Ryukyu Islands, the incorporation of metals such as Al, Ca, Mg, Si, and Pb into the skeletal structure was relatively constant, whereas that of Fe, Mn, Cu, and Ba was highly variable from the periphery of their colonies to the center (Yamada et al., 1998).

3.3. Enrichment factors

Patterns and magnitudes of EFs-Fe and EFs-Al differed substantially, but most EFs were greater than 1 (Fig. 5); this finding strongly supports the premise that Golfo Triste was impacted by

<table>
<thead>
<tr>
<th>Cores/years</th>
<th>N</th>
<th>Hg</th>
<th>Fe</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>ng/g</td>
<td>µg/g</td>
<td>µg/g</td>
</tr>
<tr>
<td></td>
<td></td>
<td>nmol/mol Ca</td>
<td>µmol/mol Ca</td>
<td>µmol/mol Ca</td>
</tr>
<tr>
<td>CO-SS-ISL</td>
<td>49</td>
<td>26.0 ± 12.9</td>
<td>16.1 ± 13.7</td>
<td>16.5 ± 7.6</td>
</tr>
<tr>
<td>1900–1996</td>
<td></td>
<td></td>
<td></td>
<td>28.9 ± 13.5</td>
</tr>
<tr>
<td>C1-MF-ALC</td>
<td>66</td>
<td>12.8 ± 5.0</td>
<td>6.0 ± 1.93</td>
<td>7.9 ± 5.3</td>
</tr>
<tr>
<td>1930–1996</td>
<td></td>
<td></td>
<td></td>
<td>9.8 ± 3.4</td>
</tr>
<tr>
<td>C2-MF-ISL</td>
<td>66</td>
<td>282.1 ± 540.0</td>
<td>219.9 ± 179.3</td>
<td>10.1 ± 9.9</td>
</tr>
<tr>
<td>1934–1999</td>
<td></td>
<td></td>
<td></td>
<td>31.1 ± 16.0</td>
</tr>
</tbody>
</table>

| Note: | CO-SS-ISL: Siderastrea siderea; C1-MF-ALC and C2-MF-ISL: Montanastraea foveolata. |
large inputs of Hg (Kamau, 2002). High values of EFs-Fe matching our three chronologies occurred in the 1950s, 1960s, 1970s, and 1980s (Fig. 5), whereas those of EFs-Al matched all three chronologies only in the 1960s and early 1990s. EFs-Fe and EFs-Al differed by as much as two orders of magnitude, probably because of differences in the rates of incorporation of Fe and Al into the calcareous matrix (Kennedy, 1986). Chronologies of EFs-Fe and EFs-Al were too incongruent for further analysis. Even so, although regional rainfall data were neither correlated nor cross-correlated to EFs, local maxima of rainfall anomalies matched EFs peaks in the 1940s, 1960s, and 1980s. EF peaks recorded in the 1950s and 1970s occurred when rain was frequent but continuously and rapidly decreasing in intensity.

In this study, the earliest maxima of EFs-Fe dated back to the mid 1900s, early 1910s, and 1920s and were found in CO-SS-ISL (Fig. 5A). Early peaks of EFs-Al were found in the same core around the 1920s. High concentrations of Hg between the 1900s and 1930s were probably associated with early anthropogenic activities such as mining, wood-cutting and burning, and deforestation (sensu Guzman and Garcia, 2002). These activities began in Venezuela in the late 19th century mostly due to the expansion of human settlements, the logging of forests for the wood industry, and the development of commercial crops such as cocoa, coffee, and sugarcane (Grau, 1972, 1995). Deforestation increased Hg deposition in the neighboring aquatic systems directly due to its effect on soil erosion and indirectly by contributing to the increase of particulate materials carried away by runoff and rivers (Roulet et al., 2000). At the end of the 19th century, the Aroa River valley was exploited by several parties involved in copper mining and smelting, both well-known sources of Hg (Wright and Welbourn, 2002).

Differences between the EF patterns in CO-SS-ISL and C2-MF-ISL, obtained from two different coral species living in the same area, were smaller than those existing between any of these cores and C1-MF-ALC, suggesting a strong locality effect. Because the entrance of the lagoon in which the colony of M. faveolata sampled in Alcatraz was growing and was opened only partially to the sea, we speculate that the influx rates of suspended particles and the rates

**Fig. 5.** Average of metal enrichment factors (EFs) in coral cores and standardized rainfall anomaly. Hg/Fe (●), Hg/Al (○), and average rainfall (black line). (A) S. siderea, core C0-SS-ISL, (B) M. faveolata, core C1-MF-ALC, and (C) M. faveolata, core C2-MF-ISL.

