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Polycyclic Aromatic Hydrocarbons in Sediments from Pueblo Viejo, Tamiahua, and Tampamachoco Lagoons in the Southern Gulf of Mexico

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The coastal lagoons of the Gulf of Mexico have great ecological and economic importance from the point of view of fishing (primarily as regards the farming of oysters). At the present, there are two oyster-farming regions in the State of Veracruz. The first, and most important, is in the northern part of the state where 3,056 fishermen settle and who farm oysters in Tampamachoco, Tamiahua and Pueblo Viejo Lagoons. Similarly, they contribute up to 90% of the national production of oysters and shrimp (Restrepo 1995).

Recent studies have demonstrated that pollution problems are severe in Pueblo Viejo and Tampamachoco Lagoons, and that productivity in these systems has been seen to dwindle considerably, given that they are receiving input from anthropogenic sources of organic, inorganic and biological pollutants, which are putting human health at risk (Botello *et al.* 1992).

Within the pollutants determined in mexican coastal areas of the Gulf of Mexico, oil and petroleum hydrocarbons are considered of paramount importance, because the continental shelf of Tamaulipas, Veracruz, Tabasco and Campeche States represents one of the most productive areas for crude oil in the world. It has several marine platforms, an intensive tanker traffic including storage areas and industrial ports for loading and unloading of crude oil representing a high risk zone for oil pollution (Botello *et al.* 1993).

Thus, it is necessary to determine the current state of pollution, and most of all the levels of PAHS's in these lagoon systems, given that as a result of their hydrophobicity and strong affinity for particulates, the PAH's may accumulate in sediments and bioaccumulate in fish and shellfish at levels several orders of magnitude greater than that found in source effluents (Huntley *et al.* 1995).

In addition, when the particles of polluted sediments are suspended they can affect directly the filter feeding organisms (Eertman *et al.* 1995) and more importantly, because laboratory studies have demonstrated that some PAH's are mutagenic and carcinogenic (Clansky and Winstedt 1992; Grimmer 1993).

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MATERIALS AND METHODS

The lagoons of Pueblo Viejo, Tamiahua and Tampamachoco [Fig 1] are located in the Coastal Plains of the Gulf of Mexico, between the towns of Tuxpan and Tampico, in the north of the State of Veracruz. The area of this study is limited by the outer geographic co-ordinates of 20° 57', 22 13' latitude, and 97°19', 98°80' longitude, forming part of the hydrological basins of the Tuxpan and Pánuco rivers.

Surface sediments were taken during May and September (1994) and March (1995) from 15 sampling sites by means of a small stainless steel van Veen grab sampler (6 L) and frozen (4°C) in glass jars previously cleaned and rinsed with bidistilled acetone. In the laboratory these were defrosted, and dried during 48 hr at 45°C then the sediments were sifted in a mesh to 0,25 mm.

The analytical procedures for extraction and purification of PAH's were carried out by the method of CARIPOL (1986) according to U.N.E.P. (1992). Each set of samples (6) was accompanied by a complete blank and a spiked blank which was carried through the entire analytical scheme in a manner identical to the samples. 10 g of dried sediment were soxhlet extracted with methanol (100 ml) and KOH, and standard additions were added before extraction. The aromatic standard addition contains Phenanthrene or Fluoranthene 200 µl. The saturated and aromatic fractions were purified by adsorption chromatography using 20 cm long columns, packed with alumina (5% deactivated with water). The extracts containing fraction 1 (saturates) and fraction 2 (aromatics) were rotoevaporated to 2 ml and analyzed by gas chromatography.

Quantification of the aromatic fraction was make by means of a Hewlett Packard gas chromatograph model 5890 equipped with 30 m x 0.25 mm ID x 0.25µm bonded 5%-phenilmethylsilicone, fused silica column (temperature programmed 40 - 300°C at 6 °C/min). Nitrogene was used as carrier gas (flow 1 ml/mm). In this study was used a mixture with well-known standards of the "Chemical Service" PPH-10M. The limit of detection for individual aromatic compounds was 0.01 µg/g and recovery yields were up to 90%.

Also, the total organic carbon was determinated and its analysis was based on method of Gaudette *et al.* (1974). In which exothermic heating and oxidation with K^2CrO_7 and concentrated H_2SO_4 are followed by tritation of the excess dichromate with 0.5 N $Fe(NH_4)_2(SO_4).6H_2O$.

RESULTS AND DISCUSSION

Table 1 shows the different total concentrations determined in the three studied lagoons, as well as the type of sediment and percentage of organic carbon in each sampling site.

