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Distribution of Mercury in Surficial Sediments from Todos Santos Bay, Baja California, México

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Abstract During 2004 the spatial distribution of total Hg in sediments from Todos Santos Bay, Baja California, México was studied to evaluate the degree of environmental impact in this bay. The results showed low concentrations and no Hg enrichment at any site. These findings suggest natural levels of Hg in the water of Todos Santos Bay. The regional distribution of Hg/Fe shows lower values in the East and higher in the West of the bay. No significant correlations ($p < 0.05$) were found between Hg and organic matter or particle size, suggesting that the distribution of Hg is not controlled by these variables.

Keywords Mercury · Sediments · Baja California

There is a globally distributed variety of anthropogenic sources of Hg to the environment. However, a high proportion of the direct inputs to aquatic systems have been controlled in the majority of the developed countries (Fitzgerald and Lamborg 2003). In contrast, anthropogenic inputs of Hg via emissions to the atmosphere are currently of great concern. Due to Hg emissions to the atmosphere, which are associated with coal burning and high temperature processes (waste incineration), Hg global cycling have been significantly altered (Fitzgerald et al. 1998; Mason et al. 1994). The high volatility of elemental Hg (main form Hg in atmosphere) (Mason et al. 1994) and large residence time in the atmosphere (Gustin et al. 1999), allows this element to be widely distributed across the earth. Once in the atmosphere, Hg oxidation in both clouds (Munthe 1992), and aerosols (Mason et al. 1992), will transform Hg^0 into the ionic form Hg^{2+} which will be eventually removed through dry or wet deposition to soils or sediments (Schroeder and Munthe 1998). Then, sediments act as sinks of Hg through biologically or abiotic mediated reduction of Hg^{2+}, resulting a supersaturation with a posterior evasion of Hg^0 (Amyot et al. 1997; Kim and Fitzgerald 1986) and/or methylation of Hg^{2+}, resulting in the accumualtion of highly toxic methymercury (MMHg) in sediments which eventually could be bioaccumulated in biota.

The Bay of Todos Santos is located 100 km south of the US–México border, on the Pacific coast of the Baja California Peninsula. This bay has an area of 330 km^2 and an average depth of 50 m (SEMAR 1974). The bottom sediments are composed of mixture of mud (silt–clay) and sand (Emery et al. 1957). Adjacent to the bay is the city of Ensenada with a population of 400,000 inhabitants. This bay is exposed to potential pollution through domestic and industrial effluents, shipping and fishing traffic, and associated pollutants from agricultural run-off from various point sources (Romero-Vargas 1995). The bay can be considered a region whose sediments trace metals levels are relatively low, except for the zone encompassed by the 1.15 km^2 port zone and marina (Romero-Vargas 1995). No information has been published to date concerning values of Hg in the bay sediments. This study investigates the spatial distribution of total Hg in surficial sediments of Todos Santos Bay in order to evaluate the degree of environmental impact and to provide baseline measurements for monitoring purpose

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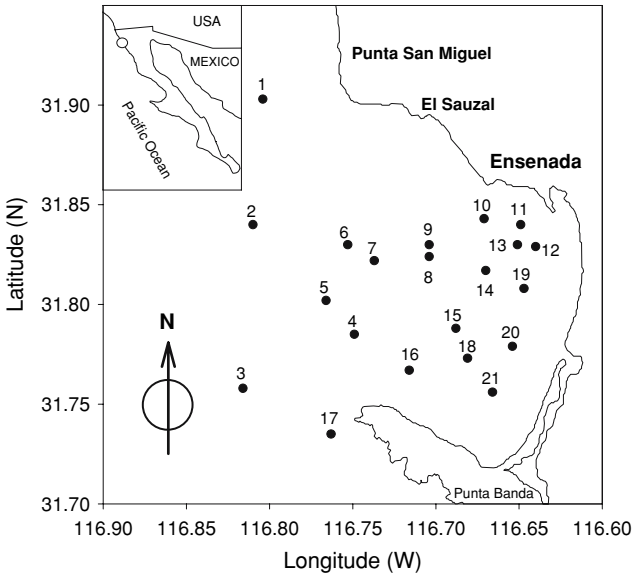

Fig. 1 Study area in Todos Santos Bay, Baja California, México

in this bay. Also this work reports measurements of organic matter and grain size to analyze the influence of these variables on the concentration and distribution of Hg in sediments.

