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Levels of Organic Pollution in Coastal Lagoons of Tabasco State, Mexico; I: Petroleum Hydrocarbons

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The concentration of fossil hydrocarbons in marine environments has increased in recent years, mainly due to intensive exploitation of oil and the large number of oil industry accidents (NATIONAL ACADEMY OF SCIENCE, 1975). In coastal zones affected by oil spills and continuous hydrocarbon discharges up to 236 ug of hydrocarbons have been detected in oysters per g of wet tissue (EHRHARDT, 1972). In sediments affected by an oil spill in Buzzards Bay, U.S.A., BLUMER and SASS (1972) found up to 12,000 ppm of hydrocarbons more than a year after the accident had occurred.

There has been great interest in the determination of hydrocarbon levels in bivalves such as clams, oysters and mussels, because these organisms are useful indicators to determine the state of oil pollution in coastal areas (FARRINGTON and QUINN, 1973; CLARK and FINLEY, 1973).

This paper presents a basic study of the concentrations and source of hydrocarbons (fossil or biogenic) found in sediments and oysters of coastal lagoons and estuaries of the state of Tabasco, México. It is a response to the urgent need for this type of analysis generated by the current expansion of the oil industry in the coastal areas of the Gulf of México.

METHODS AND RESULTS

More than 100 samples of sediments and oysters (Crassostrea virginica) were collected in 27 stations located in the Carmen-Machona and Mecoacán lagoons in Tabasco, México, during four periods: October, 1979; January, March and May, 1980 (Fig. 1). Hydrocarbons were extracted from these samples and purified.

The sediments, collected with a Van Veen dredge, were immediately frozen at -20° C (CLARK, 1966). The oysters were collected manually, the valves removed, and then they were also frozen at -20° C. The samples preserved in this manner were sent for analysis to the Instituto de Ciencias del Mar y Limnología (Institute of Ocean Sciences and Limnology) in México City.

75 g of lyophilized sediment were extracted from each sample with 150 ml of methanol and 150 ml of benzene in reflux for six hours. The two fractions (methanol-benzene) were saponified with 175 ml

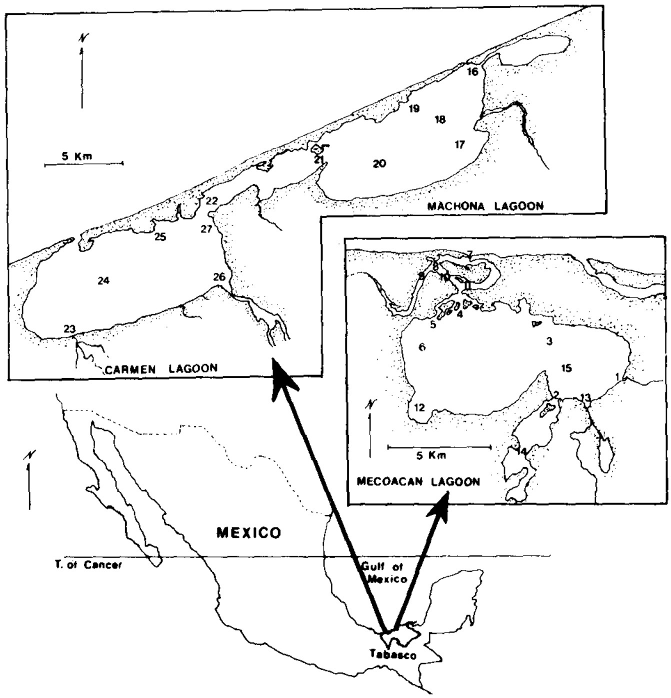

Figure 1. Sampling locations.

of methanolic KOH at 20% (w/v) for six hours. The non-saponifiable compounds were purified by means of a chromatography column packed with silica-gel and aluminium oxide in a 4:1 ratio, both with activity degree I. The extract was eluted with 25 ml of hexane, 25 ml of benzene and 25 ml of methanol. The hexane and benzene fractions were collected separately, evaporated to total dryness and analyzed by gas chromatography.

The extraction of hydrocarbons from oysters was carried out with 5 g of freeze-dried oysters, which were extracted and purified simultaneously with 200 ml of methanolic KOH at 20% in constant reflux for 12 hours and then treated according to the procedure describe above for sediments.

