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Pollution by Petroleum Hydrocarbons in Sediments from Continental Shelf of Tabasco State, Mexico

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The Wider Caribbean is potentially one of the largest oil producing areas in the world. Major petroleum production areas include Louisiana and Texas, USA; the Bay of Campeche, Mexico; Lake Maracaibo, Venezuela; and Gulf of Paria, Trinidad; all of which are classified as production accident high-risk zones.

About 5 million of barrels are transported every day in the Caribbean, thus generating an intense tanker traffic. It has been estimated that oil discharges from tank washings within the Wider Caribbean could be as high as 7 million barrels/year.

For all those reasons petroleum pollution is considered as the major environmental problem in the Wider Caribbean area and increasing day to day due to the use of petroleum as the main energy source (Rodriguez 1981).

On the other hand, the continental shelf of Tabasco state actually represents one of the most productive areas for crude oil in the Gulf of Mexico. It has several marine platforms, as well as intensive tanker traffic including storage areas as the Port of Dos Bocas with a capacity for more than 2 x 10^6 barrels representing a high risk zone of oil pollution.

The continental shelf of Tabasco is one the most productive areas for fishing and its coastal zone has important coastal lagoons with high productivy used mainly for acquaculture activities. The climate in the area is typically tropical with an intensive rain season of approximately 200 cm of precipitation per year.
Strong north winds are the most important climate features during autumm and winter seasons.

MATERIALS AND METHODS

The study area was located between the mouth of Frontera River and Mecoacan Lagoon at $92^0$44'00''- $93^0$06'00'' W longitude and 18^0 28'08'' - $19^0$25'09'' N latitude as presented in Figure 1. Samples of surficial sediments were collected by using a Van Veen grab sampler of 10 kg of capacity, during the cruise OGMEX-VII aboard the R/V "Justo Sierra" in January 1989.

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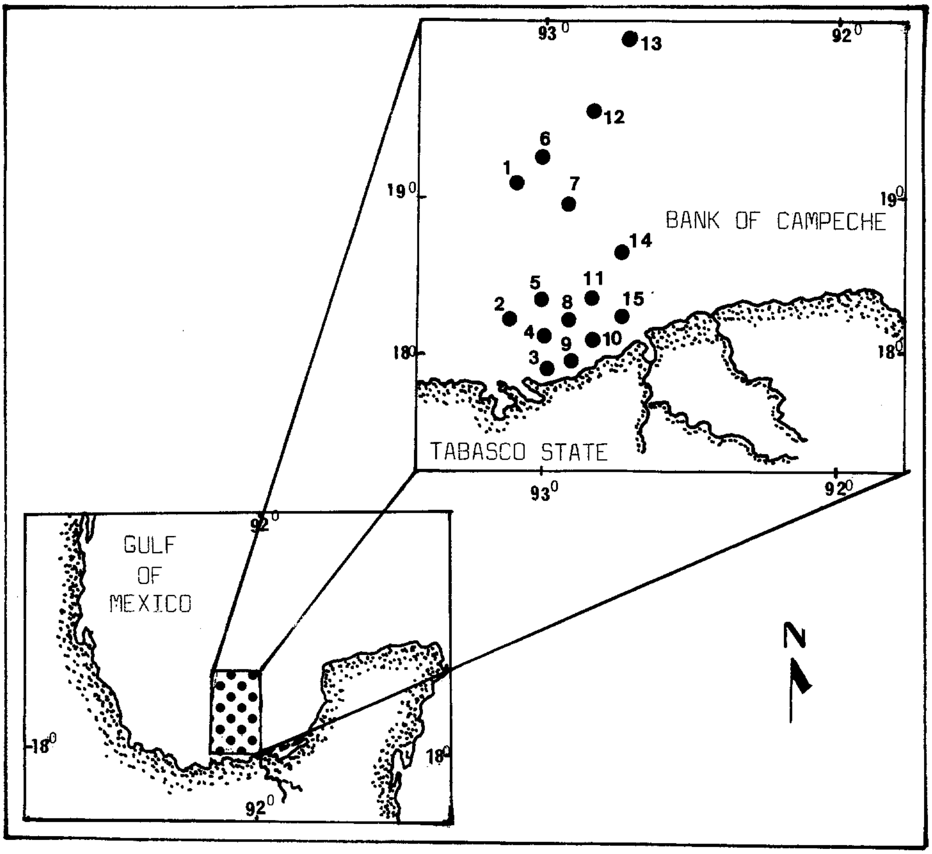

Figure 1. Map of the coast of Tabasco State showing sampling locations.

After collection the samples were placed in glass jars previously cleaned with hexane and dichloromethane bidistilled and kept frozen at $-4^{0}C$ until analysis.

The analytic procedure for the extraction and purification of the hydrocarbons fractions was the recommended by the Caripol-IOCARIBE Manual (1986). The sediments were digested by using a solution of KOH-Methanol (5% in vol) for 3 hrs, then the organic phase was extracted using hexane bidistilled (Aldrich) and purified in chromatography columns (30 cm long, 1.5 i.d.) packed with activated alumina and eluting with hexane and CH_4Cl_2.