**Fig. 6.** Standardized standard deviation of the enrichment factor (sdEFs) and standardized rainfall anomaly. Hg/Fe (●), Hg/Al (○), average rainfall (black line). (A) S. siderea, cores C0-SS-ISL, (B) M. faveolata, core C1-MF-ALC, and (C) M. faveolata, core C2-MF-ISL. Arrows indicate increments in the EFs that do not correspond with the increments in the rainfall.
of sedimentation there were different of those existing in the open sea reef in which the other two colonies were growing. Further data and research is required to test this hypothesis.

The patterns exhibited by sdEFs were very homogeneous within all three chronologies. We found four periods in which sdEFs were very high, and each corresponded roughly to a decade (1950–1990; Fig. 6). High sdEF values also occurred in the early 1940s in CO-SS-ISL and C1-MF-ALC (Fig. 6) and in the late 1940s, in C2-MF-ISL. The latter was matched only by corresponding but smaller peaks in the other coral chronologies (Fig. 6). Both sdEFs-Fe and sdEFs-Al chronologies from C1-MF-ALC differed from those of the other two cores in that they lacked the enormous peaks in the 1970s. Based on previous results, we speculate that these differences are also the product of locality effects (Fig. 6).

Peaks of sdEFs occurring in the 1940s were associated with large and increasing rainfall anomalies and resulted from increasing runoff (Fig. 6). A similar association was observed between sdEF peaks and rainfall maxima that occurred in the 1960s and the early 1980s (Fig. 6). On the other hand, peaks of sdEFs occurring in the 1950s and 1970s were associated with periods in which rainfall anomalies were relatively high but rain intensity was constantly and rapidly decreasing, suggesting that the maximum concentrations of Hg during these decades were best explained by considering the combination of runoff and the sudden availability of Hg in the environment.

Since 1957, industries such as INVEPAL (formerly VENEPAL) contributed heavily to the polluting Golfo Triste. However, oil-related industries established during the second half of the 20th century released the most Hg into local marine environments. The Morón petrochemical complex began activities in 1958 (Ministerio Energía y Minas, 1994), and the production of ammunition and explosives began in 1968 (known as CAV1M since 1977) (Iglesias et al., 1998). The occurrence of high values of sdEFs from the coral cores during the late 1950s matched the timing of when the fertilizer and the chlorine-caustic soda plants of the Morón petrochemical complex began operation (Ministerio Energía y Minas, 1994). Between 1958 and 1977, these plants processed approximately 3,000 barrels of crude oil every day, produced 150,000 metric tons of fertilizer every year (Hinestroza, 2001), released Hg-rich emissions to the atmosphere, and discharged their wastewater and residues directly into the gulf.

High values of sdEFs were also found in the 1970s. The chlorine-caustic soda plant ceased operations in 1977 (Ministerio Energía y Minas, 1994) at which time it released several tons of Hg into the environment in the form of solid wastes discharged into the nearby Caño Alpargatón River. Other industries that are considered to be relevant sources of heavy metal pollution, such as the fertilizers plants CAVIM, and INVEPAL, are still operating today. Perhaps this explains why after 60 years of a continuous decline in rainfall and runoff in the region (Fig. 3), concentrations of Hg in the environment have not diminished in recent decades.

Our results suggest that some marine environments in Golfo Triste have been impacted by Hg since the first decades of the 20th century and that levels of Hg in coral skeletons are similar to or higher than those in other impacted areas of the world. Rivers and runoff supply most of the Hg available in the region, but subtle clues point to previously undetected records of Hg release by local industries. Certainly, further work is required to untangle the complex historical dynamics of Hg in this economically important region of Venezuela.

Acknowledgements

We would like to thank C. Bastidas, E. Brunetti, A. Croker for their logistical support while sampling at Golfo Triste; we are also grateful to A. Oliveros for laboratory assistance and to Laboratorio de Desechos Tóxicos (USB) for metal analyses. P. Zanders made helpful comments to improve this manuscript. This work was sponsored by FONACIT (Project G-2001000599) and the Smithsonian Tropical Research Institute.

References


Ravichandran, M., Baskaran, M., Santschi, P.H., Bianchi, T.S., 2000. Increase in mercury contamination recorded in lacustrine sediments following deforestation in the central Amazon. Chemical Geology 165, 243–266.


