Bull. Environ. Contam. Toxicol. (2003) 70:1213–1219

DOI: 10.1007/s00128-003-0111-4

Bulletin of Environmental Contamination and Toxicology

# Mercury in Bottom Sediments of the Tropical Rio Marabasco, Its Estuary, and Laguna de Navidad, Mexico

A. O. M. Willerer,[1] F. S. Kot,[2] E. N. Shumilin,[3] S. Lutsarev,[4] A. J. M. Rodríguez[3]

[1] CEUNIVO, University of Colima, Manzanillo, Colima, Mexico
[2] Institute of Water and Ecological Problems, Far Eastern Branch of Russian Academy of Sciences, 65, Kim Yu Chen Street, Khabarovsk, 680000, Russia
[3] Interdisciplinary Marine Science Center, Av. IPN s/n, col. Playa Palo de Santa Rita, Apdo Postal 592, La Paz, Baja California Sur, 23096, Mexico
[4] P. P. Shirshov Institute of Oceanology, Russian Academy of Sciences, Moscow, Russia

Received: 14 August 2002/Accepted: 14 March 2003

Mercury (Hg), one of the trace elements of great environmental concern (Botkin and Keller 2000; Gray et al. 2002), may also be important for the health of the population of southwestern Mexico, in particular for the coastal zone of the states of Colima and Jalisco. This area belongs to the tectonically active province of the Sierra Madre del Sur, which is rich in mineral deposits. Hg-ore deposits of the Arrayanal (Monografía 1994), the abandoned "Mina Martínez" Hg-ore mines (González-Reyna,1956), and the "Peña Colorado" iron-ore mines in Sierra El Mamey near Minantitlán are located in the upper watershed of the tropical Rio Marabasco. The river, born in the Sierra Manantlán at 1200 m altitude, had a mean annual water discharge of 12.8 $m^3s^{-1}$ from Oct 2000 to Sept 2001, with maximum of 66.1 $m^3s^{-1}$ (Registro de los datos …2001), although it has reached 742 $m^3s^{-1}$ in recent years (Estudio Hidrológico…1995). In its lower course, the river supplies fresh water for the irrigation of a large agricultural area, the Cihuatlán plantations, and finally flows into Laguna de Navidad, part of the famous international resort zone. Because of these reasons, knowledge of the ambient levels of Hg is of significant environmental and practical interest for a State of Colima and Mexico.

To contribute to the basic knowledge of the situation, the Hg contents in the sediments of the Rio Marabasco, its delta, and the adjacent Laguna de Navidad were analyzed, and the results are reported here.

## MATERIALS AND METHODS

Samples of surface sediments were taken using a Van Veen grab sampler on 12-14 October 2000 all along the course of Rio Marabasco, its delta, and the shallow (0.2 to 4.0 m depth) semiclosed Laguna de Navidad, which receives water and suspended matter from this river during most of the year. Sample locations are presented in Figure 1. The samples were air-dried, homogenized in an agate mortar, and subsampled for textural, mineralogical, and chemical analysis. Details of this study as well as lithologic, mineralogical, and geochemical information obtained will be presented and discussed in a separate paper.

*Correspondence to:* E. N. Shumilin

The Hg content was measured by the cold vapor technique using a Yuliya-2-Hitachi flameless atomic absorption spectrophotometer (Kot et al. 1999). The detection limit, defined as three times the standard deviation of the procedural

