Bull. Environ. Contam. Toxicol. (1998) 61:80-87

Bulletin of Environmental Contamination and Toxicology

Hydrocarbon and Organochlorine Residue Concentrations in Sediments from Bay of Chetumal, Mexico

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Received: 11 April 1998/Accepted: 18 May 1998

The southeastern portion of the Yucatan Peninsula is characterized by high diversity, interlinked ecosystems. It has been estimated that 25% of the total reptile and mammalian species are of conservation value, either because they are endangered, threatened, or endemic (Dotherow et al. 1995). In this area is the Bay of Chetumal, along the border between Mexico and Belize, which is an important part of the range of the West Indian manatee (*Trichechus manatus*). The Mexican side of the bay has been declared recently a sanctuary of the manatee (Lock 1997).

In June of 1996, several thousand Hardhead Catfish (*Arius felis*) died in the Bay of Chetumal. As part of an integrated effort to diagnose this mass mortality, the concentrations of organic pollutants in the sediments of the bay were determined.

MATERIALS AND METHODS

The Bay of Chetumal is a 67 km long and 12 km wide, 1098 km^2, estuary at the Southeast comer of the Yucatan Peninsula. It is located between 18 21' and 18 52' N, and 87 54' and 88 23' W. It is a shallow lagoon with a mean depth of 3.28 m (Chavira-Martínez *et al.* 1992). It is connected to the Caribbean Sea through a shallow 19 km opening. There are freshwater inputs from the Rio Hondo and Laguna Guerrero. The Rio Hondo is the border between Mexico and Belize, and is a major source of pollutants to the Bay. It drains through a highly developed sugar cane zone. The city of Chetumal discharges roughly 200 m^3/day of raw sewage into the *bay*, with an increase in the levels of phosphates and nitrates/nitrites (Ortiz and Saenz 1997).

Surface sediments were collected in 17 stations at the Bay of

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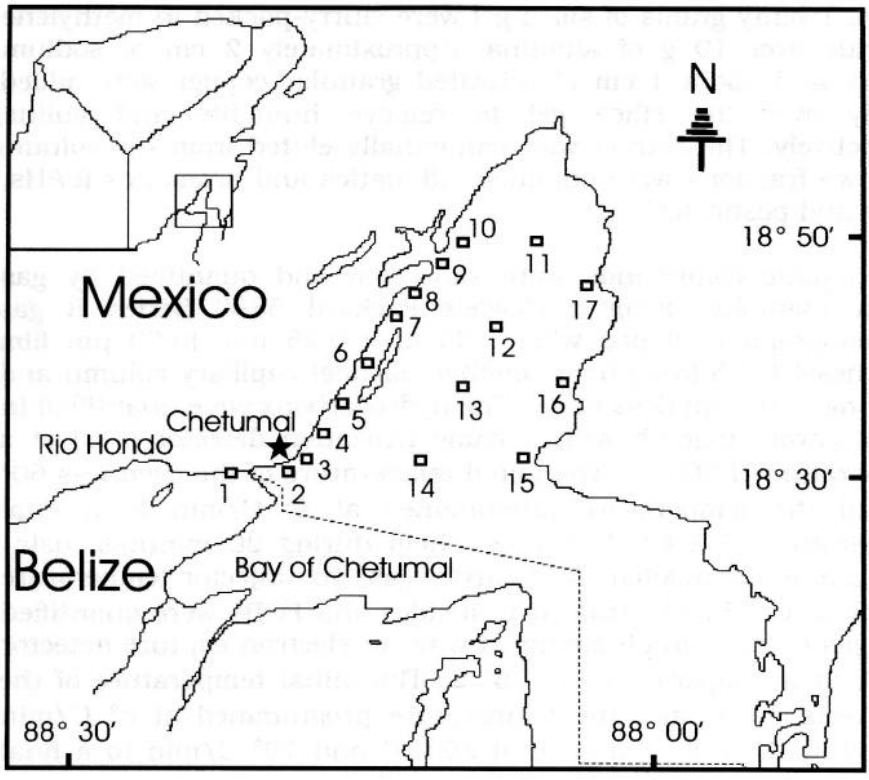

Figure 1. The Bay of Chetumal, on the border between Mexico and Belize, and the sampling stations.

