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Trace Metals in Sediments from Bahia de Chetumal, Mexico

V. García-Ríos,[1] G. Gold-Bouchot[2]

[1] Department of Marine Resources, Cinvestav del IPN, Unidad Mérida, Apdo. Postal 73-Cordemex, Mérida, Yucatán 97310, Mexico
[2] Centro EPOMEX, Universidad Autónoma de Campeche, Av. Agustín Melgar S/N, Campeche, Campeche, Mexico

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Bay of Chetumal, an important habitat for the West Indian manatee (*Trichechus manatus*), is located southeast of the Yucatan Peninsula (Fig. 1) on the border between Mexico and Belize (Lock, 1997). It is a shallow estuarine coastal lagoon with several freshwater inputs from rivers, the main being the Rio Hondo that sets the border between the two countries. The influence of the Caribbean Sea is limited to the southeastern area. There are pollution problems in the Bay, such as inputs of urban sewage (Ortíz and Sáenz, 1997), the presence of organochlorine pesticides used in agricultural areas (mainly sugar cane) on the margins of Rio Hondo (Euán-Avila *et al*, 2002), and hydrocarbon inputs through sewage from the city of Chetumal, and outboard motor activities. The distribution of organochlorine compounds (pesticides and PCBs) and hydrocarbons in sediments has been described (Noreña-Barroso *et al.*, 1998), and the toxicity of sediments established (Zapata-Perez *et al.,* 2000).

The objective of this study was to evaluate the concentrations and speciation of seven heavy metals (Zn, Pb, Ni, Cu, Cd, Fe and V) in the sediments of the bay, as a contribution to the knowledge and rational management of the bay.

MATERIALS AND METHODS

Surface sediments were collected at 16 sampling stations at the Bay of Chetumal in August 1999 (rainy season) and June 2000 (dry season; Fig. 1). Sediments were sampled using a 0.1 m^2 Van Veen grab. Percentage of sand, clay and silt were determined with the Bouyoucos hydrometer method and organic matter determined using the Walkley and Black wet oxidation method (Franco *et al.,* 1985).

To evaluate the speciation of metals (Zn, Pb, Ni, Cu, Cd, Fe and V) in the different fractions of the sediments, and thus their bioavailability, a sequential extraction procedure was applied (Pempkowiak *et al.*, 1999). Briefly, sediment samples were extracted sequentially with: 0.11 M acetic acid, to obtain metals loosely adsorbed to the surface of sediment particles; 0.05 M hydroxylamine hydrochloride, to isolate metals associated with manganese and iron oxides/hydroxides; 1 M ammonium

Correspondence to: G. Gold-Bouchot

acetate after digestion with 8.8 M hydrogen peroxide, to isolate metals bound to organic matter; finally, to obtain metals incorporated into clay minerals lattices,

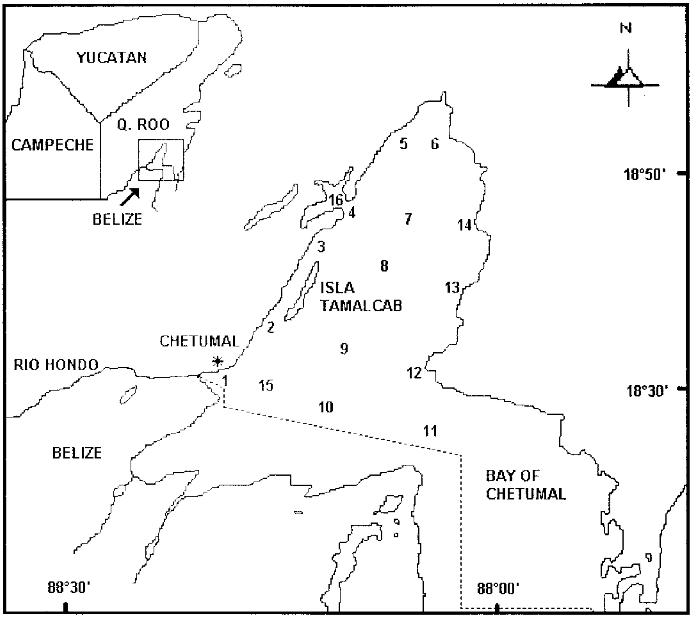

Figure 1. Map of Chetumal Bay, showing the sampling stations.

fuming nitric acid was added overnight, then hydrogen peroxide, and finally refluxed. Metals adsorbed to the surface of sediment particles are considered the most bioavailable. Metals were quantified in each fraction using a Perkin Elmer Spectrum Emission Plasma 400 ICP. As part of the quality control procedures, intercalibration sample IAEA-356 was measured along with the samples.