For the hydrocarbon analysis, a Perkin-Elmer gas chromatograph, Model 910, was used, equipped with flame ionization detector, linear temperature programmer and capillary columns 30 m long with an internal diameter of 0.25 mm, packed with OV-101. Nitrogen was used as carrier gas. The temperature was programmed from 70 to 225° C, with an increase of 3° C per minute. The compounds were identified by comparison with the retention indices of a previously analyzed standard containing normal paraffins, ranging from C_{14} to C_{32}, aromatic hydrocarbons and pristane and phytane.

RESULTS AND DISCUSSION

TABLE 1 shows the total hydrocarbon concentration for sediments, represented in ug/g (ppm) of dry weight).

Table 1. Total hydrocarbon concentration in sediments (ppm).

Station	October 1979	January 1980	March 1980	May 1980
1	27	19	54	64
2	65	59	44	41
3	83	108	61	55
4	26	99	95	53
5	11	39	53	29
6	31	46	29	21
7	1060	29	33	47
8	305	124	79	15
9	48	71	36	43
10	90	24	57	48
11	68	65	40	44
12	32	-	40	15
13	25	73	64	23
14	35	28	43	40
15	74	50	53	39
16	32	49	113	31
17	54	47	59	29
18	46	38	77	28
19	83	15	57	41
20	52	22	32	28
21	28	20	57	36
22	150	19	40	35
23	33	23	60	36
24	53	37	76	7
25	33	94	72	23
26	35	18	108	32
27	57	32	72	20

The majority of values obtained for sediments (80%) are below 70 ppm; i.e., they correspond to hydrocarbon concentration in coastal areas considered to be non-polluted (NATIONAL ACADEMY OF SCIENCE, 1975; BLUMMER and SASS, 1972). The highest concentration (1060 and 305 ppm) reflect the influence of oil spilled in the Ixtoc-I accident, which was carried to the coast by tropical storm "Henry" in September, 1979. The remaining values between 80 and 150 ppm (18%) are probably due to fluvial discharges and run-off from adjacent areas where exploration, exploitation and crude oil refinement are carried out.

The results obtained in May, 1980, are all less than 70 ppm, which could indicate that fossil hydrocarbons do not remain in the sediments of the lagoon studied because of the great dynamism of the coastal ecosystems, which favor dispersion, weathering and biodegradation of hydrocarbons.

Figure 2 represents a chromatogram of the hexane fraction from sediments of the Mecoacán lagoon. It shows a series of peaks of n-paraffins in a range from n-C_{15} to n-C_{33}, with a clear predominance of odd-numbered n-paraffins, principally C_{15}, C_{17}, C_{29}, C_{31} and C_{33}, a pattern which is common for recent non-polluted marine and freshwater sediments.

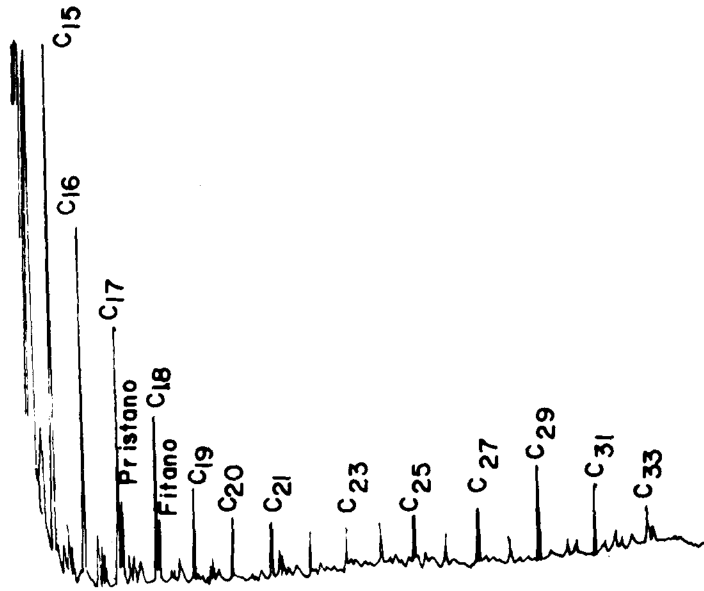

Figure 2. Chromatogram of the hexane fraction from Mecoacán lagoon.

