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Distribution and Enrichment of Silver and Cadmium in Coastal Sediments from Bahía Todos Santos, Baja California, México

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Abstract Silver, cadmium and iron were studied in sediment from Bahia Todos Santos, Baja California, México during 2004. Results showed that the spatial distributions of these metals were very similar to that of organic carbon and fine grain size, with values increasing from the inner to the outer parts of the bay. High concentrations and enrichments of silver (0.051–0.071 μg g^{-1} dry weight) and cadmium (1.9 μg g^{-1} dry weight) in Bahía Todos Santos were associated to harbor dredging activities and to coastal upwelling, respectively. However, the distribution of silver and cadmium in most of the study area is controlled by grain size and organic carbon content.

Keywords Heavy metals · Bahía Todos Santos · Mexico · Coastal sediment

Sediments may act as an important sink of heavy metals. Although a significant proportion of the metals is buried, metal can partly be mobilized to the water column due to processes such as organic matter diagenesis and reductive dissolution of iron and manganese oxides (Forstner 1989). Due to this mobilization, studies of heavy metals in marine sediments are very important and could provide information not only about the transport and fate of contaminants in marine sediments, but also about the overlying water quality (Wang et al. 2003).

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Bahía Todos Santos (BTS) is located 100 km south of the México-USA border on the northwest coast of Baja California, México. BTS has an approximated area of 330 km^2. Most of the area (90%) is 10–50 m deep. However, there is a narrow 400 m deep submarine canyon located between Todos Santos Islands and Punta Banda (Fig. 1). The city of Ensenada, with 400,000 inhabitants, is located in the inner part of the bay. During many years BTS has been environmentally affected by domestic and industrial effluents; fishing and boat traffic; and agricultural runoff. During the last 5 years, dredging and disposition of dredged materials, mainly from the harbor has increased substantially. As a consequence of sediment disposal into BTS, the risk of environmental pollution has been increased. The aim of this study is to assess the spatial distribution and enrichment of Ag and Cd in marine sediments from BTS, and to determine whether or not factors such as effluents, traffic, agricultural runoff, and/or disposal of dredged sediment are important in the modification of the natural conditions.

Materials and Methods

A total of 21 superficial sediment samples were studied from BTS during April 2004 cruise aboard the Matamoros vessel (Fig. 1). Triplicates samples were collected from the central part (upper 3 cm) of a Van Veen grab using a Teflon spatula, stored in previously acid-washed polypropylene centrifuge flasks, and kept frozen prior to analysis.

Sediments digestion was made according to 3050B method from SW-846 protocol of the Environmental Protection Agency (EPA 1996). Briefly, 1 g of dry sediment was weighed in 30 mL acid-washed Erlenmeyer flask,