Normality was verified with the Shapiro-Wilks test, and the significance of seasonal changes in concentrations of the metals were obtained with a nonparametric Mann-Whitney test using Statistica Software (StatSoft, 1991). Spatial distribution maps of the heavy metals in the different sediment fractions were made with Surfer Software (Golden Software, 1999).

RESULTS AND DISCUSSION

Shapiro-Wilks normality test indicated that results were non-normal, then non-parametric tests were applied. Analysis of the intercomparison sample showed recoveries from 75 to 98% of consensus values.

Sediments in the Bay are coarse (>85% sand); however, temporally the percentages change. Percent sand and clay were higher during the rainy season (sand $P=0.04$; clay $P=0.01$), and silt was higher during the dry season ($P = 5.2 \times 10^{-4}$). Organic matter did not present significant differences between the two seasons (P = 0.3). The spatial distribution of different particle sizes changed seasonally. In the dry season sand was restricted to the outlet of Hondo River, but clay, silt and organic matter had the highest concentrations at the center of bay. This pattern seems to be consequence of currents.

Median total concentrations (± interquantile range, in μg/g dry weight) of metals, and the percentage of each metal associated with each sediment fraction, are given in Table 1. Metal total concentrations in the two seasons were in the order: Fe>V>Ni>Pb>Zn>Cu>Cd. There were no significant differences in median concentrations of metals between seasons, except for Cu and V. Non-parametric Mann-Whitney tests indicated that the difference is highly significant (Cu, P = 0.01; V, $P = 7.7 \times 10^{-7}$).

Table 1. Concentrations of heavy metals (in two seasons) in fractions of sediments in Bay of Chetumal (n = 16)

	TOTAL	IQ RANGE	ADSORBED TO THE SURFACE OF SEDIMENT PARTICLES	ASSOCIATED WITH MN AND FE OXIDES/HYDR OXIDES	BOUND TO ORGANIC MATTER	INCORPORATED INTO CLAY MINERALS LATTICES
Rainy season						
	g/g		%	%	%	%
Zn	6.14	2.97	4.00	0.00	0.00	95.38
Pb	23.92	1.85	3.75	5.86	2.93	88.03
Ni	27.43	16.47	11.01	13.30	7.71	69.82
Cu	4.49	0.91	3.37	5.81	2.39	87.66
Cd	1.45	0.3	2.42	6.1 7	0.80	90.32
Fe	867.71	550.08	0.00	0.01	0.18	99.81
V	70.15	29.09	4.79	2.15	1.84	91.36
Dry season						
Zn	5.59	1.44	1.01	0.00	1.02	97.83
Pb	22.98	4.3	4.80	6.29	5.93	82.58
Ni	27.83	12.46	9.30	10.66	4.95	76.38
Cu	5.10	0.86	3.91	5.89	4.36	86.67
Cd	1.57	0.23	3.44	5.92	5.37	85.42
Fe	825.91	416.11	0.00	0.01	0.14	99.84
V	139.90	33.11	2.15	1.08	0.96	95.71

Zn and V were mostly adsorbed to the surface of sediment particles (1 to 5%); Pb, Ni and Cu were associated with manganese and iron hydroxides (6 to 13 %); finally, Fe was complexed with organic matter (0.2 %). Ni (19 to 24 %) and Pb (9 to 11%) were the most bioavailable metals (adsorbed to surfaces of sediment particles and associated with manganese and iron hydroxides).