Figure 3 shows the chromatogram for sediments from station number 7, located at the outlet of the Mecoacán lagoon into the Gulf of México, which received a large quantity of crude oil. This figure shows and even distribution of n-paraffins from C_{14} to C_{35}, with no predominance of odd-numbered carbons. The presence of pristane and phytane noted here is a typical of hydrocarbons from crude oil.

The total hydrocarbon levels obtained from the tissue of Crassostrea virginica are shown in Table 2, expressed in ug/g (ppm) of dry weight.

In contrast to the values obtained for sediments, which to a large degree do not reflect pollution, the results obtained for oysters coincide with those reported by other researchers for bivalves from lagoons, bays and canals affected by oil industry activities and accidents (BLUMER et al., 1970); EHRHARDT, 1972; FARRINGTON and QUINN, 1973, SAMMUT and NICKELS, 1978; BOTELLO, 1978). The greatest concentrations of hydrocarbons in oysters were observed principally in October, 1978, which may indicate that these organisms had bioaccumulated compounds or adsorbed particles of oil from the Ixtoc-I accident in the Gulf of México. In general, the values obtained for oysters indicate a chronic (i.e., constant and incipient) pollution, which allows these mollusks to demonstrate their capacity to bioaccumulate hydrocarbons.

With reference to the distribution patterns of n-paraffins in the

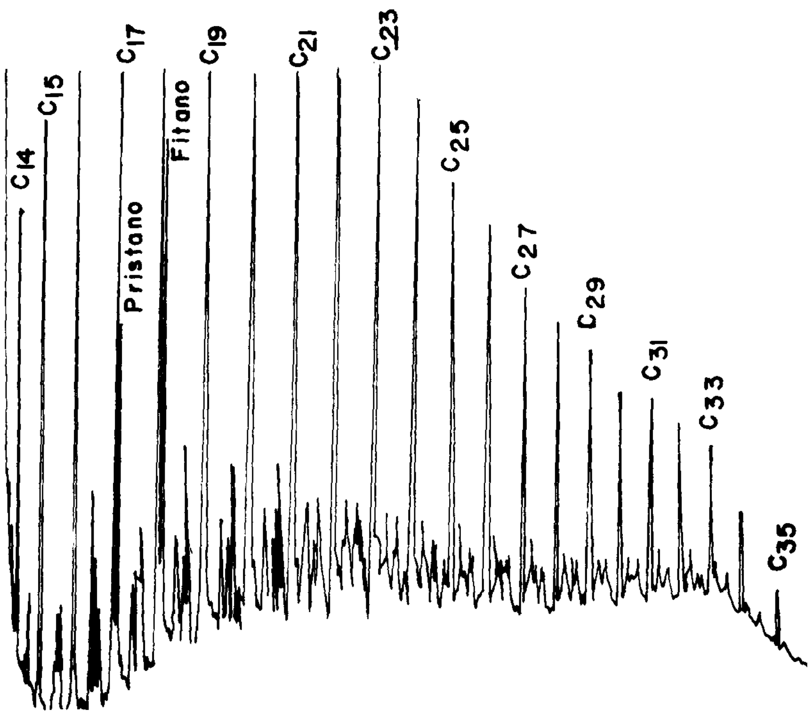

Figure 3. Chromatogram of the Hexane fraction of the sampling site No. 7, after arrival of crude oil from the Ixtoc-I.

Table 2. Total hydrocarbons from <u>Crassostrea virginica</u> tissue.

Station	October 1979	January 1980	March 1980	May 1980
2	52	55	-	33
3	164	40	62	42
4	3371	60	39	40
5	2388	66	8	48
6	41	56	21	38
10	130	-	22	38
11	280	81	23	48
13	722	-	29	93
19	1842	138	60	300
20	-	-	72	40
21	34	118	61	31
22	-	208	106	30
25	-	76	96	1120
27	352	62	52	350

organisms analyzed, the corresponding chromatogram (Fig. 4) reveals the presence of saturated compounds in a range from n-C_{14} to n-C_{29}. There is a notable "hump" which includes in addition to the n-paraffins, certain olefins and cyclical saturated hydrocarbons which are not clearly resolved by the chromatography column used in the analysis.

