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Levels of Reactive Mercury and Silver in Sediments from the Port of Ensenada, Baja California, Mexico

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Silver and mercury, two of the three most toxic of the elements (with Cu) to invertebrates and algae in marine and estuarine ecosystems (Bryan and Hummerstone 1977; Fisher et al. 1984), share similar characteristics: both elements are free of strong complexation by dissolved organic ligands (Miller and Bruland 1995) and are also dominated by chloride complexation in oxic seawater (Clark 1994; Miller and Bruland 1995). Furthermore, both Ag and Hg are very particle-reactive under fresh- and seawater conditions (Wang and Driscoll 1995, Ravizza and Bothner 1996, Wen et al. 1997). However, anthropogenic Ag is introduced into the aquatic environment mainly through the discharge of wastewaters (photographic industry, x-ray applications, and electronics; Ravizza and Bothner 1996), whereas Hg is introduced mainly from atmospheric deposition (coal combustion and waste incineration) and industrial discharge (antifouling paint for the hulls of ships, slimicides for use in the lumber and paper pulp industries, pesticides, and seed dressings in agriculture and in pharmaceuticals; Clark 1994).

Silver produces toxic and sublethal responses in microorganisms and marine invertebrates (Luoma et al. 1995) because its ions are rapidly taken on biological surfaces, of the rapid intracellular accumulation of silver, and its interference with copper metabolism (Bryan 1971). It is generally assumed that Ag is bioaccumulated through the assimilation of either $AgCl^o(aq)$ or Ag^+, the dominant species in fresh and brackish waters, respectively (Reinfelder and Chang 1999). Elemental Hg^o and methylated Hg are neurotoxic (effects that are generally irreversible), while inorganic Hg salts are nephrotoxic (Hamasaki et al. 1995). Particularly important is methyl mercury (MeHg), which due to its ability to pass biological membranes, its high chemical stability, and its low concentrations in excreta from organisms is the only mercury species that biomagnifies to a higher degree in food chains (e.g., Cabana and Rasmussen 1994, Fischer et al. 1995). In this work, a sediment core from the port zone of Ensenada, Mexico, was analyzed for mercury and silver associated with the reactive fraction (which includes carbonates, Fe and Mn oxyhydroxides, iron monosulfides, organic matter, pyrite), which takes into account most of the components potentially capable of participating in the formation, transformation or dissolution of other

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mineral phases (and associated trace metals), or in their incorporation into living organisms. The objective of this study was to analyze the distribution of reactive Ag and Hg in a sediment core from the port zone of Ensenada, Baja California, Mexico.

This zone is located approximately 100 km south of the US-Mexico border, on the Pacific coast of the Peninsula of Baja California, inside the Bay of Todos Santos (Fig. 1). Generally, the bay can be considered as a region whose sediment trace metal levels are relatively low (Romero-Vargas-Márquez 1995), except for the zone encompassed by the port zone and marina (Fig. 1), covering an area of 1.15 km^2. Here, total metal concentrations (Cu, Zn, Cd, Fe, Ni, Cr, Al and Mn) can represent from 1.1 to 14.3 times the average trace metal concentration of the bay sediments (Romero-Vargas-Márquez 1995). Metals tend to accumulate in this zone because: (1) it is a low-energy zone in which fine-grained sediments tend to accumulate and, due to their higher surficial area, also tend to incorporate higher concentrations of trace metals; (2) it is the zone of discharge of urban runoff water through the seasonal stream Arroyo Ensenada, especially during the winter rainy season; (3) of the contributions from marine vessels normally docked in the port and marina areas; and (4) of the presence, within the port zone, of dry docks with activities such as reparation and maintenance of marine vessels that involve liberation of antifouling paint from ship hulls and use of mine tailings for sand blasting operations. Actually, works are underway to build a new dock facility for recreation cruise vessels inside the port zone. Construction of this dock will involve dredging approximately 1,500,000 m^3 of sediments from which 300,000 m^3 will be transferred outside of the port zone, whereas the rest will be used as fill for the new facilities.