Chetumal (Fig. 1) in November, 1996 with a 0.1 m^2 Van Veen grab, and the samples were transported to the laboratory in Merida for further analysis. Hydrocarbon and chlorinated organic compound concentrations were determined according to procedures described in Sericano *et al.* (1990) and Wade *et* al. (1993). The sediment samples were freeze-dried before the analysis. Approximately 30 g of sediment (dry weight) were extracted with hexane and methylene chloride during 8 hours each in a soxhlet apparatus. The methylene chloride extract was concentrated from approximately 300 mL to 20 mL in a flat-bottomed flask equipped with a three-ball Snyder column condenser and then it was mixed with the hexane extract. The hexane fraction was also concentrated and then transferred to a Kuderna-Danish tube to concentrate the extract to a final volume of 2 mL using a continuous stream of nitrogen.

The sediment extracts were fractionated by alumina:silica column chromatography. The alumina was partially deactivated with 1 % distilled water (w/w) and the silica gel with 5 % distilled water

(w/w). Twenty grams of silica gel were slurry-packed in methylene chloride over 10 g of alumina. Approximately 2 cm of sodium sulfate and about 1 cm of activated granular copper were added evenly over the silica gel to remove humidity and sulfur, respectively. The extract was sequentially eluted from the column and two fractions were obtained: aliphatics and aromatics (PAHs, PCBs and pesticides).

The organic compounds were separated and quantified by gas chromatography using a Hewlett Packard 5890 Series II gas cromatograph equipped with a 30 m x 0.25 mm (0.33 pm film thickness) HP-5 (5% phenyl-methyl silicone) capillary column and working in the splitless mode. The hydrocarbons were quantified in a gas chromatograph with a flame ionization detector (FID) at a temperature of 300°C. The initial temperature of the oven was 60° C and the temperature programmed at 6° C/min to a final temperature of 290° C that was held during 20 minutes, using nitrogen as the auxiliary and carrier gas. The injector temperature was 280° C. The chlorinated pesticides and PCBs were quantified in a gas cromatograph equipped with an electron capture detector (ECD) at a temperature of 325° C. The initial temperature of the oven was 70° C and the temperature programmed at 5° C/min until 140° C, 1.5° C/min until 250° C and 10° C/min to a final temperature of 300° C that was held during 5 minutes: using helium as the carrier gas and nitrogen as auxiliary gas. The injector temperature was 275° C. The compounds were identified and quantified using standards from Ultra Scientific. Quality assurance of the analytical procedure included the addition of internal standards and the analysis of a procedural blank for each set of samples.

RESULTS AND DISCUSSION

Concentrations of organochlorine compounds are given in Table 1, along with the median and interquantile range. The highest median concentrations were for hexachlorocyclohexanes (1.46 ± 1.94 ng/g) and DDTs (1.43 ± 0.97 ng/g). Median concentration of total PCBs was 2.96 ± 1.72 ng/g. The individual stations with the highest concentrations were stations 1, 2, 4 and 17 with 8.93, 8.12, 8.40 and 13.54 ng/g of total pesticides. For PCBs, the highest concentrations were found in stations 2 and 17, with 6.12 and 9.28 ng/g, respectively. The lowest concentrations were found in stations 12 for pesticides (2.94 ng/g) and 3 for PCBs (1.23 ng/g).

Table 1. Concentrations of organochlorine compounds, in ng/g, in sediments from Bay of Chetumal, Mexico.