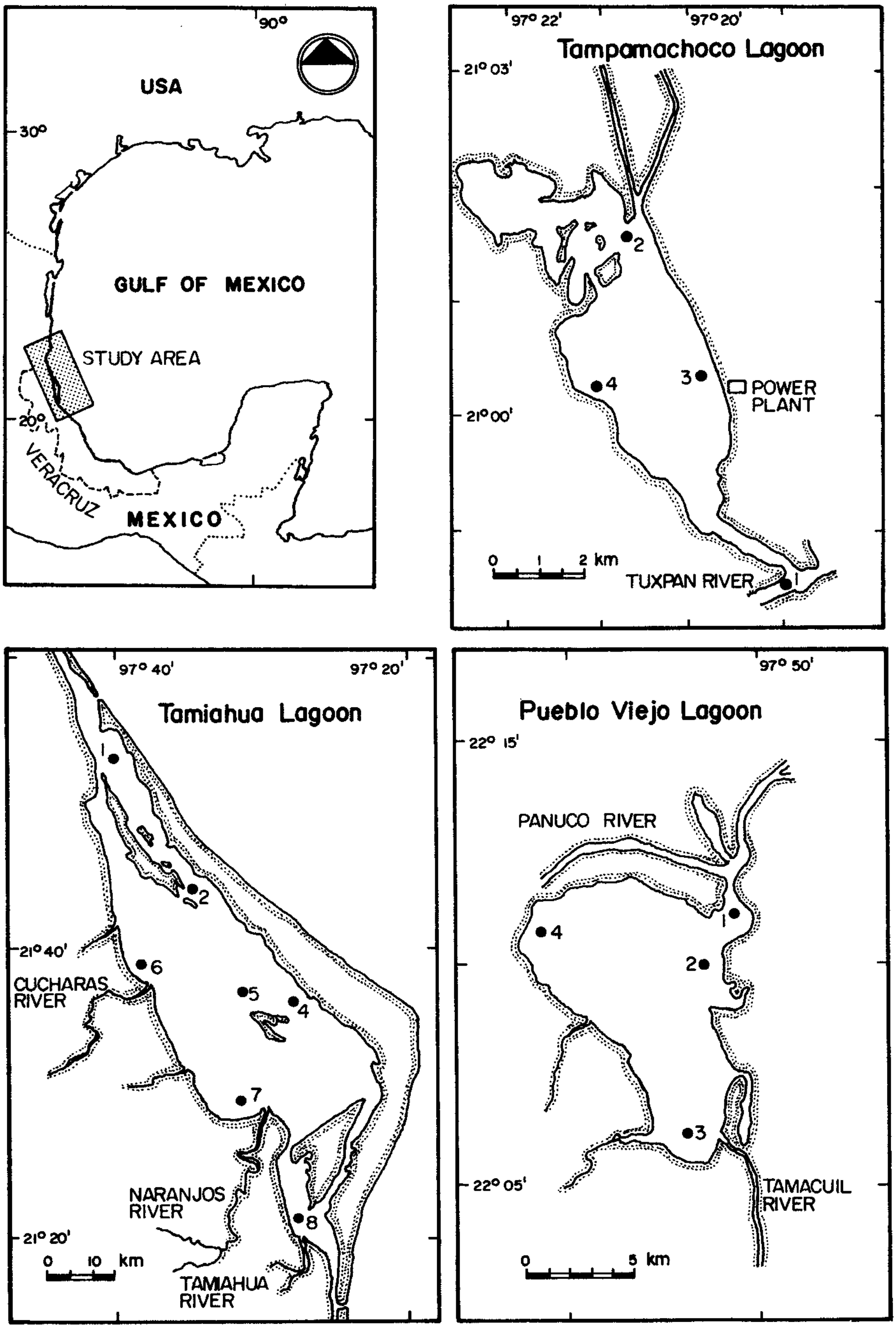

Figure 1. Sampling sites for sediment in coastal lagoons, northeast Gulf of Mexico

In Pueblo Viejo Lagoon, the location showing the highest total concentrations of PAH's was station number 1 with 5.21 µg/g, located in the northern, which receives input from the River Pánuco, bordering the industrial area of Tampico, and which river also passes through various towns. The lowest levels (2.05 µg/g) were detected in station number 2 (Barranco Amarillo), near where there is no settlements or any farming activity.

For Tamiahua Lagoon, station number 4 (Cabo Rojo), with 8.14 µg/g, showed the highest values of total PAH's, followed by station number 6 (Estero de Cucharas) and 7 (Estero Tancochín) with 4.94 and 3.2 µg/g respectively. The accumulation of organic compounds was favorable in station number 4, given that it is in an area for the deposit of silty-clay sediment, demonstrating that the sorption of these xenobiotics which stick to the particles depends not only on the electric charge of the particles in the estuaries, but also on the types and degree of aggregation of the particles available. In the case of stations 6 and 7, both localities receive the influence of two rivers of significant channels, which give their names to the creeks; similarly, an oil pipeline crosses between the creeks El Mamey and Tancochín.