MATERIALS AND METHODS

Samples were obtained from one core collected in the port zone (Figure 1) at approximately 6 m water depth on November 2, 1998. Hg and Ag concentrations measured at the core location are probably lower-end range levels since the areas showing the higher concentrations of organotin compounds and metals in superficial sediments are generally those located at the western part of the port zone (Macías-Carranza et al. 1997, Romero-Vargas-Márquez 1995). A plastic core liner (7.2 cm internal diameter) was introduced into the sediment, retrieved and capped underwater by a diver who transferred it to a boat. The core liner was always maintained in a vertical position to keep perturbation to a minimum. The color of the sediment was black throughout the core, suggesting the presence of appreciable quantities of iron monosulfides and, by extension, the prevalence of reducing conditions in the sediments. All material involved in the sampling and analysis was metal-free. Once in the laboratory, the sediment was extruded and sliced every 1-cm under a nitrogen atmosphere. Each sediment section was then transferred to 50-mL plastic centrifuge tubes, centrifuged at 6,000 rpm for 30 min to separate the interstitial water from the sediment, and the pore water extracted with the aid of plastic syringes. Next, the interstitial water was filtered through a

25 mm diameter cellulose membrane filter with a nominal pore size of 0.45 μm and stored in plastic vials for later analysis of dissolved sulfate. Pore water concentrations of this anion were determined using the gravimetric method of Howarth (1978), which has a detection limit of approximately 0.3 mM. The percentage of recovery, using Copenhague seawater of known salinity, was 110 ± 5 % (n =3).

Wet sediment samples were subjected to a chemical sequential extraction scheme developed to separate trace metals associated with sedimentary pyrite (Huerta Diaz and Morse, 1990). Briefly, the method involves the digestion of the equivalent of 2.5 g of dry sediment (calculated from its water content) at room temperature during 16 h with 20 mL of HCl 1N (HCl fraction; includes carbonates, Fe and Mn oxyhydroxides, and iron monosulfides). The residue is then treated with two successive digestions of HF 10M (1 and 16 h, respectively) at room temperature (silicate fraction, essentially includes clays). Finally, the resulting residue is dissolved with 10 mL of concentrated HNO_3 during two hours at room temperature (pyrite fraction). After each digestion, the samples were centrifuged at 6,000 rpm for 20 min, the supernatant decanted and kept in low density polyethylene bottles for later analysis of Hg and Ag. Calibration curves obtained from Ag standards dissolved in water acidified with HNO_3 and in 1N HCl solutions were similar, indicating the absence of Ag precipitation with chloride ions while using 1N HCl to digest the sediment samples. In contact with the HCl, all the samples smelled strongly of H_2S, produced by the decomposition of iron monosulfides, confirming the presence of important quantities of this mineral.

The Hg and Ag associated with the silicate fraction were not analyzed, since this fraction does not participate in processes involved in early diagenesis. Here we will discuss only the results obtained for the reactive fraction (RF), which takes into account most of the components potentially capable of participating in the formation, transformation or dissolution of other mineral phases (and associated trace metals), or in their incorporation into living organisms. This operationally-defined fraction will be represented by the sum of the metal concentrations (Me) from the HCl and pyrite fractions (*i.e.*, Me-RF = Me-HCl + Me-pyrite). For the special case of Hg and Ag, their RF concentrations can be considered as near-total, since the contribution of the silicate fraction to the total concentrations of Hg and Ag is generally assumed to be negligible (e.g., Rivera-Duarte and Flegal 1997, Mercone et al. 1999). Results obtained for the HCl and pyrite fractions will be discussed in a separate article. Trace metal concentrations were measured by atomic absorption spectrometry (Thermo Jarrel Ash model Smith Hieftje 12); silver by graphite-furnace-, and mercury by cold-vapor-atomic absorption spectrophotometry (Instrumental Laboratory Atomic Vapor Accessory 440). In no case the values of the blanks exceeded the limits of detection of Hg (0.13 nmol g^{-1} for both fractions) or Ag (0.020 nmol g^{-1} and 0.0011 nmol g^{-1} for the HCl and pyrite fractions, respectively). The limits of detection were calculated as three times the standard deviation of the procedural blanks.