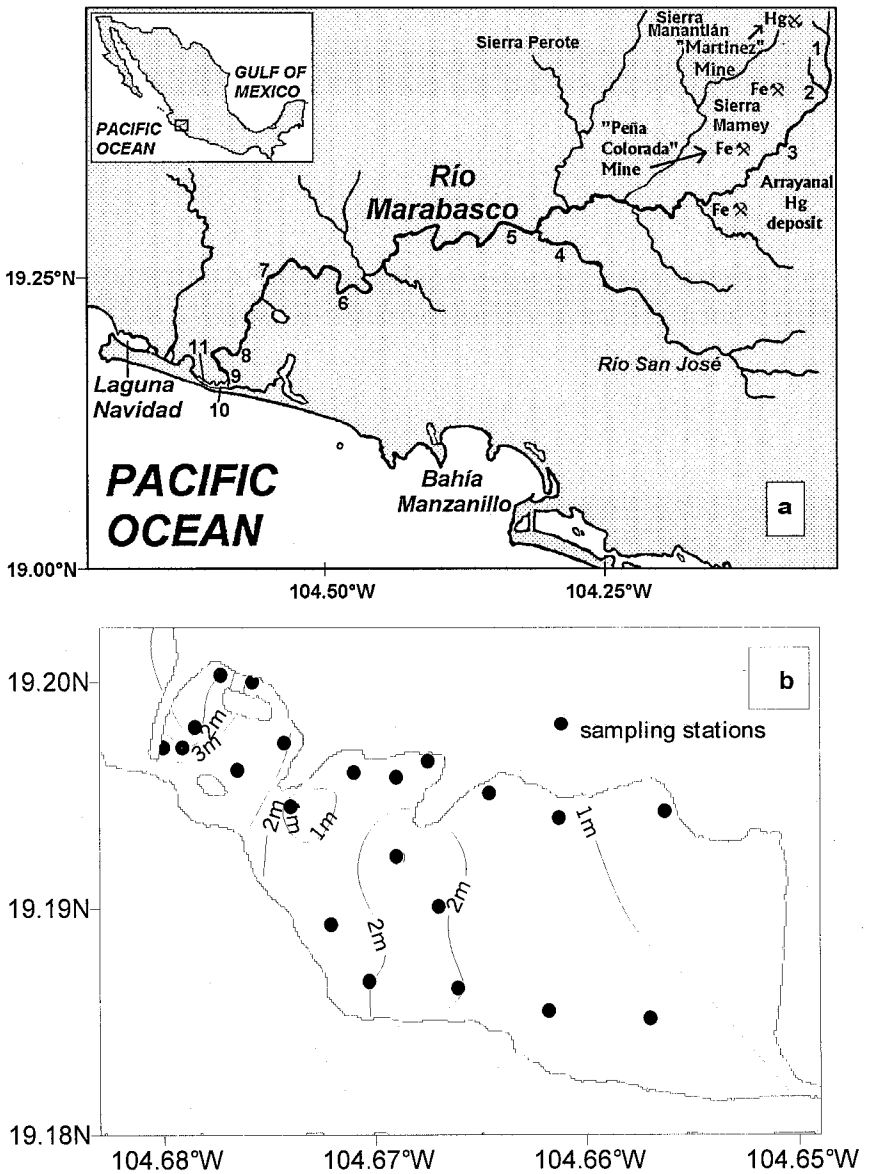


**Figure 1.** Study area and sampling site locations: a)Rio Marabasco and its delta; b) Laguna de Navidad

blank expressed per unit sample analyzed, was 2 ng $g^{-1}$. The major matrix elements Al and Fe, representing the content of aluminosilicates and iron oxides-hydroxides, were measured by flame atomic absorption spectrophotometry (Shumilin et al. 2001) after strong acid digestion (Ultrex quality $HNO_3$, HCl, and HF) of 200 mg aliquots in open teflon beakers at 130 $^0$C. The method of determination of total carbon (TC) and organic carbon (OC) in sediments is based on the rapid combustion of two samples (with and without treatment by hydrochloric acid) in a tubular furnace at 850 $^o$C and with oxygen as the carrier gas.The resulting carbon dioxide is carried away by the oxygen flow into a coulomb cell of the express-analyzer AN-7529, where it is absorbed by solution of barium hydroxide at an exactly defined pH. The carbonate content is calculated as the difference between TC and OC (Ljutsarev 1987). The results of the analysis of the standard reference material "NBS 1646 "Estuarine sediment" fell within the 15% standard deviation limits, considered as acceptable by US EPA recommendations. The treatment of data was done using the software STATISTICA (Statistica 2001). The spatial distribution of Hg in the surface sediments of the Laguna de Navidad was drawn by using the SURFER-32 software (Surfer 1995).

## RESULTS AND DISCUSSION

The results of the determination of Hg, Al, Fe, carbonates, and OC in the surface sediments from the Rio Marabasco , its delta, and Laguna de Navidad are presented in Table 1. Variations of Hg contents in the stream sediments along the river course are shown in Figure 2, while the spatial distribution of Hg concentrations in the surface sediments of Laguna Barra de Navidad is given in Figure 3.