Table 1 The geographic positions in the sampling sites

	Geographic position	
Sampling sites	Latitude	Longitude
1	31.903	116.804
2	31.840	116.810
3	31.758	116.816
4	31.785	116.749
5	31.802	116.766
6	31.830	116.753
7	31.822	116.737
8	31.824	116.704
9	31.830	116.704
10	31.843	116.671
11	31.830	116.651
12	31.829	116.640
13	31.840	116.649
14	31.817	116.670
15	31.788	116.688
16	31.767	116.716
17	31.735	116.763
18	31.773	116.681
19	31.808	116.647
20	31.779	116.654
21	31.756	116.666

Materials and Methods

During April 2004, sediment samples were collected at 21 stations throughout Todos Santos Bay (Fig. 1). The geographic positions in the sampling sites are shown in Table 1. Samples were collected using a Van Veen grab from which a surficial sediment sample ($\sim$90 g) was taken with a plastic spatula from its central part. The sediment was stored in previously acid-washed 50 mL polypropylene centrifuge tubes and kept a -20°C upon return to the laboratory. For total Hg determinations, 0.5 g of dry sediment was weighed into 30 mL precleaned acid-washed pyrex flasks and digested in 3 mL of trace metal grade concentrated HNO_3, 9 mL concentrated HCl and 5 mL $K_2Cr_2O_7$. The acidfied samples were heated and maintained with constant reflux for 4 h at 100 $\pm$ 5°C. The sample digest solutions were placed in polypropylene centrifuge tubes, and 50 mL of deionized water was added. Hg was determined by Cold Vapour-AAS with a Varian SpectraAA 220 equipped with a vapor generator VGA-77. The detection limit obtained for Hg was approximately 9 ng g^{-1}. For total Fe determinations, 1.5 g of wet sediment was digested with 2.5 mL of trace metal grade concentrated HNO_3 and 10 mL

Table 2 Concentrations of total Hg, Fe, organic matter (OM), and mean grain size (MGZ) in sediments (dry weight)

Site	Hg (ng g^{-1})	Fe (%)	OM (%)	MGZ (ϕ)
1	20.66	1.28	0.40	3.19
2	63.47	2.17	0.78	4.29
3	*ND	4.01	2.03	5.03
4	13.19	3.70	2.74	5.13
5	41.40	1.81	0.50	3.47
6	16.51	1.06	0.40	3.17
7	26.74	2.56	0.96	4.41
8	20.84	2.66	1.07	4.44
9	*ND	1.04	0.14	3.23
10	*ND	1.72	0.60	3.71
11	*ND	1.44	0.52	3.92
12	14.69	1.58	0.31	3.88
13	*ND	1.41	0.48	3.41
14	11.24	1.03	0.23	3.14
15	10.80	1.51	0.38	3.78
16	*ND	2.02	0.74	4.38
17	19.88	2.90	0.57	3.98
18	*ND	1.06	0.28	3.31
19	*ND	1.23	0.19	3.11
20	16.92	1.05	0.31	3.42
21	*ND	0.54	0.19	2.76
Mean	23.03 $\pm$ 15.20	1.08 $\pm$ 0.91	0.66 $\pm$ 0.64	3.77 $\pm$ 0.65
Range	10.8–63.47	0.54–4.01	0.14–2.74	2.76–5.13

*ND = Not detectable

HCl following the method 3050B described by US-EPA (1996). Iron concentrations of the digested solution were measured using a Smith Hieftje 12 Thermo Jarrel Ash (TJA) AAS using air-acetylene flame. The detection limit obtained for Fe was approximately 0.8 μg g^{-1}. Blank samples and certified reference material for marine sediment MESS-3 (National Research Council of Canada), were routinely analyzed with each batch of samples to evaluate the accuracy and precision of the analytical methodology. Certified and measured values were in general agreement, with recovery efficiency of approximately 98% for Hg and 90% for Fe. Organic matter and grain size determinations were done according to Mook and Hoskin (1982) and Daessle et al. (2002) respectively.