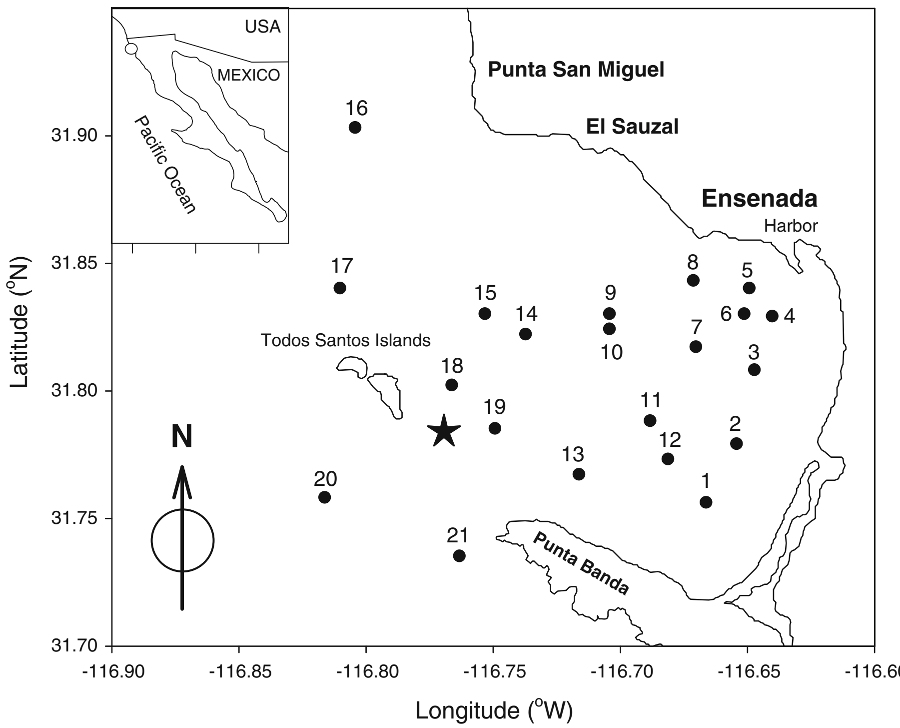

Fig. 1 Study area and sampling sites. Stars show dredging dumping sites location

2.5 mL of HNO_3 11 N and 10 mL of HCl 10 N (both trace metal grade) were added and left at room temperature overnight. Following, temperature was increased at 95 ± 5°C and sediments were digested at constant reflux during 5 h. Sample digestion solutions were placed in acid-washed 50 mL polypropylene centrifuge tubes until instrumental analysis. Iron quantification was made by air-acetylene flame atomic absorption using a Varian SpectrAA 220 FS equipment. On the other hand, a Varian SpectrAA 8809 atomic absorption spectrophotometer equipped with graphite furnace was used for Ag and Cd analysis. Sediment grain size (GS) (% <0.63 µm) was determined using a Horiba (model LA-910) laser/tungsten particle size analyzer according to the methodology described by Daesslé et al. (2002). A LECO (model CHNS-932) carbon analyzer was used to determine organic carbon (OC). Blank samples and certified reference material for marine sediment MESS-3 (National Research Council of Canada) were analyzed with each batch of samples to evaluate accuracy and precision of the analytical methodology. Certified and measured values were in general agreement, with recovery efficiency of 90%, 95%, and 90% for Fe, Ag and Cd, respectively. Detection limits for Fe, Ag, and Cd were 0.76, 0.01, and 0.001, respectively.

In order to identify Ag and Cd enrichments in BTS, metal-Fe baselines were elaborated. According to Schiff and Weisberg (1999) and Noblet et al. (2003), baselines relationships represent the prediction of which is considered as natural concentrations; thus, any concentration above that baseline limits would represent enrichment.

Results and Discussion

In general, Ag, Cd, and Fe showed similar spatial distributions patterns, with higher concentrations in the deeper outer limits of the bay and the submarine canyon (Fig. 2a, b, c respectively).

The spatial distribution profiles of Ag showed a strong increasing gradient toward the submarine canyon (Fig. 2a). The average concentration of Ag (0.027 µg g^{-1} dry weight) of inner bay stations (3, 4, 5, and 6) is less than half the average concentration (0.057 µg g^{-1} dry weight) of outer stations (18 and 19). This suggests that high concentrations of Ag in sites 18 and 19 could be the result of dredging material dumping in the submarine canyon, which is near to those particular sampling sites. High concentrations of Ag in organisms, sediments, and water in the coastal waters of Southern California and Baja California have been attributed to domestic and industrial outfalls (Martin et al. 1988; Muñoz-Barbosa et al. 2004; Muñoz-Barbosa et al. 2000; Sañudo-Wilhelmy and Flegal 1992). The harbor of the city of Ensenada has been impacted for many years by both kinds of discharges; thus, sediments dredging, transportation, and disposal, could affect places next to the zones where these activities have taken place.