The Hg content in surface sediments of the river varies from 2 ng $g^{-1}$ to 22 ng $g^{-1}$ (mean 9.4 ± 7.8 ng $g^{-1}$), all representing background levels for soil and river bed sediments (Gray et al. 2002). The lowest Hg content (3 to 8 ng $g^{-1}$) is found for sediments of Sts.1 and 2, upstream of the Peña Colorada iron mine near the village of Upper Minatitlán, and at St. 4, from a non-contaminated tributary, Rio San Jose, draining the Sierra El Perote. The highest Hg levels (17 to 22 ng $g^{-1}$) were detected in the sediment samples from Sts.3,5, and 8, which were also richer in OC (0.53% to 1.70 %) (Fig. 2; Meyer, personal communication). This type of Hg enrichment is a natural geochemical phenomenon, Hg having a high affinity with organic matter during migration across terrigenous environments. Thus, the Hg-ore deposits and mines of the drained territory have not produced elevated Hg contents in bottom sediments of the river and estuary.

The content of Hg in the surface sediments of the Laguna de Navidad varies from 2 to 32 ng $g^{-1}$, with a mean concentration of 15 ± 9 ng $g^{-1}$. (Table 1, Fig. 3). All of these Hg contents reflect natural background levels in sedimentary material. Their apparent variation is presumably controlled by the grain-size of the sediment particles and by their organic matter concentrations; the finer the

particles the richer they are in OC and the higher is the Hg content in the sediments. This is similar to that reported for the spatial distribution of Hg in surface sediments of the subtropical Laguna de La Paz, southeastern Baja California Peninsula (Kot et al.1999).

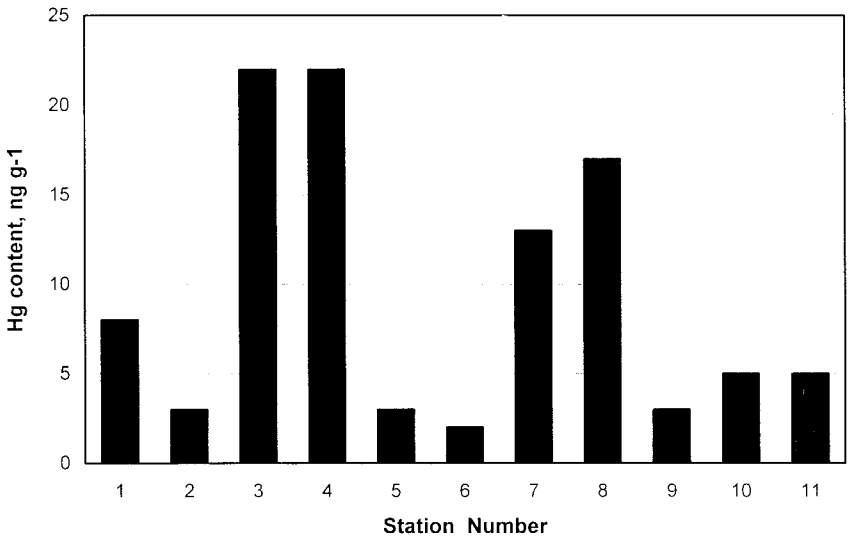


**Figure 2.** Mercury distribution in the surface sediments along the Rio Marabasco

**Table 1.** Contents of Al, Fe, carbonates, OC, and Hg in surface sediments from the Rio Marabasco, its delta, and Laguna de Navidad

| Sample locations | Al, % | Fe, % | Carbonates, % | OC, % | Hg, ng $g^{-1}$ |
|---|---|---|---|---|---|
| Rio Marabasco and its delta | 0.6-8.0<br>8.7±0.7 | 1.1-7.2<br>4.2±2.3 | 0.9-5.1<br>2.2±1.4 | 0.02-1.70<br>0.55±0.53 | 2-22<br>9.4±7.8 |
| Laguna de Navidad | 5.3-10.7<br>8.2±1.7 | 0.6-5.0<br>2.9±1.9 | 1.4-17.2<br>4.8±4.5 | 0.1-7.1<br>1.6±1.5 | 2-32<br>15±9 |

