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Baseline

Total mercury in sediments from mud volcanoes in Gulf of Cadiz

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Mercury emissions into the environment have both natural and anthropogenic sources. Natural sources include volcanic activity, erosion of mineral deposits (the earth's crust contains 0.5 parts per million of mercury) (Gochfeld, 2003; Gustin, 2003), association with hydrocarbons (Miedaner et al., 2005; Wilhelm et al., 2006), and volatilization from the oceans, whereas man related sources include metal smelting, coal combustion, chemical synthesis/use, and waste incineration (SEC, 2005). Between 2700 and 6000 tons of elemental mercury are released per year via natural means to the biosphere through degassing from the earth's crust and oceans (Tchounwou et al., 2003). Industrial wastes and the combustion of fossil fuels add up to an additional 2000–3000 tons of mercury to the environment (ATSDR, 1999). Natural and anthropogenic sources led to a significant enhancement in environmental exposure and deposition, increasing the existing global Hg pool created by past releases (SEC, 2005).

Mercury has high affinity for suspended particles, which can lead to its extraction from the water column and its accumulation in the sediments. Thus, sediments function as a deposit and also as a source of mercury to porewaters and biota (Ramalhosa et al., 2001, 2006; Ram et al., 2003). It is also well known that methylation processes, mediated by bacteria in sediments, convert mercury into methylmercury, the most toxic lipophilic form (Heyes et al., 2006; Kim et al., 2006). This organic mercury is readily bioavailable, accumulating along food chains due to bioconcentration and biomagnification (Baeyens et al., 2003; Gochfeld, 2003; Tchounwou et al., 2003). Therefore, mercury is now acknowledged as a global, diffuse and chronic problem (SEC, 2005) due to its high toxicity to humans, ecosystems and wildlife.

Mud volcanism and fluid flow processes at active continental margins with high sedimentation rates, and in accretionary wedges such as in the Gulf of Cadiz (GC), have an important role in the hydrological budgets, biogeochemical cycles and physical properties of sediments. Fluid flow and mud volcanism also make a potentially important contribution to the geochemical budget of metals in the ocean and in the atmosphere. Fluid advection through the sediments provides an efficient mechanism for the upward transport of reactive components and trace gases, where methane is one of the most important, and has an impact on the mineralization within the shallow sediments and on the chemistry and benthic biota. The widespread occurrence of fluid escape processes has been recognized in a variety of different marine settings and throughout the geological record (Campbell et al., 2002; Peckmann and Thiel, 2004). The nature and composition of the expelled fluids and materials from the fluid escape structures and mud volcanoes (MV) can give valuable information on the geology and geochemistry of the deeper sediments.

The Gulf of Cadiz, located south of Iberia is an area with extensive evidence of hydrocarbon-rich gas seepage, manifested by the presence of mud volcanoes, pockmarks, diapiric ridges and the formation of methane-related authigenic carbonates (Gardner, 2000, 2001; Mazurenko et al., 2002; Pinheiro et al., 2003; Somoza et al., 2003). The first mud volcanoes were discovered in this area in 1999 (Gardner, 2000, 2001) and since then they have been extensively investigated in the framework of several national and international projects (INGMAR; MVSEIS; HERMES). Most of the geochemistry studies dealing with mud volcanoes in this area have focused either on the characterization of the gas composition in gas hydrates and in interstitial fluids, or

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on the sediment geochemistry, mainly related to the abundance of major elements. Data on metals content, especially mercury, are still scarce for mud volcanoes. In this study, we show, for the first time, results for the abundance of mercury in the hydrocarbon gas-rich sediments of mud volcanoes in the Gulf of Cadiz, and we investigate the role of these structures as traps or sources of mercury.

The sediment samples analyzed in this study were retrieved using a gravity corer from several mud volcanoes of the Gulf of Cadiz (Fig. 1 and Table 1). They were acquired during two scientific cruises, in the scope of the Euromargins MVSEIS Project (01-LEC-EMA24F; PDCTM72003/DIV/40018). These cruises, TTR-14 and TTR-15, were carried out on board the R/V Professor Logachev within the framework of the Training Trough Research Programme of the Intergovernmental Oceanographic Commission of UNESCO (UNESCO/IOC), in the summers of 2004 and 2005, respectively.