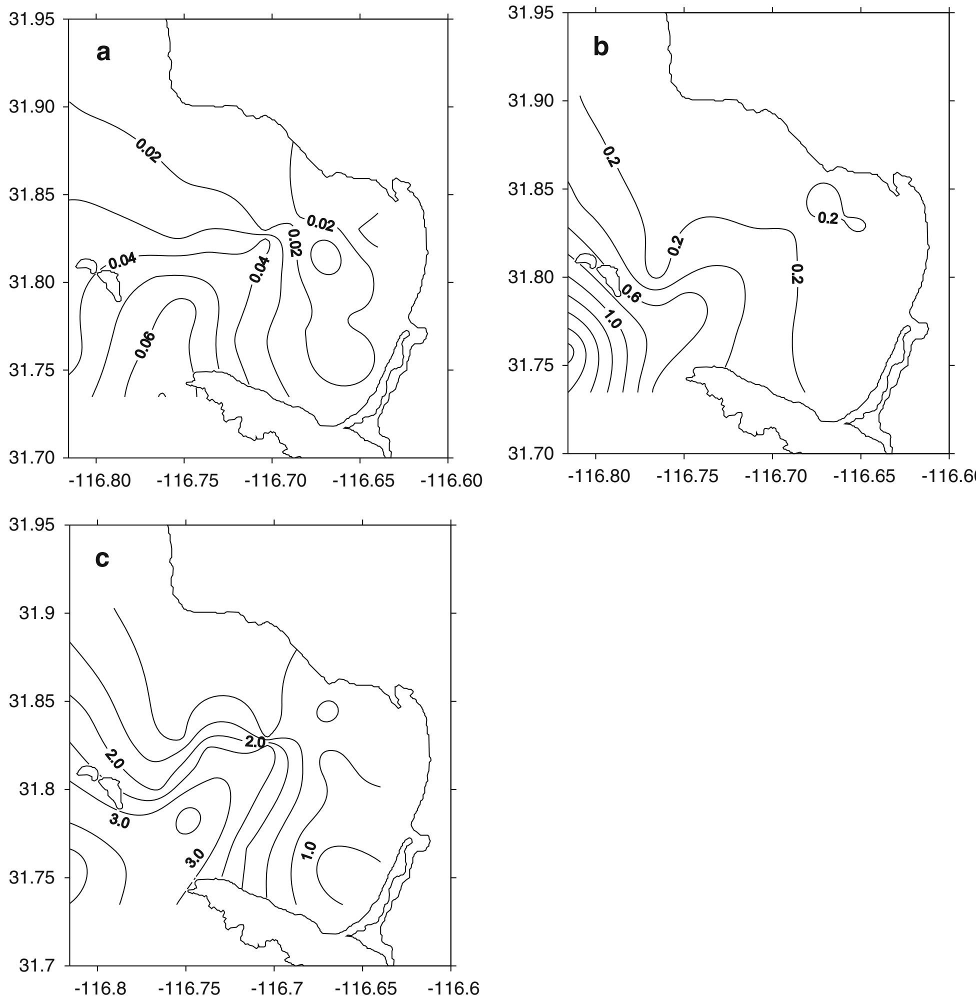

Fig. 2 Spatial distribution of Ag (**a**), Cd (**b**), and Fe (**c**). Numbers in line contours represent concentrations in μg g^{-1} (dry weight) for Ag and Cd, and percentage for Fe

Similarly to Ag, the geographical profiles of Cd showed lower concentrations in the inner part of BTS and higher in the outer sites (Fig. 2b). However, not all the sites that showed high concentrations of Cd in the outer part are the same as in the case of Ag. Sampling stations 18 (common to Ag) and 21 showed the highest concentrations of Cd (0.75 and 1.9 μg g^{-1}, respectively). In contrast to Ag, the biogeochemical cycle of Cd in the ocean has been linked to natural processes. Studies about metals in the northwest coast of Baja California have found that cadmium in mussels (Muñoz-Barbosa et al. 2000; Segovia-Zavala et al. 2003), sediments (Daesslé et al. 2000; Muñoz-Barbosa et al. 2004), and water (Sañudo-Wilhelmy and Flegal 1991; Segovia-Zavala et al. 1998) cannot be linked to anthropogenic sources. On the contrary, all these studies found that coastal upwelling is a very important factor in explaining the high concentrations found.

Cadmium involvement in the organic matter regeneration in the water column results in a nutrient-like vertical profile for this metal (De Baar et al. 1994). As a consequence, as in the case of nutrients, upwelling could be an important mechanism of Cd transport to the coastal zone surface waters. In a comparative study to determine the concentration of metals in organisms from polluted and clean places, Gutiérrez-Galindo and Muñoz-Barbosa (2001) found that Cd concentrations in the polluted place (Harbor of the City of Ensenada) were much lower that concentrations in the clean place (south side of Punta Banda). These authors concluded that Cd brought by upwelling to the coastal zone was the factor producing high Cd concentrations in the organisms of Punta Banda. Punta Banda is about 2.5 miles from the sampling sites where this study's highest Cd concentrations were found. Thus, it is likely that the same mechanism is affecting the Cd concentrations in both, organisms and sediments.