1	0.29	0.16	0.17	0.08	0.88	0.73	0.12	0.44	5.83	0.23	8.93	1.90
2	0.51	0.27	n.d.	0.57	0.99	1.61	0.47	0.50	3.21	n.d.	8.12	6.12
3	0.23	0.25	n.d.	0.45	3.06	0.85	0.36	0.28	1.43	0.17	7.08	1.23
4	0.91	0.13	0.10	0.23	1.96	1.48	0.31	0.20	2.90	0.18	8.40	2.05
5	0.18	0.23	0.12	0.05	1.52	0.33	0.21	0.27	1.70	0.18	4.79	2.71
6	0.35	0.13	n.d.	0.44	1.46	0.87	0.00	n.d.	1.77	0.18	5.20	2.96
7	0.20	0.10	0.11	0.05	1.12	0.92	0.24	n.d.	0.70	0.21	3.65	1.27
8	0.30	0.25	0.14	0.58	2.66	1.09	0.37	0.28	1.43	0.16	7.27	3.25
9	0.28	0.10	n.d.	0.46	3.30	0.84	0.01	0.35	1.71	0.17	7.22	3.32
10	0.47	0.16	n.d.	0.64	3.07	1.23	0.00	0.41	1.01	n.d.	6.99	3.42
11	0.44	n.d.	0.21	0.39	0.91	1.41	0.25	0.32	2.88	n.d.	6.81	4.69
12	0.29	0.12	n.d.	0.10	0.76	0.67	0.06	0.07	0.87	n.d.	2.94	4.60
13	0.22	0.16	n.d.	0.19	1.17	0.08	0.53	0.21	0.82	0.22	3.61	2.82
14	0.28	0.00	n.d.	0.48	1.29	0.26	0.36	0.66	0.85	n.d.	4.19	3.77
15	0.33	n.d.	n.d.	0.12	2.93	0.57	0.33	0.15	1.98	0.48	6.88	2.55
16	0.43	0.16	0.21	0.58	0.93	1.02	0.00	n.d.	1.24	n.d.	4.59	1.97
17	1.78	0.47	n.d.	0.99	6.77	1.70	0.59	n.d.	1.25	n.d.	13.54	9.28
Med	0.30	0.16	0.00	0.44	1.46	0.87	0.25	0.27	1.43	0.17	6.88	2.96
IQ Range	0.16	0.13	0.12	0.45	1.94	0.55	0.30	0.28	0.97	0.19	2.68	1.72

N.d.=Not Detected *Drins=Aldrin+Endrin+Dieldrin † Pentachloroanisole ‡ Pentachorobenzene

The concentrations of hydrocarbons, with the medians and interquantile range, are given in Table 2. The highest concentrations, for all hydrocarbon fractions, were observed in station 17, at the northeast of the Bay. High concentrations were also observed in stations 14 and 15, in the central portion of the Bay. The concentrations of low molecular weight PAHs (those with two and three rings: 0.27 µg/g) were always lower than those of the high molecular weight (four and five rings; 2.176 µg/g), which indicates that the PAHs found here are pyrogenic (Wade et al. 1994; O'Connor 1992; Barrick and Prahl 1987). A nonparametric Mann-Whitney U-test test indicates that the difference is highly significant ($U=284$; $P=8.5x10^{-7}$). A confirmation of the pyrogenic source for these hydrocarbons is that the concentration of the alkyl derivatives (0.14 µg/g) is lower that that of the parent compounds (2.2 µg/g) ($U=289$; $P=3.5x10^{-7}$) (Colombo et al. 1989).

The spatial distribution of hydrocarbons in the Bay is different than that for pesticides (Figs. 2 and 3). The distribution for total organochlorine compounds has a maximum at station 17, at the northeast comer of the Bay (Fig. 2), whereas hydrocarbons have a secondary maximum in the middle of the Bay (Fig. 3). These differences could be due to the circulation pattern in the Bay and/or different sources and environmental pathways for both types of pollutants.

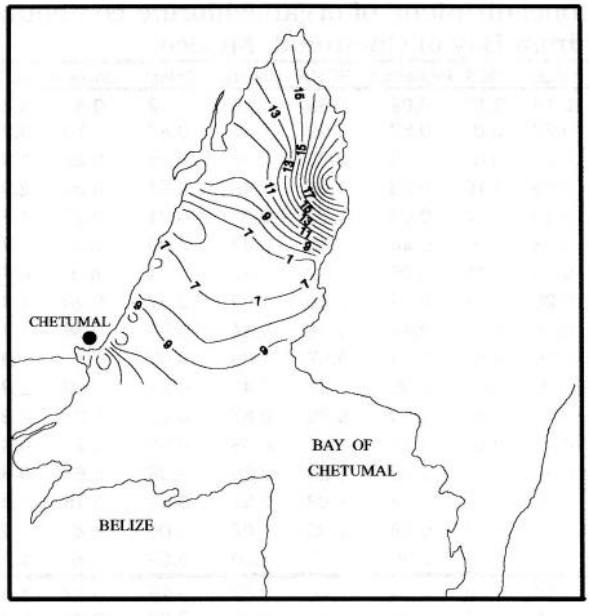

Figure 2. Spatial distribution of total organochlorine compounds (in ng/g)) in recent sediments from Bay of Chetumal.