Six cores (AT518, AT522, AT526, AT540, AT543 and AT544) from TTR14 and six cores (AT578, AT579, AT590, AT592, AT596 AND AT598) from TTR15 were studied. Core AT518 was taken from a control site with hemipelagic sediments, away from mud volcanoes; Core AT522 was collected on the crater of Ginsburg MV; Cores AT540, AT579 and AT578 were taken from the crater on one of the flanks, close to the crater, and from the flank but away from the crater of the Meknés MV, respectively; Cores AT543 and AT544 were taken from the Captain Arutyunov MV; Cores AT592, AT596 and AT598 were taken from the Semenovich, Porto and Bonjardim MVs (Table 1). Each core was divided into sections of 10 cm in length (corresponding to about 100 g of sediment) in order to determine the total mercury concentrations, the percentage of fine particles ($\%F < 63$ μm) and the organic matter content.

After collection, the sediment samples were immediately frozen on board. The number of samples for each core depended on the retrieved core length. In the laboratory, sediment samples were freeze-dried, homogenised and manually sieved using a 1 mm mesh size nylon sieve. The percentage of fine particles was determined by wet sieving about 5 g of dried sediment through a sieve of 63 μm mesh. The organic matter content was estimated by the Loss on Ignition (LOI) at 500 °C during 4 h (Williams, 1985). Sediments for total mercury analysis were directly analysed by atomic absorption spectrometry (AAS) with thermal decomposition, using an Advanced Mercury Analyser (AMA) LECO 254 (for further details see Costley et al., 2000). The accuracy and precision of the analytical methodology for mercury determinations were assessed by replicate analysis of certified materials, namely NRC MESS-3 estuarine sediment. Certified (91 ng $g^{-1} \pm 9$ std) and measured values (94 ng $g^{-1} \pm 6$ std; $n = 70$) were in agreement, and precision of replicates analysis ranged between 0.33 and 3.6%. Spearman coefficients (r_s) were calculated to determine the correlation between total mercury concentrations,