An approximation was made regarding the sedimentation rate by using the method introduced by Berner (1978). The assumption behind this method is that the initial slope of sulfate concentration (C) vs. depth (x) profile is directly proportional to the rate of sedimentation (ω). The initial slope $(\partial C/\partial x)_0$ represents the straight line connecting the uppermost data points in the profile which are still below the bioturbation zone. The empirical equation has the form (Berner 1978):

$$\omega = -B\left(\frac{\partial C}{\partial x}\right)_0 \qquad (1)$$

where B represents a constant of proportionality equal to one if $(\partial c/\partial x)_0$ is expressed in mM per centimeter of sediment and ω is in cm a^{-1}. As suggested by the black color observed in the sediment, the strong smell of H_2S in all samples, and the visual lack of benthonic organisms in the sediments, it is reasonable to assume that anoxic conditions were present throughout the core and, therefore, that bioturbation was essentially absent in these sediments. According to Berner (1978), sedimentation rates calculated using equation (1) are probably correct to within a factor of two. It was further assumed that dredging has been restricted to the main navigation channel of the port zone, and that dredging has been absent from the zone where the sediment core was collected. Furthermore, it also was assumed that the sedimentation rate was the same throughout the sediment core. Analysis of the pore water sulfate profile showed that a fairly good linear portion ranged from 1-10 cm depth ($r^2 = 0.65$, $n = 9$, $p < 0.01$; insert in Fig. 2a), with a slope of -1.25 ± 0.35 mmol L^{-1} cm^{-1} and, therefore, an approximate sedimentation rate of 1.25 ± 0.35 cm a^{-1}.

RESULTS AND DISCUSSION

Whether a coastal region will be a sink or a source of Ag and Hg will depend largely on the redox conditions of the environment. Particularly important are semi-enclosed urban estuaries with intense shipping activity and heavy industry, similar to our study area. These areas tend to favor relatively large contributions of contaminants and often need regular dredging to keep them open for ship navigation. Although the area occupied by these regions can be small relative to the total coastal area, the amounts of sediments (and associated trace metals) exported from these regions to the open ocean, or to pristine coastal zones are not. Over 364×10^6 tons of dredging spoil were dumped in northwest European and U.S. waters in 1986 alone (Clark 1994).

As shown in Fig. 2b, the concentrations of Hg-RF remained fairly constant with sediment depth, fluctuating around an average value of 0.58 ± 0.23 nmol g^{-1} ($n = 43$). However, relatively large variations in concentration also were present (RSD = 40%), with values ranging from 0.10 (19-20 cm) to 1.3 nmol g^{-1} (16-17 cm). Our average values can be considered low since they are similar to pre-industrial levels measured in the Saguenay Fjord, Canada (0.50 ± 0.25 nmol g^{-1}; Gagnon et