It is noteworthy that in older studies (Romero-Vargas-Marquez (1995), mean Cd concentrations in sediments from BTS, near the dumping site, were 3 times higher than the mean concentration inside the Harbor of Ensenada. We

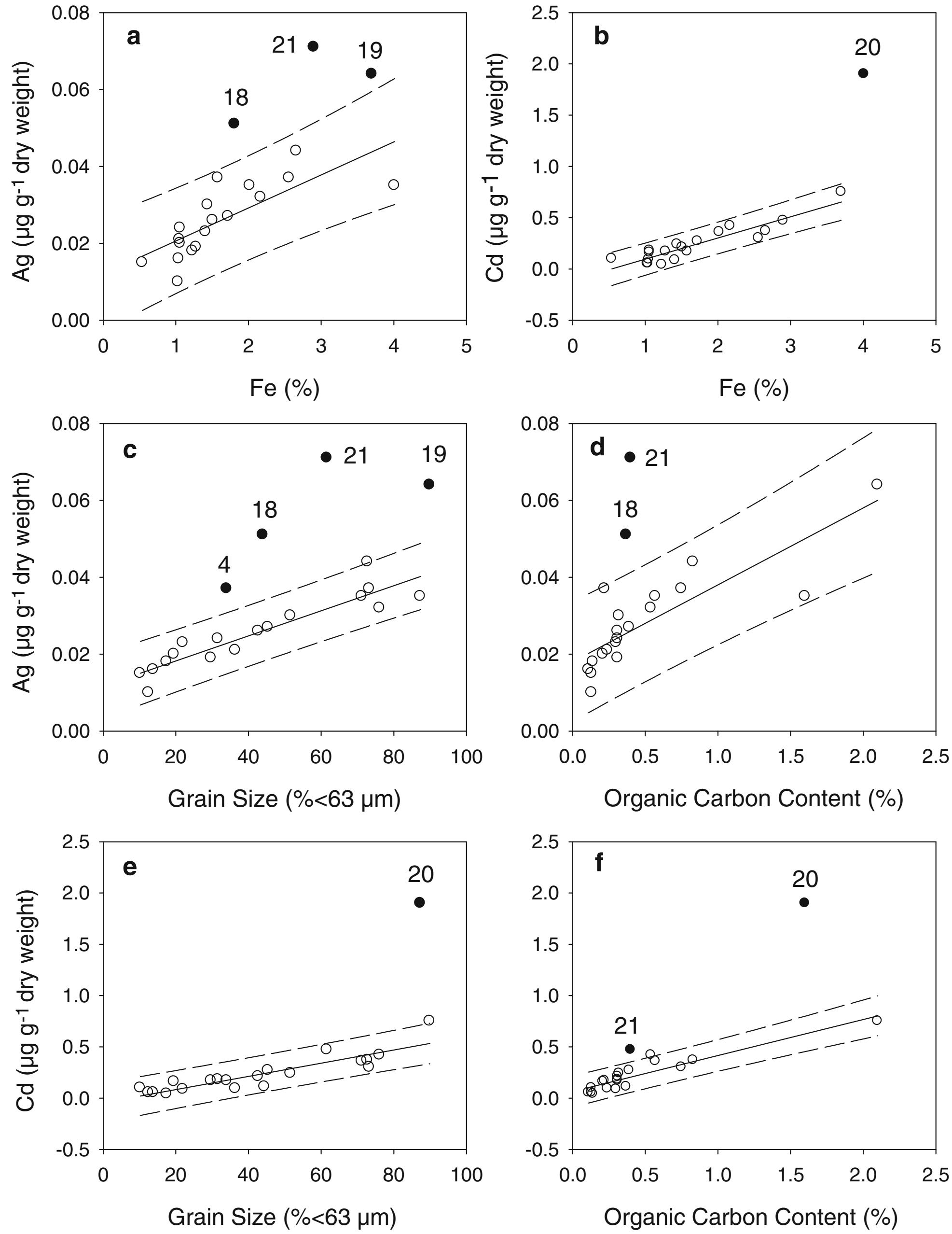

Fig. 3 Metal-Iron, Metal-Grain Size, and Metal–Organic Carbon content plots. Sites which fall within the regression prediction interval (*dotted lines*) are considered unenriched (*hollow symbols*), and sites which fall above the regression prediction interval are considered enriched (*filled symbols*)