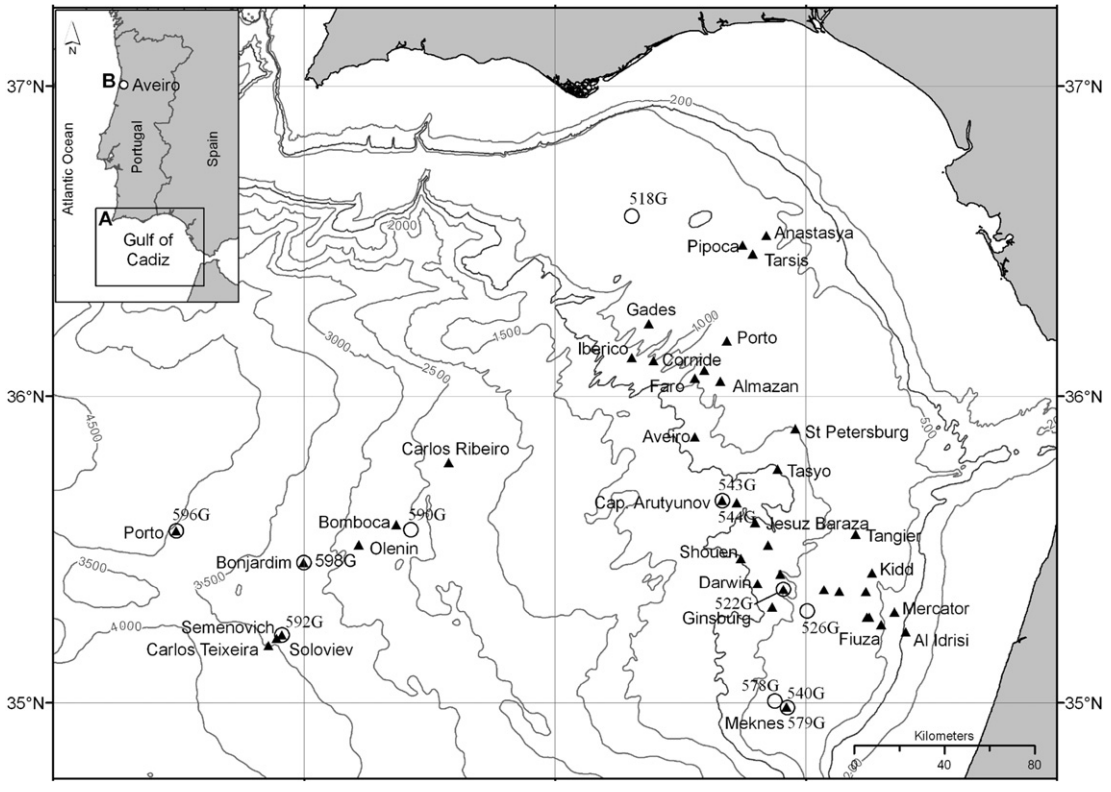

Fig. 1. Map of the Gulf of Cadiz with the location of the known mud volcanoes and the location of the gravity cores used in this study. Inset illustrates the location of the Gulf of Cadiz (A) and the location of the Ria de Aveiro, used as a comparison site (B).

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Table 1
Location of sampling sites and associated mud volcanoes

Station number	Mud volcano/structure	Latitude	Longitude	Water depth (m)
TTR14 - AT518G	Background (pelagic sediment)	36°, 34, 998	07°, 41, 186	696
TTR14 - AT522G	Crater of Ginsburg mud volcano – MM (mud breccia)	35°, 22, 417	07°, 05, 299	912
TTR14 - AT526G	Domelike structure	35°, 18, 135	06°, 59, 693	862
TTR14 - AT540G	Mud volcano	34°, 59, 070	07°, 04, 413	701
TTR14 - AT543G	Captain Arutyunov mud volcano – MM	35°, 39, 688	07°, 19, 981	1345
TTR14 - AT544G	Captain Arutyunov mud volcano – MM	35°, 39, 707	07°, 20, 012	1330
TTR15 - AT578G	Background off Meknés mud volcano – MM (pelagic sediment)	34°, 59, 49′	07°, 04, 54′	762
TTR15 - AT579G	Slope of Meknés mud volcano – MM	34°, 59, 30′	07°, 04, 46′	747
TTR15 - AT590	Sunk ship with coal – PM	34°, 59, 04′	08°, 34, 36′	2586
TTR15 - AT592G	Semenovich mud volcano – PM	35°, 13, 44′	09°, 05, 24′	3242
TTR15 - AT596G	Porto mud volcano – PM	35°, 33, 82′	09°, 30, 53′	3878
TTR15 - AT598G	Bonjardim mud volcano – PM	35°, 27, 65′	08°, 59, 99′	3064

MM is Moroccan margin and PM is Portuguese margin.

the percentage of fine particles (%$F < 63$ μm) and the organic matter content (% OM). For all statistical tests the significance level was 0.05.

Vertical profiles of total mercury content in the cores are presented in Fig. 2. Concentrations varied from 9.0 to 86.2 ng g^{-1}. Cores AT518, AT578, AT543 and AT544 have