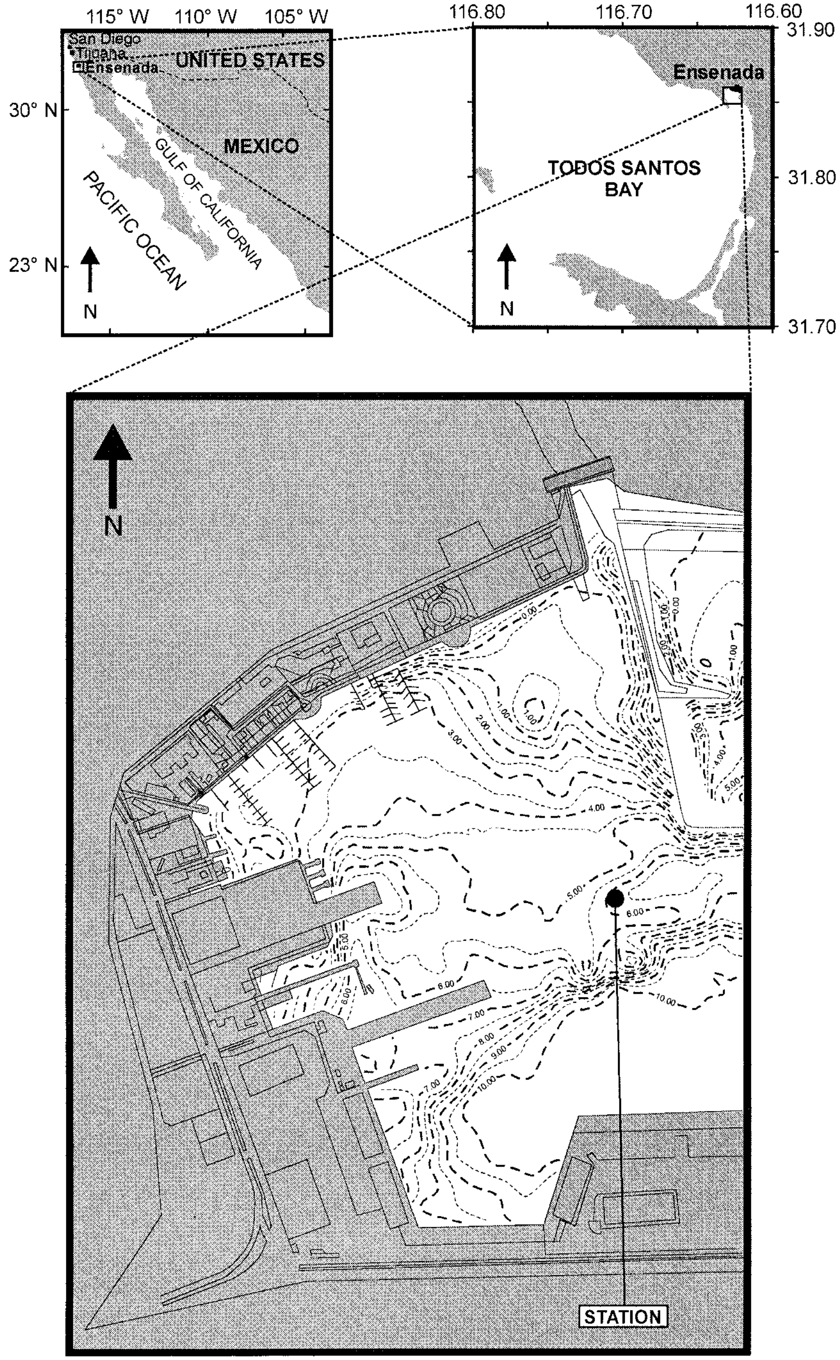

Figure 1. Station where the sediment core was collected, located in the port zone and marina of the Bay of Todos Santos (water depths in meters).