The fractions of saturated and aromatic hydrocarbons were analyzed by capillary gas chromatography using a Hewlett Packard Model 5890 equipped with a phenyl-methyl silicone 5% capillary column (25 m x 0.25 mm i.d.). Nitrogen was the carrier gas. Injection was performed on splitless mode at 280°C. The oven temperature was programmed from 40 to 300°C at 6°C/min. Detector temperature was

300° C. n-C_{28} was the internal standard for the saturated fractions and a mixture of PAHs (Chem Service, West Chester PA 19381) containing 15 aromatic compounds, was used as an external standard for the aromatic fraction. Recovery percentage for both fractions was 90%.

Also, a series of blanks were carried out before and after chromatographic analysis to reconfirm the presence of aliphatic and aromatic compounds. The identification and quantification of these organic compounds were carried out by its retention time compared with an internal standard (Supelco Inc. Belafonte PA 16823) Type of sediments and grain size analysis was performed by using the combined dry sieve and pipette method (Folk 1974). The percentage of organic carbon (%TOC) in the sediments was determined by titration using diphenylamine and ferrous sulphate 1N (Gaudette et. al. 1974) as color indicators.

RESULTS AND DISCUSSION

At present, the literature regarding the presence of petroleum hydrocarbons in the Wider Caribbean is very sparse.

Recent analysis carried out in sediments of coastal areas of United States from Tampa Bay, Florida., up to Corpus Christi, Texas (Wade et. al. 1988), Cartagena Bay, Colombia (Garay 1986), and Coatzacoalcos River, Mexico (Farran et. al. 1987) show high concentrations of petroleum hydrocarbons in these sites as a clear indication of industrial and oil activities. Indeed, the study area had been impacted by the effects of two big oil spills, the Ixtoc-I in 1979 and the Abkatun I in 1985 (Soto et. al. 1981).

Table 1 shows the sediment types, organic carbon content as well as the concentration of aliphatic and aromatic hydrocarbons present in sediments analyzed. The average size for sediments were: <muds 0.062 mm, sandy muds <2 mm and slime muds >2 mm. All values obtained for petroleum hydrocarbons in sediments are below 10 ug/g of dry weight i.e., they correspond to hydrocarbon concentrations in coastal areas considered to be non-polluted (Farrington 1985).

The highest concentrations (stations 5, 6, 10, 11 and 15) indicate the influence of oil activities carried out in the area. The remaining values are probably due to fluvial discharges and run-off from adjacent coastal areas. In a previous study conducted in coastal lagoons of Tabasco, Botello et. al. (1983) reported higher concentrations of petroleum hydrocarbons up to three orders of magnitude compared with the results of this study, due mainly to the effects of the Ixtoc-I oil spill.

The chromatography analysis of the aliphatic fraction reveals the presence of n-paraffins with slight odd-even ratio with predominance of the C_{17}, C_{21}, C_{25}, C_{27}, C_{29} and C_{31}, a pattern common for non-polluted marine sediments, marine phytoplankton and terrestrial vegetation (Clark and Blummer 1967).

Table 1. Type of sediments, total organic carbon (%) content and concentration (ng/g dry wt) from the continental shelf of Tabasco State, Mexico.

Sampling site	Type of sediments	% TOC	Aliphatics C17-C31	Aromatics ng/g	Total Hydrocarbons ng/g
1	slime mud	1.12	23	504	527
2	slime mud	0.19	15	471	486
3	slime mud	0.50	134	627	761
4	slime mud	0.50	109	832	941
5	slime mud	0.83	195	1439	1634
6	sandy mud	0.40	208	1186	1394
7	slime mud	0.35	147	1096	1243
8	mud	0.44	170	816	986
9	mud	0.68	202	992	1194
10	sandy mud	0.83	199	1174	1373
11	mud	0.50	79	1709	1788
12	mud	0.78	28	455	483
13	sandy mud	0.73	N.D	501	501
14	mud	0.68	122	864	986
15	mud	1.07	255	3120	3375