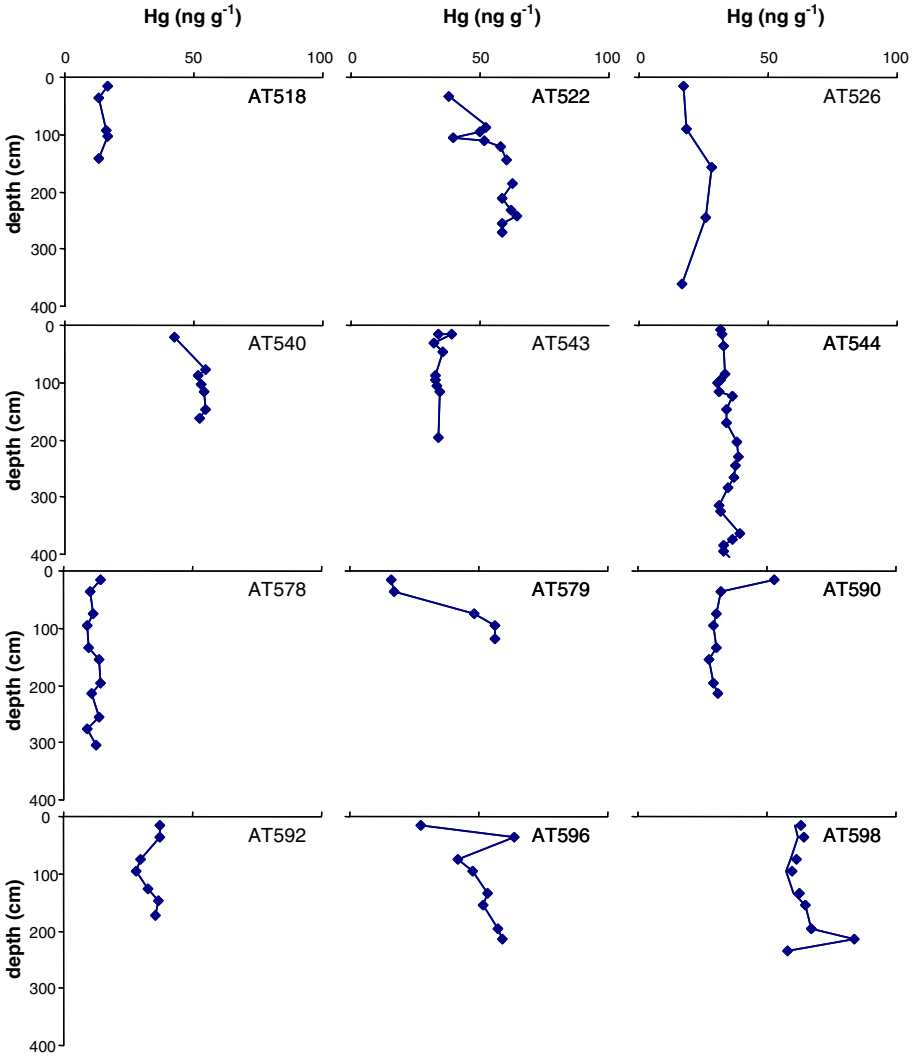

Fig. 2. Vertical profiles of total mercury concentrations (ng g^{-1}) in the sediment cores from TTR14 and TTR15 cruises in the Gulf of Cadiz. Location of the cores is shown in Fig. 1 and Table 1.

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a nearly constant mercury concentration along the profiles. The lowest levels were found in cores of pelagic sediment (AT518 and AT578) which are considered to contain background levels with concentrations ranging between 13.1–16.8 ng g^{-1} and 9.0–14.4 ng g^{-1}, respectively (Fig. 3c). Core AT526 was taken on a dome structure which is not a mud volcano, and it is among the cores with lower mercury concentrations (16–28 ng g^{-1}) showing values comparable to the background cores levels.

Except for AT526 and superficial values for core AT579 (15.9–17.3 ng g^{-1}), all other mud volcano cores have higher mercury concentrations, with mean values ranging between 32.9 and 66.1 ng g^{-1}.

In cores AT522, AT540, AT579 and AT596 mercury concentrations in deeper layers are higher than in superficial layers. AT590 (a non-volcano core) was the only core with higher concentrations at the top and constant levels with depth. This corresponds to an area of a shipwreck with a cargo of coal.

Mercury peaks exhibited by some cores were observed at different depths. For example, cores AT596 and AT598 have similar levels in the middle section but AT596 displayed a peak in the top layer and AT598 a subsurface peak.

In these sediments, the $\%F < 63$ μm ranged from 52% to 98% (mean value of 79.2% and std. of 9.9%) with more than four fifths of the results above 70% (Fig. 3a). The organic matter content ranged from 2.4 to 7.1% (with almost 83% of results below 5%) (Fig. 3b).