Table 1 Pearson correlation coefficients

	Ag	Cd	Fe	GS	OC
Ag	1.00				
Cd	0.82	1			
Fe	0.88	0.83	1		
GS	0.86	0.94	0.91	1	
OC	0.84	0.86	0.94	0.91	1

All correlations are significant at $p < 0.05$

GS percentage of grain size lower than 63 μm in diameter, *OC* organic carbon content (%)

do not have sampling sites inside the Ensenada's harbor so we cannot make the same comparison.

In order to obtain a regional spatial distribution of Cd and Ag in sediments, results from this study were compared with those found by Schiff and Weisberg (1999), and Daesslé et al. (2000) in Southern California (SC) and Bahía Vizcaino, Baja California Sur, México (BV), respectively. Sediment digestion in SC and this study are similar (HNO_3–HCl); however, Cd concentrations from BV study are the result of the sum of the adsorbed, carbonates, Fe–Mn oxihydroxides, organic matter and sulphides fractions. Despite this discrepancy, cautious comparisons can be made. The Southern California region, which is located to the north of our study area, is a highly populated area with a very high economical development, resulting in a higher production and disposal of contaminants to the environment. On the other hand, BV is far away from heavily populated cities and the industrial activity is practically absent, which suggests that the bay has not been environmentally affected. The highest Ag concentration found in this study (0.071 $\mu g\ g^{-1}$) is one order of magnitude lower than the average concentration found in SC (0.34 $\mu g\ g^{-1}$; $n = 248$). In contrast, the highest Cd concentration found in this study (1.9 $\mu g\ g^{-1}$) is one order of magnitude higher than the average concentration found in SC (0.33 $\mu g\ g^{-1}$) and is similar to that found in BV (1.25 $\mu g\ g^{-1}$). The anthropogenic origin of Ag suggests a higher impact in SC than in BTS. On the other hand, the natural origin of Cd gives good reason for the higher Cd concentrations in almost pristine environment than in polluted places.

Tefry and Presley (1976) suggest that the Metal/Fe ratio may be used to distinguish between sediments with natural trace element levels and those which have been enriched or contaminated. To identify enriched stations, regression analyses between metals and Fe were carried out (Fig. 3a, b). Data that fell above the 99% prediction interval of these regressions were discarded, and regression analysis was done again using the remaining data. This procedure was repeated until no data fell above the 99% prediction interval. The eliminated data was plotted again to show the enriched sites. Ag/Fe relationship shows enrichments in sampling sites 18, 19, and 20 (Fig. 3a). Sampling sites 18 and 19 are very close to the dumping sites of dredged sediments from the harbor, which suggests that dredging activities could be responsible for these enrichments. On the other hand, Cd/Fe relationship shows that only sampling site 21 is enriched (Fig. 3b). This site is located southwest of Punta Banda, very close to the place where high concentrations of Cd where found in mussels and attributed to coastal upwelling (Gutiérrez-Galindo and Muñoz-Barbosa 2001).

Finally, the influence that GS and OC may have on metal enrichment is assessed. Overall, there is a significant correlation between GS and OC, and the concentration of Ag and Cd (Table 1). These correlations suggest that Ag, Cd and OC concentrations are, as expected, predominantly controlled by grain size. However, there are some stations that fall above the correlations line limits. Thus, in order to identify enrichments with respect to GS and OC, a similar method to the described above for Cd/Fe relationships was used. Silver relationships with GS and OC showed several enriched sampling sites. In the case of Ag/GS relationship (Fig. 3c), enriched samples 18 and 19 are near to the dumping site, and enriched station 4 is the closest to Ensenada City Harbor, which is the place where dredging takes place. Silver/OC relationship showed enrichments in sampling sites 18 and 21 (Fig. 3d), site 18 is located near to the dumping site. In general, the enrichment of Ag in these sites could be due to the dredging activities. On the other hand, Cd/GS, Cd/OC and Cd/Fe ratios only showed enrichments in sampling site 21 (Fig. 3e, f).