Results and Discussion

The total Hg concentration and percentages of Fe, organic matter and grain size (Φ) results are summarized in Table 2. Sediment Hg concentration ranged from 10.8 to 63.5 ng g^{-1} dry weight with an average value of 23.0 ng g^{-1}. The higher concentrations of Hg were found in the northwestern part of the study area (Site 2; 63.4 ng g^{-1} d.w.) and near the islands (Site 5; 41.4 ng g^{-1} d.w.). The average Hg concentration found in the Todos Santos Bay is similar to that in La Paz Lagoon (20 ng g^{-1}), Baja California Sur, México (Kot et al. 1999). The Hg concentrations in surficial sediments of our study area were lower than typical background values for uncontaminated marine deposits; the background level for Hg in sea sediments is reported between 50 g g^{-1} and 80 ng g^{-1} (Fujii 1976) and baseline levels of total Hg in uncontaminated sediments are in the order of 30 ng g^{-1} (Bryan and Langston 1992). Estimated from core horizons, deposited before the sediment was impacted by human activities, baseline Hg levels in San Francisco Bay are 60 ng g^{-1} (Hornberger et al. 1999) and 59 ng g^{-1} in the Yatsushiro Sea (Tomiyasu et al. 2000). The concentrations of Hg in this study are also lower than the average

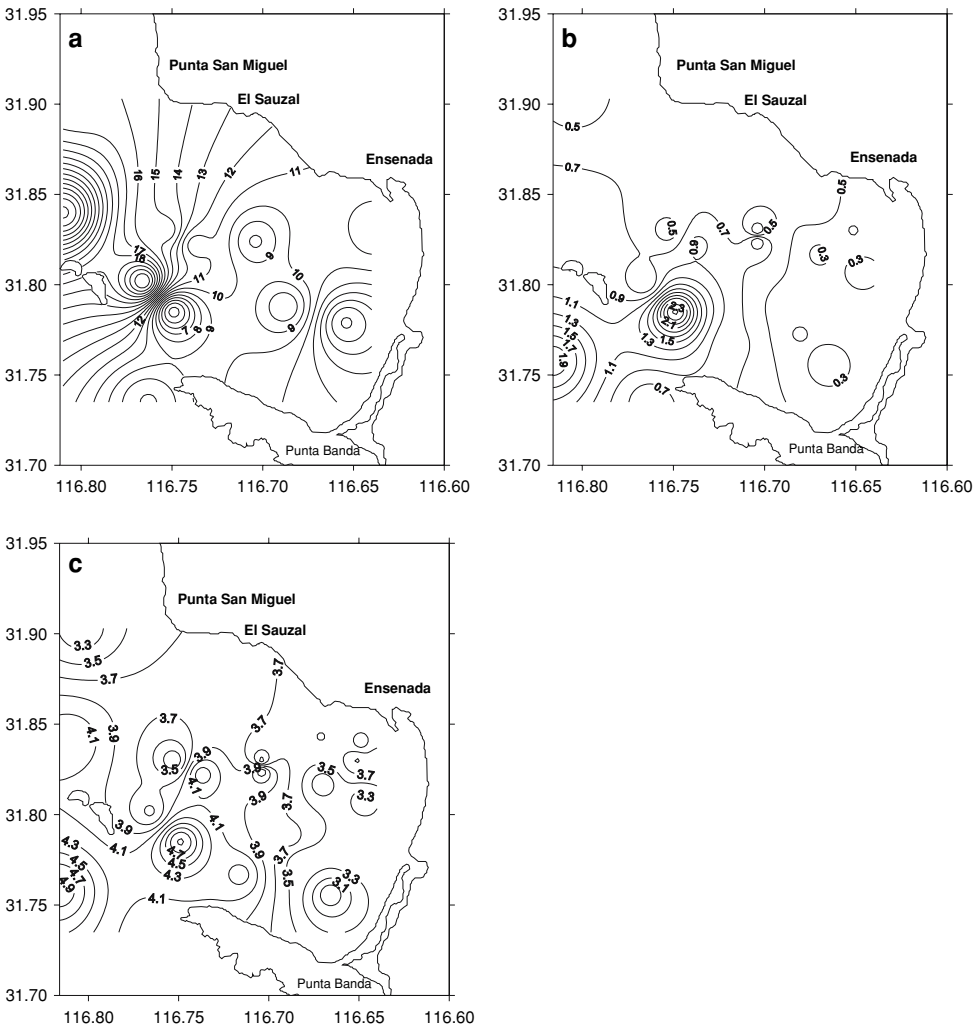

Fig. 2 Spatial distribution of Hg normalized by Fe (**a**), % organic matter (**b**), and (ϕ) mean grain size (**c**) in surficial sediments from Todos Santos Bay