The Spearman coefficients (r_s) between mercury concentrations, fine fraction and organic matter content were calculated for all cores, but only for cores AT522, AT544, AT579 were significant correlations at a 5% significance level found. For the AT522 core, a positive correlation

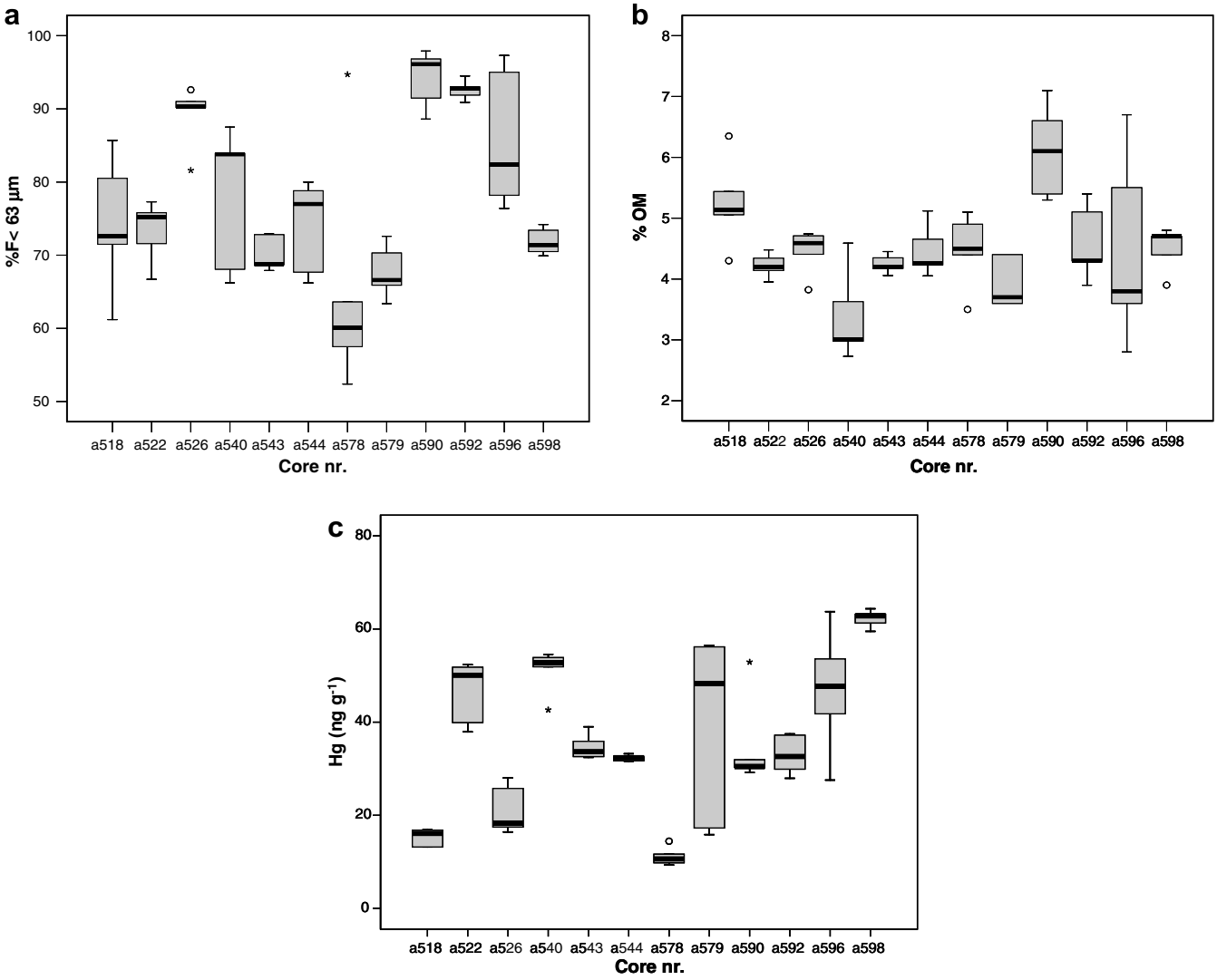

Fig. 3. (a) Box and whisker plots of percentage of fine particles ($\%F < 63$ μm), (b) organic matter content and (c) total mercury (ng g^{-1}) in the sediment cores from TTR14 and TTR15 cruises in the Gulf of Cadiz. Median concentrations and interquartile range (IQR) are plotted. Whiskers represent the highest and lowest values excluding "outliers" (represented by dots and considered as cases with values between 1.5 and 3 × IQR from the 75th percentile or 25th percentile). Asterisks represent cases with values more than 3 × IQR from the quartiles.