References

Daesslé LW, Carriquiry JD, Navarro R, Villaescusa-Celaya JA (2000) Geochemistry of surficial sediments from Vizcaíno Bay, Baja California. J Coastal Res 16:1133–1145

Daesslé LW, Ramos SE, Carriquiry JD, Camacho-Ibar VF (2002) Clay dispersal and the geochemistry of manganese in the northern Gulf of California. Cont Shelf Res 22:1311–1323

De Baar HJW, Saager PM, Nolting RF, Van der Meer J (1994) Cadmium versus phosphate in the world ocean. Mar Chem 46:261–281

EPA (1996) Acid digestion of sediments, sludges and soils (Method 3050B). Revision 2:1–12

Forstner U (1989) Contaminated sediments. Springer, Heidelberg

Gutiérrez-Galindo EA, Muñoz-Barbosa A (2001) Short-term temporal variability of Ag, Cd, and Cu in *Mytilus californianus* and the effectiveness of this organism as bioindicator. Cienc Mar 27:269–288

Martin M, Stephenson MD, Smith DR, Gutiérrez-Galindo EA, Flores-Munoz G (1988) Use of silver in mussels as a tracer of domestic wastewater discharge. Mar Pollut Bull 19:512–520

Muñoz-Barbosa A, Gutiérrez-Galindo EA, Flores-Muñoz G (2000) Mytilus californianus as indicator of heavy metals on the northwest coast of Baja California, Mexico. Mar Environ Res 49:123–144

Muñoz-Barbosa A, Gutiérrez-Galindo E, Segovia-Zavala J, Delgadillo-Hinojosa F, Sandoval-Salazar G (2004) Trace metal enrichments in surficial sediments of the northwest coast of Baja California, Mexico. Mar Pollut Bull 48:587–603

Noblet JA, Zeng YZ, Baird R, Gosset RW, Ozretich RJ, Phillips CR (2003) Southern California Bight 1998 Regional Monitoring Program, Southern California Coastal Water Research Project

Romero-Vargas-Marquez IP (1995) Metales pesados y sus fracciones químicas en sedimentos de la Bahía de Todos Santos, Baja California, México, Universidad Autónoma de Baja California, Ensenada. Baja California, México, p 86

Sañudo-Wilhelmy SA, Flegal AR (1991) Trace elements distributions in coastal waters along the US-Mexican boundary: relative contributions of natural processes vs. anthropogenic inputs. Mar Chem 33:371–392

Sañudo-Wilhelmy SA, Flegal AR (1992) Anthropogenic silver in the Southern California Bight: a new tracer of sewage in coastal waters. Environ Sci Technol 26:2147–2151

Schiff KC, Weisberg SB (1999) Iron as a reference element for determining trace metal enrichment in Southern California coastal shelf sediments. Mar Environ Res 48:161–176

Segovia-Zavala JA, Delgadillo-Hinojosa F, Alvarez-Borrego S (1998) Cadmium in the coastal upwelling area adjacent to the California-Mexico border. Estuar Coast Shelf S 46: 475–481

Segovia-Zavala JA, Delgadillo-Hinojosa F, Vidal-Talamantes R, Muñoz-Barbosa A, Gutierrez-Galindo EA (2003) Mytilus californianus transplanted as upwelling bioindicators in two areas off Baja California, Mexico. Cienc Mar 29:665–675

Tefry J, Presley BJ (1976) Heavy metals in sediments from San Antonio bay and the northwest Gulf of Mexico. Environ Geol 1:283–294

Wang SX, Zhang SZ, Shan XQ (2003) Fractionation of heavy metals in different particle size sediments and its relationship with heavy metal pollution. B Environ Contam Tox 71:873–880