abundance of this element in sedimentary rocks (0.4 μg g^{-1}) (Turekian and Wedepohl 1961). Therefore, we conclude that the sediments from Todos Santos Bay are not Hg contaminated and that the Hg concentrations are within the natural range for marine sediments and provide a baseline for studying the impact of future industrial activities in this area.

To exclude variability due to grain size differences and to better compare site-to-site variations in Hg concentrations in the sediments, Hg was normalized with respect to Fe. Iron is abundant in fine-grained sediments in particular and in the continental crust in general, it also has a reactive fraction associated with particle surfaces like other contaminants and is thus commonly used for normalizing purposes (Daskalakis and O'Connor 1995). The regional distribution of Hg/Fe ratio in sediment shows lower values in the east (11) and higher (16) in the west of the study area. The maximum (18) is located near Todos Santos Island (Fig. 2a).

The mean organic matter measured in surficial sediments is 0.7%, ranging 0.1%–2.7%. The organic matter spatial distribution is shown in Fig. 2b; an increase toward the bay's deeper zones (between Punta Banda and the islands) is evident. Low organic matter values in the samples may be the result of marine sedimentation and mixing processes at the sediment water interface where the rate of delivery as well as rates of degradation by microbially mediated processes can be high (Canuel and Martens 1993). The sandy nature of this bay supports this observation. The surface sediment grain-sizes vary from medium-sand (lower depths) to silt (mud) toward the bay's central zone (deeper areas). The spatial distribution of the grain size is shown in Fig. 2c. The grain size distribution is in agreement with results from previous research that indicates the dominance of medium sand in the basin's shallow zones and an increase of mud toward in deeper zones (Riveroll-Schroeder 1985). In this study no significant correlations ($p < 0.05$) were found between Hg concentrations and organic matter or particle size, suggesting that the distribution and abundance of Hg is not controlled by these properties. Nevertheless, the organic matter and particle size do show a significant positive correlation ($r^2 = 0.903$), indicating the concomitant deposition of organic matter and fine sediment particles in the same sites, with low hydrodynamic movement.

In order to identify Hg-enriched sediments in the study area, Fe was used as a reference element and plots of Hg to Fe concentrations were made (Fig. 3). The baseline Hg–Fe obtained (BL-MEX) was compared with that reported by Schiff and Weisberg (1999) for the Southern California Bight (BL-SC). Baselines are defined as the relationship between the abundance of Fe and Hg in non impacted sites. The results showed no Hg enrichment at any site. This points to low natural background levels of Hg in the waters of Todos Santos Bay as well as limited anthropogenic inputs.

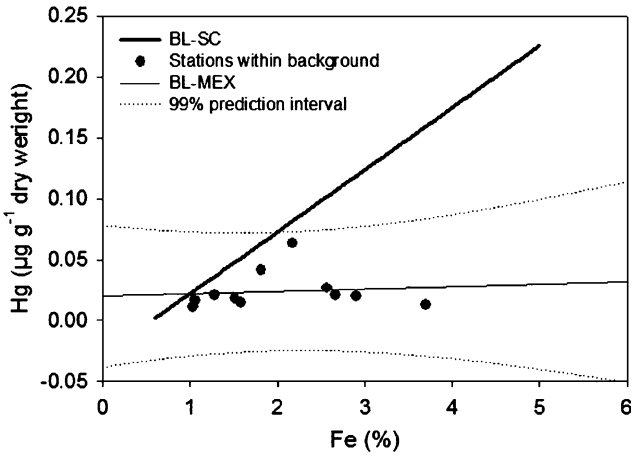

Fig. 3 Mercury–iron plots (BL-MEX) overlaid with reference element baseline in Southern California (BL-SC) (Schiff and Weisberg 1999). Sites which fall with the prediction interval are considered unenriched; sites which lie above the prediction interval are considered enriched

References

Amyot M, Gill GA, Morel FMM (1997) Production and loss of dissolved gaseous mercury in coastal seawater. Environ Sci Technol 31:3606–3611