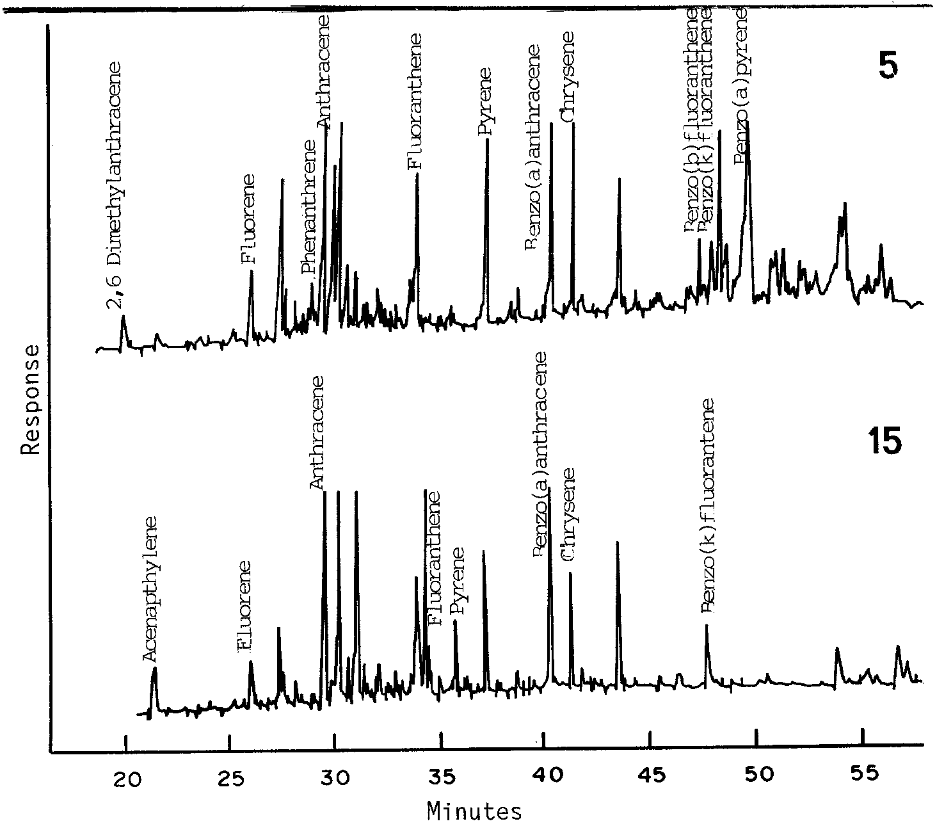

Figure 2.- Gas chromatograms of sampling sites 15 and 5, showing the presence of polycyclic aromatic hydrocarbons in sediments.

Table 2. Distribution of Polycyclic Aromatic Hydrocarbons in recent sediments from the continental shelf of Tabasco State, Mexico (ng/g dry wt).

Compounds	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Naphthalene	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
2,6 Dimethylanthracene	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	34	N.D	N.D	N.D	N.D	N.D
Acenaphthylene	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	39	N.D
Acenaphthene	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
Fluorene	N.D	N.D	N.D	N.D	N.D	84	68	N.D	N.D	87	61	66	64	69	158
Phenanthrene	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	24	N.D	N.D	N.D	89
Anthracene	149	101	100	45	158	253	262	172	112	201	128	101	50	190	79
Fluoranthene	87	151	251	305	633	98	54	70	319	310	62	61	145	41	1296
Pyrene	72	44	54	57	91	67	86	61	53	58	90	49	94	65	79
Benzo(a)anthracene	120	118	139	215	340	251	424	250	250	283	190	84	75	235	562
Chrysene	76	57	83	81	55	356	110	134	121	90	94	93	73	84	62
Benzo(b)fluoranthene	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	67	N.D	N.D	N.D	144
Benzo(k)fluoranthene	N.D	N.D	N.D	129	162	77	92	129	137	145	121	N.D	N.D	141	264
Benzo(a)pyrene	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	735	N.D	N.D	N.D	N.D
Benzo(ghi)perylene	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	147
Indo(1,2 Cd)pyrene	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	130	N.D	N.D	N.D	240
Detection limits =	10 ng/g														

Of paramount importance can be considered the presence of polycyclic aromatic hydrocarbons in marine sediments. Their presence corresponds either to concentrations of residues from high temperature processes like fossil combustions (fluoranthenes, pyrenes, chrysenes and benzopyrenes) or oil activities such as direct discharges, tanker operations, refinery processes, and accidental spills (mostly methyl derivatives and dimethyl substituted naphthalenes and phenanthrenes).

Table 2 shows the distribution of polycyclic aromatic hydrocarbons (PAHs) present in sediments of each sampling site analyzed.
The absence of naphthalenes and its methyl derivatives, which are indicators of recent oil spills is noticeable.

However, the most conspicuous PAHs are those containing 3 and 4 benzene rings, e.g., as the anthracenes, fluoranthenes, pyrenes, benzo(a)anthracenes and chrysenes. These PAHs originate through high temperature processes mainly fossil combustions (Neff 1979).

Also, it has to be pointed out that except the benzo(k)fluoranthene, PAHs with 5 or 6 benzene rings (benzo(a)pyrene, benzo(ghi)perylene), in sediments from coast of Tabasco State, are almost totally absent.

In contrast with these results, Botello et. al. (1983) reported high concentrations of PAHs specially naphthalenes and their methyl derivatives in Crassostrea virginica and sediments from coastal lagoons of Tabasco, as a direct input of fresh crude oil released during the Ixtoc-I oil spill.

Figure 2 shows two chromatograms of the aromatic fractions from sediments corresponding to stations 15 and 5, clearly showing the presence of PAHs with 3 and 4 benzene rings. Thus, the pattern of the distribution of PAHs in the sediments analyzed seems to be influenced mainly by their vicinity to potential oil pollution sources.

The concentrations of hydrocarbons reported in this study are higher than those reported previously by Al-Saad (1987) for sediments from Arabian Gulf, but are in the same range as those published by Wade et. al. (1988) for sediments from the Gulf of Mexico especially the coasts of Texas, Louisiana, and Florida, which are under the pressure of intensive oil tanker traffic showing high levels of petroleum pollution (Atwood et. al. 1987).

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