The total concentrations in five of seven metals, are considered by NOAA in their Sediment Quality Guidelines (Long and Morgan, 1990). Only nickel concentrations exceeded the ER-L (30 g/g). More than half the stations exceeded it in both samplings, and only station 14 in the dry season exceeded the ER-M (50 g/g), thus

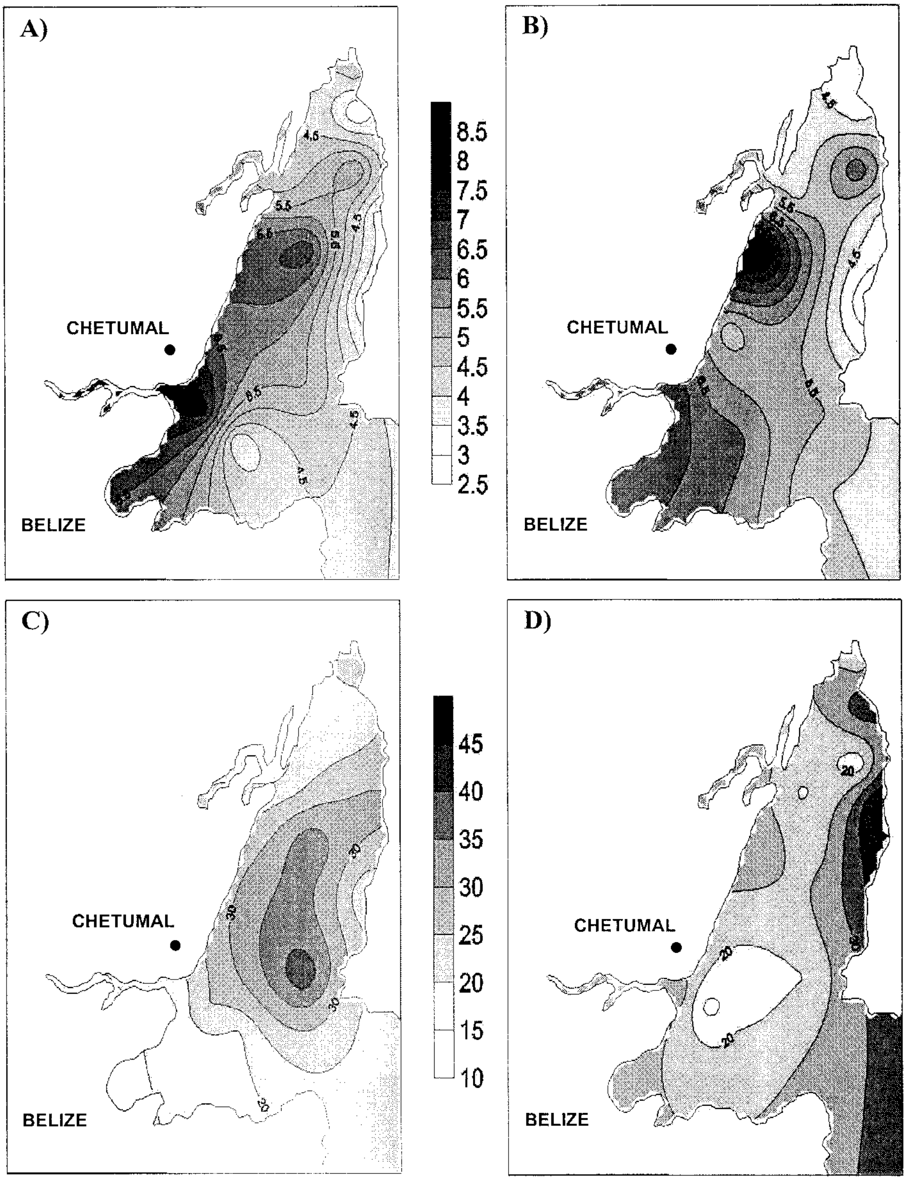

Figure 2. Spatial distribution of total Zn (g/g dry weight) in A) rainy season and B) dry season; and total Ni (g/g dry weight) in C) rainy season and D) dry season, in sediments of Bay of Chetumal.

total metal concentrations in the bay can be considered as not dangerous. High V concentrations were observed in marine sediments in the Mexican State of Veracruz (VazquezGutiérrez *et al.,* 1991). However, the highest concentrations of all metals were those incorporated into the mineral structure of the sediments (79 a 99%), which makes their bioavailability low.