Above: range of values (dry weight basis); below: average ±*sd.*

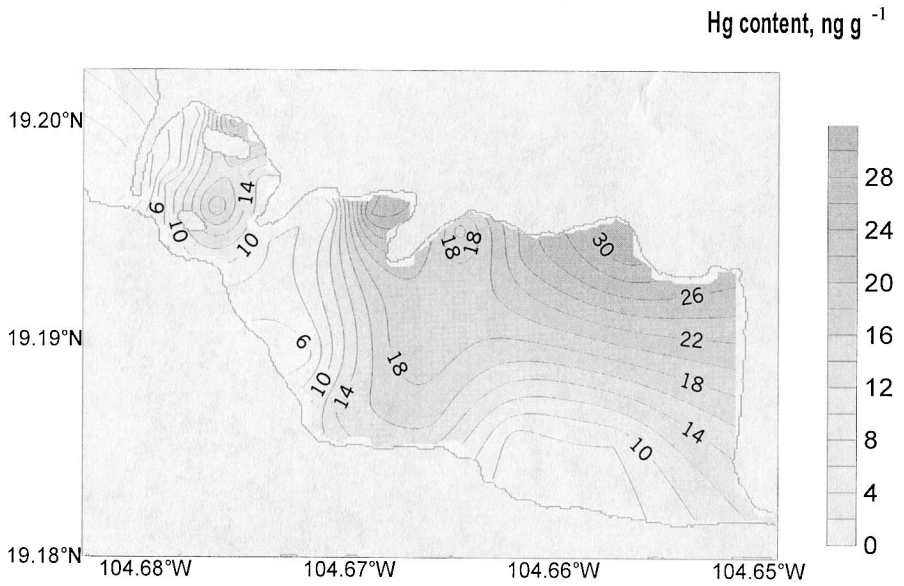


**Figure 3**. Spatial distribution of Hg in surface sediments from Laguna de Navidad

Both correlation and principal component analyses of the data were performed to more precisely evaluate the association of Hg with the principal constituents of the sediment matrix for the whole set of samples (Table 2).

**Table 2.** Correlation matrix showing association of Hg with major components of the sediments of the Rio Marabasco and the Laguna de Navidad.

| | Al | Fe | Carbonates | CO | Hg |
|---|---|---|---|---|---|
| Al | 1.00 | | | | |
| Fe | 0.98 | 1.00 | | | |
| Carbonates | 0.97 | 0.95 | 1.00 | | |
| CO | 0.99 | 0.98 | 0.97 | 1.00 | |
| Hg | 0.86 | 0.86 | 0.82 | 0.88 | 1.00 |

This correlation matrix of the whole data set (river and lagoon sediments) firmly supports our previous observation about the importance of organic matter for the migration of Hg in the aquatic environment. The relationship between Hg and organic carbon is evidenced by the high positive correlation coefficient of 0.88. Therefore, we conclude that existing Hg deposits and ancient Hg mines situated in the drainage basin of the Rio Marabasco do not supply excess Hg to the sediments of the river and the Laguna de Navidad, leaving the river resort free of detectable anthropogenic contamination by this potentially dangerous pollutant.

*Acknowledgments.* This research was funded by a grant from the Consejo Nacional de Ciencia y Tecnología (Project CONACyT 32462T). Thanks to Dr. Ellis Glazier and Dr. Norman Silverberg for editing the English text.

REFERENCES

Botkin DB, Keller EA (2000) Environmental science: Earth as a living planet. John Wiley & Sons, Inc., New York

Estudio Hidrológico del Estado de Colima (1995) Instituto Nacional de Estadística, Geografía e Informatica Gobierno del Estado de Colima, Aguascalientes, Ags

Gerlach SA (1981) Marine pollution:Diagnosis and therapy. Springer Verlag, Berlin

González-Reyna J (1956) Riqueza minera y yacimientos minerales de México. Banco de México, México, DF

Gray JE, Crock JG, Fey DL (2002) Environmental geochemistry of abandoned mercury mines in west-central Nevada, USA. Appl Geochem 17:1069-1079

Keller E (1996) Environmental geology. 7th ed. Prentice Hall, Upper Saddle River, New Jersey, USA

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

Ljutsarev AV (1987) Determination of organic carbon in sea bottom sediments by dry combustion. Soviet Oceanology 26:533-536

Monografía Geológico-Minera del Estado de Colima (1994) Secretaría de Energía, Minas e Industria Paraestatal. Pachuca, Hidalgo, México

Registro de los datos de aforo con molinete (2001) Comisión Nacional del Agua, Servicio Hidrométrico, Estación Cihuatlán, Cuenca Río Marabasco, Jalisco. Informe técnico (in Spanish)

Statistica version 6.0. Copyright Statsoft Inc 1984-2001 Data analysis software system Statsoft Inc. Tulsa OK, USA

Shumilin E, Páez-Osuna F, Green-Ruiz C, Sapozhnikov D., Rodríguez-Meza D., Godínez-Orta L (2001) Arsenic, antimony, selenium and other trace elements

in sediments of the La Paz Lagoon, Peninsula of Baja California, Mexico Mar Pollut Bull 42:174-178
Surfer version 6.01.August 31 1995 Surface mapping system Copyright 1993-95 Golden software Inc, Golden Colorado, USA