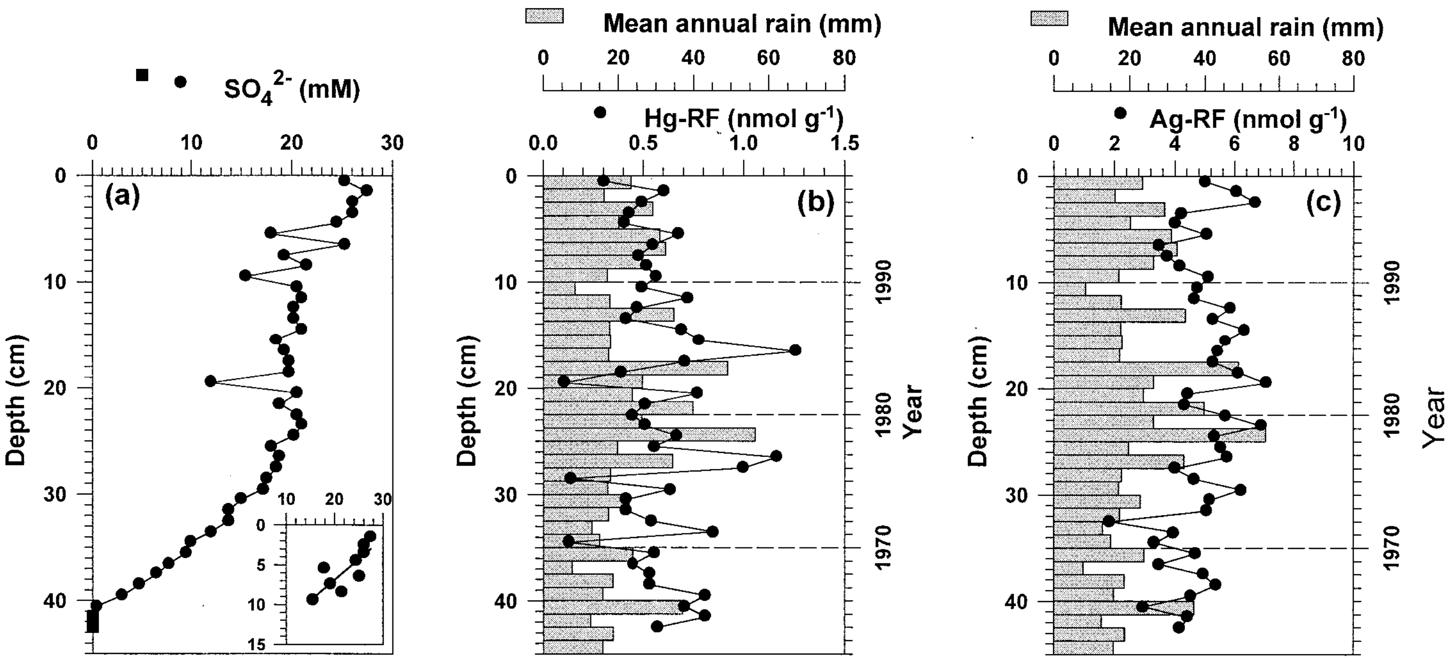

Figure 2. (a) Sediment concentration profiles of dissolved sulfate in the core collected in the port zone and marina of the Bay of Todos Santos. Inset shows the sulfate concentration values used for the linear regression analysis (line in inset) discussed in the text. Values denoted by squared symbols are below the estimated detection limit. Sediment concentration profiles of (b) Hg and (c) Ag in the reactive (RF) fraction in the core collected in the port zone and marina of the Bay of Todos Santos. Gray bars represent mean annual rain values for the city of Ensenada. Sediment chronology based on the method of Berner (1978).

al. 1997) and to background values for Swedish lake sediments (0.50 nmol g^{-1}; Regnell et al. 1997). However, they are more than five times higher than mercury concentrations measured in La Paz Lagoon, Mexico (10 ± 0.05 nmol g^{-1}; Kot et al. 1999). Furthermore, the average concentration around which the Hg-RF values fluctuated represents only two times (232%) the natural background level of Hg found in marine sediments (0.25 nmol g^{-1}; Jonasson and Boyle 1972). The shape of the profile for this fraction suggests that, on the average, the supply of mercury through urban runoff has not changed markedly with time, although seasonal variations and changes in rain intensity may have produced the variations in concentration observed in Fig. 2b. By contrast, the profile for Ag-RF shows a slight and gradual decrease in concentration levels with sediment depth during the period 1960-1985, and a decrease from 1985 to 1995 (Figure 2c). Values in this fraction ranged from 1.4 (32-33 cm) to 6.6 nmol g^{-1} (19-20 cm), with average values of 4.5 ± 1.1 nmol g^{-1} (n = 43), and smaller variations in concentration with depth (RSD = 24%) than the ones observed in Hg-RF. This average value represents approximately 6.4 times the crustal abundance of silver (~ 0.7 nmol g^{-1}; Taylor and McLennan 1985), and is comparable to levels found in sediments from environments impacted by human activities as in the Severn Estuary (4.6 nmol g^{-1}; Luoma et al. 1995), muddy superficial sediments from Puget Sound (5.3 nmol g^{-1}; Bloom and Crecelius 1987), coastal anoxic sediments from San Pedro, Santa Barbara, San Clemente and Santa Monica basins offshore from the coast of California (6.1 ± 7.6 nmol g^{-1}; Koide et al. 1986), and the northern reach of San Francisco Bay (6.5 ± 4.6 nmol g^{-1}; Smith and Flegal 1993). As was the case with Hg-RF, the relatively large changes with depth in Ag-RF concentrations (Fig. 2c) probably indicates that the variability in the supply of metals and suspended particles produced by the seasonal rains is more rapid than the time taken by the sediments to reach a new diagenetic equilibrium.