Spatially the highest metal concentrations in sediments were at the stations near the outlet of Río Hondo, except for Ni and V that had their highest concentrations near the east coast and outlet of the bay. Spatial distribution of total concentrations of Zn (Fig. 2A and 2B), Pb, Cu, Cd and Fe decrease about the mouth of bay. This tendency is possibly a consequence of contribution of terrigenous material from Río Hondo. However, the distribution of Ni (Figs. 2C and 2D) and V were more related to organic material, that is, their highest concentrations were at the center and mouth of the bay. This relation was confirmed by the high correlation coefficients of both metals with organic matter observed in all fractions of the sediments.

Ni and V displayed different characteristics from others metals: a) V highest concentration was in the dry season; b) Ni was one of the most bioavailable metals; c) Ni and V had high total concentrations; d) Ni and V have very similar spatial distribution patterns; e) Ni and V are frequently associated with petroleum hydrocarbons, that is, their presence is usually related with the presence of hydrocarbons. In this study a relationship with hydrocarbons concentration was found. In the rainy season the bioavailable fraction of Ni and V correlated with aliphatic hydrocarbons (Ni: $r = 0.62$; $P \leq 0.01$ and V: $r = 0.73$; $P \leq 0.001$). In the dry season, these metals showed a good correlation with the unresolved complex mixture (UCM) (Ni: $r = 0.64$; $P \leq 0.007$ and V: $r = 0.61$; $P \leq 0.01$) and total hydrocarbons (Ni: $r = 0.65$; $P \leq 0.006$ and V: $r = 0.62$; $P \leq 0.01$; Noreña-Barroso, Per. Com.)

The correlation structure of the bioavailable fractions, and the grain size fractions, are presented in Fig. 3, for the rainy and dry seasons, respectively. The figures show the first two axes of a Principal Component Analysis, based on a Spearman correlation matrix. During the rainy season (Fig. 3A) nickel and vanadium are strongly associated with organic matter and the clay fraction. The first two axes represent 52.6% of total variance. Cadmium, copper, zinc and iron seem to co-vary together, and have a moderate correlation with silt. Since iron is in that group then it seems to represent the normal contribution of sediments. In the dry season (Fig. 3B) nickel and vanadium are associated again with organic matter and the fine sediments, but this time the group includes lead. Iron is not included in this group; it looks close, but it is a geometric factor produced by showing only two dimensions of the ordination. Zinc seems to be associated with sand, and copper and cadmium are correlated.

In general, metal concentrations were low, and considered as not dangerous, nevertheless the relatively high concentrations of Ni and V can be attributed to