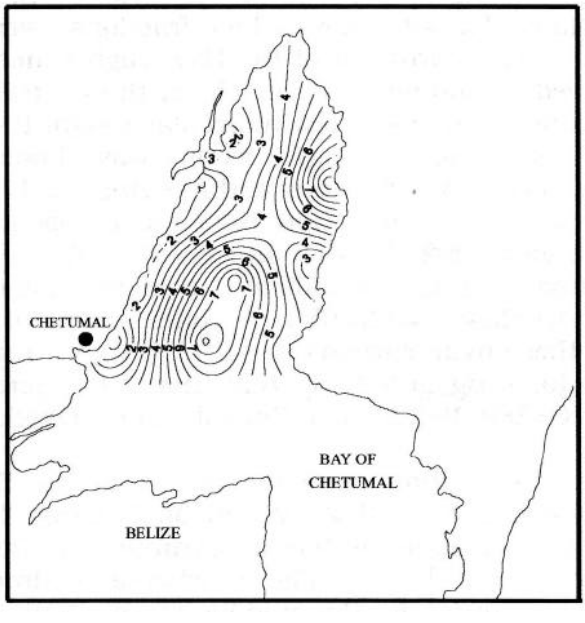

Figure 3. Spatial distribution of PAH's (in µg/g) in recent sediments from Bay of Chetumal.

Table 2. Concentrations of hydrocarbons, in µg/g, in sediments of Bay of Chetumal.

Station	2-3 Ring PAHs	4-5 Ring PAHs	Total PAHs	Aliphatics	UCM†	Total
1	0.27	2.98	3.25	3.52	8.47	15.24
2	0.31	1.07	1.38	1.49	10.13	13.00
3	0.33	0.34	0.67	1.89	3.92	6.48
4	0.24	1.97	2.20	3.74	4.65	10.59
5	0.35	1.44	1.79	7.95	6.96	16.70
6	0.09	2.10	2.19	4.58	2.17	8.95
7	0.18	1.19	1.37	0.60	0.83	2.79
8	0.43	1.04	1.47	3.04	0.64	5.15
9	0.45	3.04	3.50	3.13	2.98	9.60
10	0.40	1.20	1.60	4.81	4.54	10.95
11	0.16	3.95	4.11	2.54	3.40	10.05
12	0.14	3.65	3.79	3.44	4.09	11.32
13	0.28	7.62	7.89	16.04	8.43	32.36
14	0.17	8.05	8.21	4.83	3.01	16.05
15	0.23	3.92	4.15	6.68	5.27	16.09
16	0.18	2.17	2.34	4.17	2.84	9.35
17	0.56	8.34	8.91	18.49	13.13	40.52
Median	0.27	2.17	2.34	3.74	4.09	10.95
IQ Range	0.17	2.72	2.51	1.79	3.98	6.69

† Unresolved Complex Mixture.

The median concentration of total pesticides, 6.88 ng/g,, is higher than the average found in the Palizada River in 1992 of 4.33 ng/g (Gold-Bouchot et al. 1993) and 1993 of 1.77 ng/g (Gold-Bouchot et al. 1995). The median concentrations of total DDTs (1.43 ng/g), Chlordanes (0.87 ng/g) and PCBs (2.96 ng/g)) are all lower than the unadjusted mean values found for the northern Gulf of Mexico by the Status and Trends Program (O'Connor 1990) of 24, 3.2 and 120 ng/g, respectively.

The median concentrations of unresolved hydrocarbons is very similar to those of aliphatics (4.09 vs 3.74 µg/g), suggesting some weathering of these compounds. The overall median PAH concentration found here is 2.34 µg/g, which is much lower than the critical concentration of bong and Morgan (1990) of 35.0 µg/g, and similar to the unadjusted "high" concentration of 2.4 µg/g found by O'Connor (1990) for the northern Gulf of Mexico. The median concentration of total hydrocarbons found here (10.95 µg/g) is higher 'than those in Mecoacán, Carmen and Machona in Tabasco (an oil producing zone), where Gold-Bouchot *et al.* (1997) found values of 2.80 to 8.78 µg/g.

The concentrations of chlorinated compounds seem to be low, as compared with other regions in Mexico and the northern Gulf of Mexico; however, there is evidence that some of these compounds affect the structure of the benthic community (Salazar-Silva 1998).

The high concentrations of hydrocarbons are a cause for concern, given the importance of this ecosystem as breeding ground for the West Indian manatee and other endangered species, and because it is an ecosystem shared by two countries, which may complicate its management.

Acknowledgments. We thank the personnel and students of CET-Mar Chetumal for their help with the field work.

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