The gradual increase in Ag-RF concentrations with decreasing depth possibly can be attributed to the increasing industrialization and population growth of the region, and the concomitant increase in Ag concentration in urban runoff transferred to the port zone, mainly through the Arroyo Ensenada. Concentrations of dissolved Ag in this type of input can be significantly higher (e.g., 2-7 nmol L^{-1}; United States Environmental Protection Agency 1983) than their natural levels in open ocean (1-2.4 pM), coastal waters (3-18 pM), or bays (20-307 pM) influenced by North Pacific surface waters (Sañudo-Wilhelmy and Flegal 1992). Based on these literature values, Ag can be 8-7500 times more concentrated in urban runoff than in uncontaminated marine waters. Furthermore, coastal regions are generally regarded as efficient traps for Ag and Hg (Sañudo-Wilhelmy and Flegal 1992, Wen 1997, Smith and Schafer 1999), an important factor considering that metals delivered to the ocean by rivers, creeks and runoffs generally pass through these regions.

Assuming that Hg and Ag are transported to the study zone by precipitation runoff contributed mainly by the Arroyo Ensenada, then an association between the creek discharge and the metal concentrations in the sediments may exist. An approximate chronology for the core, based on this sedimentation rate, is shown in Figs. 2b,c for Hg-RF and Ag-RF, together with mean annual precipitation data for the City of Ensenada. As shown in these two Figures, Ag appears to increase during the period 1960-1985 and to decrease from 1985-1995, a trend that generally follows rainfall, especially during 1979-1984, when Ag and rainfall were both high. Hg was especially high during the period 1960-1985 and slightly lower from 1985 to present. These two time periods correspond with trends observed in the Ag profile, suggesting that general hydrological or climatic processes in the coastal region may be involved. Variation in mean annual temperatures may be linked to Hg trends since atmospheric deposition of this element has been found to be positively correlated with season/temperature (Mason et al. 2000). Considering the crudeness of the assumptions, these results tend to be consistent with the hypothesis that Ag is transported to the study zone mainly by particles supplied by rain and river runoff. However, Hg appears to be diluted by the sediments provided by the Arroyo Ensenada during the rainy season, suggesting that this element may be transported in a different manner to the sediments of the port zone.

According to Romero-Vargas-Márquez (1995), each time the port zone is dredged, approximately 150,000 m^3 of (anoxic) sediments are extracted and transported to other places within the Bay of Todos Santos. Furthermore, works for expanding the port facilities are underway, and it has been calculated that twice this volume of sediments will be eventually exported out of this zone. Assuming that between 150,000 to 300,000 m^3 of sediments are dredged, an average sediment density of 2.6 $g\,cm^{-3}$, and using the average Hg and Ag concentrations in the reactive fraction obtained from this study (0.58 ± 0.23 and 4.5 ± 1.1 nmol g^{-1}, respectively), it can be calculated that the amounts of Hg and Ag that can be exported out of the port zone after each dredging operation are approximately 45 ± 18 to 96 ± 36 kg and 189 ± 46 to 379 ± 93 kg, respectively. Considering the small area enclosed by the port zone (1.15 km^2) as well as the prospect of increasing dredging volumes produced by future expansions of the port facilities, the amounts of Hg and Ag involved are not only important, but they will tend to increase with time. Finally, any study involving environmental effects of metals (e.g., Hg) on biota should take into consideration other sedimentary parameters, besides reactive metals, that may affect their transfer to aquatic organisms, like organic matter, reactive Fe or acid volatile sulfide (e.g., Mason and Lawrence 1999).

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