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was found between total mercury and the percentage of fine particles ($r_s = 0.64$, $p = 0.018$, $n = 13$), while a negative correlation was found between total mercury and the percentage of organic matter content ($r_s = -0.86$, $p = 0.0001$, $n = 13$). Core AT544 also showed a significant inverse correlation between total mercury and the percentage of organic matter content ($r_s = -0.52$, $p = 0.012$, $n = 22$). Contrary to what was found in core AT522, the core AT579 showed a marginal negative correlation between fine fraction and total mercury levels ($r_s = -0.90$, $p = 0.04$, $n = 5$). Although total mercury is normally associated with high values of $\%F < 63$ μm and OM, due to the fact that mercury preferentially binds to silt/clay particles, in these sediments a positive correlation was only found in core AT522. This way, the marginal and absent correlations found could eventually be due to the fact that small particles are more abundant in estuarine than in offshore sediments and to the presence of sulphides in these sediments. Sulphides may strongly bind the mercury and make it unavailable to react with other constituents, disrupting the relationship with particle sizes. Fine fraction and organic matter content (estimated by LOI) were similar in cores collected in mud volcanoes and at the reference sites; therefore, the differences observed in mercury levels and the absence of a pattern in the observed correlations corroborates that fine fraction and organic matter content are not the main parameters controlling mercury levels.

Some mud volcano sediments displayed levels above the provisional environmental assessment criteria (EAC) of 50 ng g^{-1}. EAC's were recently established by OSPAR to express biological and/or ecotoxicological risk (Bignert et al., 2004). For values exceeding the lower EAC threshold, biological effects are possible (e.g. biomarker response, impaired growth, reproduction). Nevertheless, bioaccumulation of mercury was described in ecosystems such as deep-sea hydrothermal vent communities (Colaço et al., 2006), suggesting that bioaccumulation in organisms exposed to mud volcanoes can also be expected.

Mercury levels found in reference cores (values ranging from 9.0 to 16.9 ng g^{-1} with a mean value of 12.9 ng g^{-1}) are comparable to concentrations of 21 ng g^{-1} found in deeper strata of cores from the Adriatic Sea (Fabbri et al., 2001). Cossa et al. (2001) observed at the base of 2 meter cores collected at Gulf of Cadiz, consistent mercury concentrations of about 50 ng g^{-1}, as a result of transport by the rivers Tinto and Odiel from one of the largest sulphide deposits in the world.

Pato et al. (in press) reported mercury concentrations ranging between 1.0 to 8.6 ng g^{-1} in coastal sediments under the influence of the Ria de Aveiro lagoon NW Portuguese coast (Fig. 1). This lagoon has more than 30 tons of mercury buried in the sediments and, due to tidal forcing, this mercury is expected to be slowly and constantly released into the Atlantic Ocean. Nevertheless, despite this anthropogenic pressure, the low mercury levels found in the coastal sediments revealed that with low carbon content (ranging between 0.033% and 0.49%) and low $\%F < 63$ μm (ranging between 0.9% and 7.7%), sediment characteristics render them unable to trap, to a significant extent, the mercury that is being exported from the lagoon.

Although no clear pattern was observed between mercury levels and the organic matter content and particle size, these characteristics in sediments from mud volcanoes in Gulf of Cadiz should potentially lead to the retention of mercury. In our study, mercury enrichment was clearly observed in mud volcano sediment when compared to reference sediments (cores AT518 and AT578).

Hein et al. (2006) reported 20–40% more mercury in mud volcano sediments from offshore southern California than at a control site. In Gulf of Cadiz mud volcanoes, mercury enrichment reached a maximum of seven times the mean concentration in reference cores. Hein et al. (2006) pointed out that the high metal content in mud volcano sediments from offshore southern California is a result of leaching of basement rocks by fluid circulating along an underlying fault, which also allows for a high flux of fossil methane. This may also explain the high levels of mercury found in the sediments from the Gulf of Cadiz mud volcanoes.

In conclusion, it should be underscored that the mercury concentrations observed in sediments of mud volcanoes are very high even for such environments, and they may act both as an important repository and as an immediate source of mercury to pore waters. Such an enriched pool of mercury in the ocean environment should be monitored in order to control the potential for bioaccumulation and toxicity in marine biota living in this environment.

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