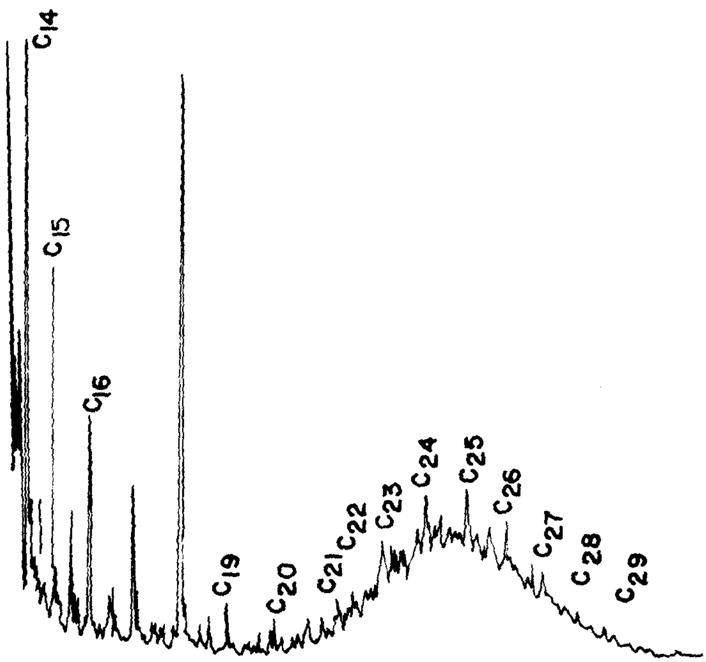

Figure 4. Chromatogram showing the pattern of n-paraffins in Crassostrea virginica from Mecoacán lagoon.

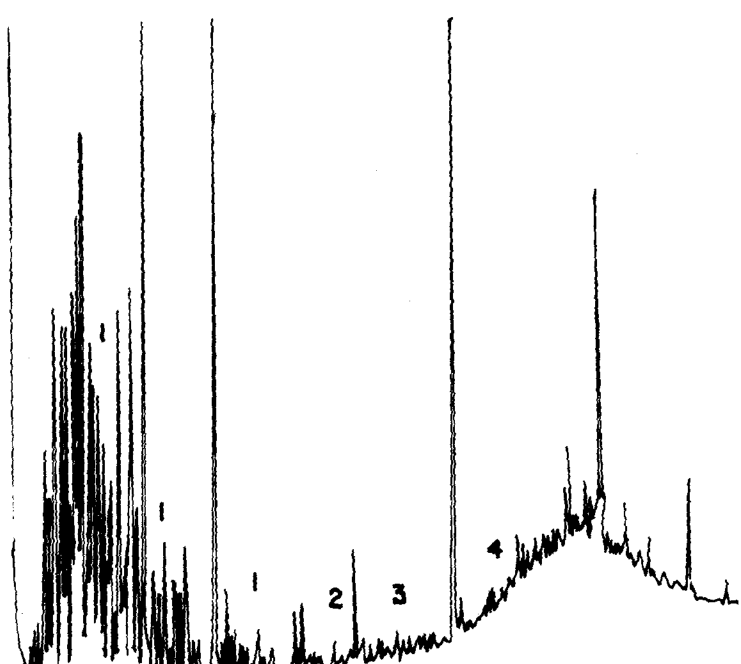

Figure 5. Chromatogram and Benzene fraction for Crassostrea virginica from Mecoacán lagoon. (1) Naphtalene and its methyl derivatives, (2) Dibenzotiophenes, (3) Anthracene, (4) Fluorene.

Figure 5 presents the benzenic fraction for C. virginica from the Mecoacán lagoon. Notable here is the presence of aromatic hydrocarbons such as the napthalenes and their methyl derivatives, the dibenzotiophenes, anthracene and fluorenes.

Since these compounds are not produced by organisms, their presence in the environment indicates pollution caused by nearby oil industry activities, which release wastes that eventually settle in sediments or tissues of the organisms analyzed.

The presence of fossil hydrocarbons in sediments and organisms tells us that these compounds undoubtely have their origin in human and industrial activities carried out near the areas studied. The Ixtoc-I spill had a considerable impact, especially on the mouths or inlet of the lagoons studied; nevertheless, due to the great dynamism of these lagoons and the high degree of natural weathering of spilt oil (BOTELLO and CASTRO, 1980), the hydrocarbons present as a result of the spill had a short time of residence.

The presence of aromatic hydrocarbons in oyster tissue (C. virginica) is clear proof that the wastes from oil industry activities are discharged into the environment and are carried by means of Tabasco's extensive hydrological net to the lagoon ecosystems, where they are stored by sediments and organisms, mainly the filterers.

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