Bryan GW, Langston WJ (1992) Bioavailability, accumulation and effects of heavy metals in sediments with special reference to United Kingdom estuaries: a review. Environ Pollut 76:89–131

Canuel EA, Martens CS (1993) Seasonal variations in the sources and alteration of organic matter associated with recently deposited sediments. Org Geochem 20:563–577

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

Daskalakis KK, O'Connor TP (1995) Normalization and elemental sediment contamination in the coastal United States. Environ Sci Technol 29:470–477

Emery KO, Gorsline DS, Uchup E, Terry RD (1957) Sediments of three bays of Baja California: San Sebastian Vizcaino, San Cristobal and Todos Santos. J Sediment Petrol 27:95–115

Fitzgerald WF, Engstrom DR, Mason RP, Nater EA (1998) The case for atmospheric mercury contamination in remote areas. Environ Sci Technol 32:1–7

Fitzgerald WF, Lamborg CH (2003) Geochemistry of mercury in the environment. In: Holland HD, Turekian KK (eds) Treatise on geochemistry. Elsevier, pp 108–140

Fujii M (1976) Mercury distribution in lithosphere and atmosphere. In: Kitamura S, Kondo M, Takizawa Y, Fujii M, Fujiki M (eds) Mercury. Kodansha Scientific, p 151

Gustin MS, Lindberg S, Marsik F, Casimir A, Ebinghaus R, Edwards G, Hubble-Fitzgerald C, Kemp R, Kock H, Leonard T, London J, Majewski M, Montecinos C, Owens J, Pilote M, Poissant L, Rasmussen P, Schaedlich F, Schneeberger D, Schroeder W, Sommar J, Turner R, Vette A, Wallschlaeger D, Xiao Z, Zhang H (1999) Nevada STORMS project: measurement of mercury

emissions from naturally enriched surfaces. J Geophys Res 104(D17):21831–21844

Hornberger MI, Luoma SN, van Geen A, Fuller C, Anima R (1999) Historical trends of metals in the sediments of San Francisco Bay, California. Mar Chem 64:39–55

Kim JP, Fitzgerald WF (1986) Sea-air partitioning of mercury in the Equatorial Pacific Ocean. Science 231:1131–1133

Kot FS, Green-Ruiz C, Paez-Osuna F, Shumilin EN, Rodriguez-Meza D (1999) Distribution of mercury in sediments from La Paz lagoon, Peninsula of Baja California, Mexico. Bull Environ Contam Toxicol 63:45–51

Mason RP, Vandal GM, Fitzgerald WF (1992) The sources and composition of mercury in Pacific Ocean rain. J Atmos Chem 14:489–500

Mason RP, Fitzgerald WF, Morel FMM (1994) The biogechemical cycling of elemental mercury: anthropogenic influences. Geochim Cosmochim Ac 58:3191–3198

Mook DH, Hoskin C (1982) Organic determination by ignition: caution advised. Estuar Coast Shelf S 15:697–699

Munthe J (1992) Aqueous oxidation of elemental mercury by ozone. Atmos Environ 26A:1461–1468

Riveroll-Schroeder EG (1985) Distribucion de materia organica en sedimentos de la Bahia de Todos Santos, Baja California. BSc Thesis, Universidad Autonoma de Baja California, Ensenada, B.C., 82 pp

Romero-Vargas IP (1995) Metales pesados y su fraccionación química en la Bahía de Todos Santos, Baja California, México. Bsc Thesis, Universidad Autónoma de Baja California, Ensenada, B.C., 86 pp

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

Schroeder WH, Munthe J (1998) Atmospheric mercury -an overview. Atmos Environ 32:809–822

SEMAR (1974) Estudio geográfico de la región de Ensenada, Baja California, México. Dirección General de Señalamiento Marino. Eds. México

Tomiyasu T, Nagano A, Yonehara N, Sakamoto H, Rifardi OK, Akagi H (2000) Mercury contamination in the Yatsushiro Sea, south-western Japan: spatial variations of mercury in sediment. Sci Total Environ 257:121–32

Turekian KK, Wedepohl KH (1961) Distribution of the elements in some major units of the Earth's crust. Bull Geol Soc Am 72:175–192

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