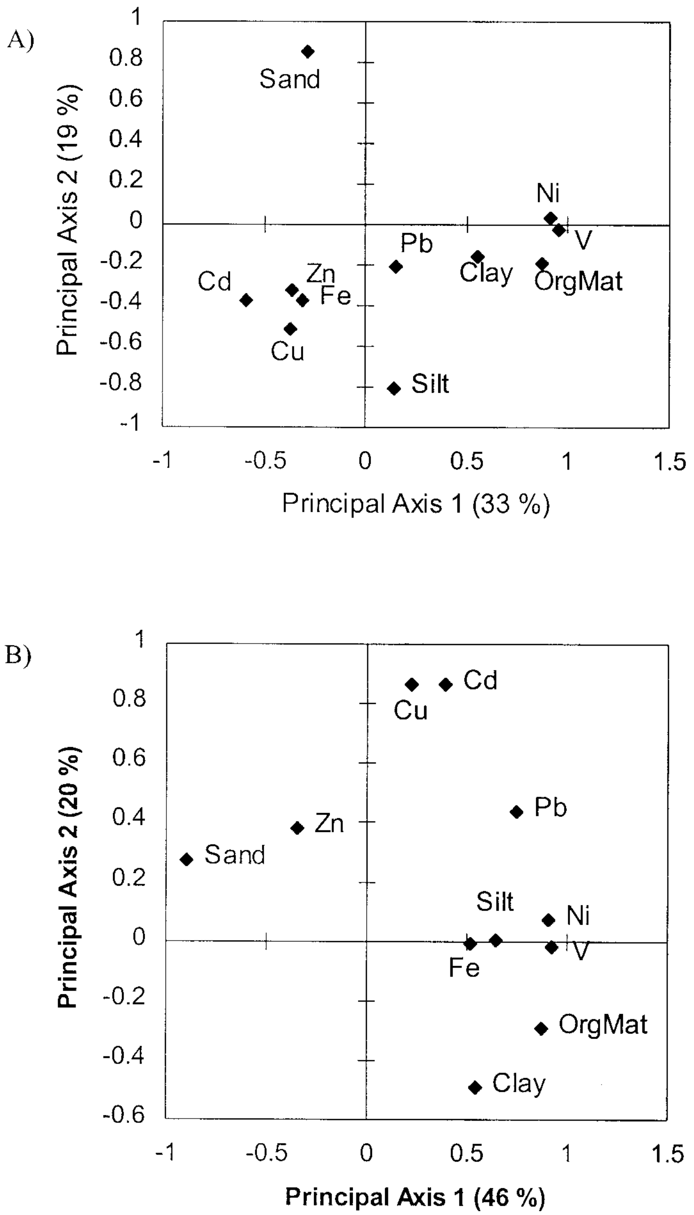

Figure 3. Principal component analysis (on a Spearman correlation matrix) of the bioavailable fraction of metals in sediments, and grain size fractions, from Bay of Chetumal, México for the A) Rainy, and B) Dry seasons.

pollution by hydrocarbons. This is an important factor to consider in the management of Bay of Chetumal, because hydrocarbon (and thus Ni and V) sources to the bay can be controlled.

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REFERENCES

Euán-Avila JI, Liceaga-Correa MA, Rodríguez-Sánchez H (2002) Caracterización de fuentes no puntuales de contaminación agrícola en el municipio de Othón P. Blanco en Quintana Roo y su potencial influencia en la Bahía de Chetumal. In: Rosado-May FJ, Romero-Mayo R, De Jesús- Navarrete A (ed). Contribuciones de la ciencia al manejo costero integrado de la Bahía de Chetumal y su área de influencia. Universidad Autónoma de Quintana Roo, Chetumal, Quintana Roo, México.

Franco J, De la Cruz G, Cruz A, Rocha A, Navarrete N, Flores G, Kato E, Sánchez S, Abarca LG, Winfield I, Bedia CM (1985) Manual de Ecología. Ed. Trillas, México.

Golden Software (1999) Contouring and 3D surface mapping for scientists and engineers. Golden Software, Inc. USA.

Lock N (1997) Transboundary protected areas between Mexico and Belize. Coastal Management 25: 445-454.

Long ER, Morgan LG (1990) The Potential for Biological Effects of Sediment-Sorbed Contaminants Tested in the National Status and Trends Program. NOAA Technical Memorandum NOS OMA 52. NOAA Office of Oceanography and Marne Assessment. Ocean Assessments Division, Seattle, WA. 173 p.

Noreña-Barroso E, Zapata-Pérez O, Ceja-Moreno V, Gold-Bouchot G (1998) Hydrocarbon and organochlorine residue concentrations in sediments from Bay of Chetumal, México. Bull Environ Contam Toxicol 61: 80-87.

Ortíz MC, Sáenz JR (1997) Detergents and Orthophosphate inputs from urban Discharges to Chetumal Bay, Quintana Roo, Mexico. Bull Environ Contam Toxicol 59: 486-491.

Pempkowiak J, Sikora A, Biernacka E (1999) Speciation of Heavy Metals in Marine Sediments vs their Bioaccumulation by Mussels. Chemosphere 39(2): 313-321.

StatSoft, Inc. (1991) CSS:STATISTICA. Tulsa, Oklahoma, United States of America.

Vazquez F, Sánchez M, Alexander H, Delgado D (1991) Distribution of Ni, V and Petroleum hydrocarbons in recent sediments from the Veracruz coast, Mexico. Bull Environ Contam Toxicol 46: 774-781.

Zapata-Pérez O, Simá-Alvarez R, Noreña-Barroso E, Guemes J, Gold-Bouchot G, Ortega A, Albores-Medina A (2000) Toxicity of sediments from Bahia de Chetumal, Mexico, as assessed by hepatic EROD induction and histology in Nile Tilapia Oreochromis niloticus. Mar Environ Res 50: 385-391.