At the western area of Tamiahua, PAH's are generated by the constant traffic of small boats going about their fishing business from La Laja to Tancochin. The La Laja fishing co-operative has some hundred boats, and in the central and southern parts of the system there are approximately 350 small vessels.

The sampling stations that showed the lowest concentrations, are station number 5 (on the north of La Isla del Toro) with 0.67 µg/g, and station number 8 (Estero Tampache) with 0.58 µg/g. These two sites are characterized by sandy sediment, which does not favour the adsorption of PAH's. On the other hand, they are both zones influenced by currents because of their proximity to the mouths of Tamiahua Lagoon.

In Tampamachoco Lagoon, the greatest PAH levels were reported at station 3 (9.39 µg/g) situated facing the Thermoelectric Power Station. It is important to notice that the values in this location were the highest detected at all stations in the three lagoons studied. Station 4 (Paso Daniel) with 4.71 µg/g, receives the influence of a natural oil-spring called Oro Negro; and station 1, which receives the inflows from the Tuxpan river, registered a PAH's concentration of 3.15 µg/g.

Station 2 (Estero Jácome) showed the lowest total PAH concentrations with 0.67 µg/g. Here the sediment is predominantly silty-clay, which would lead to the expectation of high PAH concentrations. The fact of not finding them is evidence that the distribution of these aromatic compounds in Tampamachoco is determined more by proximity to direct input, rather than by the type of sediment found locally.

Of the three lagoons studied, in Pueblo Viejo 44% of the PAH totals corresponded to those made up of 4 benzene rings, and 9% were 5 ring compounds (among them are Benzo(k)fluoranthene, Benzo(b)fluoranthene and Indene, which are of pyrogenic origin); then come the 2 ring compounds (Acenaphthene) with 25%, and 3 ring compounds with 22% (Acenaphthylene and Fluorene). This demonstrates the input of recent hydrocarbons, which are very volatile and of petrogenic in origin. The results corroborated the fact that the entry of PAH's to the system also has an anthropogenic origin.

For Tamiahua Lagoon, the greatest percentage of total PAH's corresponded to 4 ring aromatics (64%), followed by 3 ring compounds (27%). Both originate from the pyrolysis of gasolines and oils from the launches, the burning of mangrove and pasture, as well as being introduced into the system by the inflows of the rivers.

In Tampamachoco, the 4 and 3 ring compounds present the highest percentages, 4 rings (58%) and 3 rings (18%) respectively. Therefore the PAH's determined also derive from the pyrolysis of fuels and lubricants, coming from the discharges of the Thermoelectric Power Station as well as petrogenic sources.

According to the predominant compounds, the following sequences were obtained for Pueblo Viejo: Benzo(k)fluoranthene (1.39 µg/g) > Indene (1.35) > Acenaphthene (0.69) > Phenenthrene (0.59) > Benzo(b)fluoranthene (0.51).
Tamiahua: Indene (1.63 µg/g) > Benzo(a)anthracene (1.46) > Pyrene (1.36) > Benzo(a)pyrene (0.46) > Fluorene (0.38).
Tampamachoco: Benzo(a)anthracene (2.75 µg/g) > Pyrene (1.11) > Phenanthrene (1.1) > Benzo(k)fluoranthene (0.74) > Benzo(a)pyrene (0.42).

Of the former compounds, Benzo(a)pyrene is considered potentially carcinogenic in humans (Neff 1979; Martel *et al.* 1986; Kennish, 1992). Nevertheless, in the present study this aromatic was detected exclusively in Tamiahua lagoon at station number 6 (0.46 µg/g), and in Tampamachoco at station number 3 (0.42 µg/g), facing the Thermoelectric Power Station.

With regard to the correlations between the concentration of PAH's and the type of sediment (sand, silt or clay), the values obtained were not significant ($p = >0.05$). On the other hand, on establishing a direct correlation between the organic carbon (C.O.%) and the PAH's determined in the sediments of each lagoon system, the coefficients were the following: Tamiahua $r= 0.62$, Pueblo Viejo $r= -0.65$, and Tampamachoco $r= -0.74$. This demonstrates that the PAH concentrations are independent of the percentages of organic carbon present in the lagoons. The correlation coefficients for Pueblo Viejo and Tampamachoco contradict the sorption theory, which is sustained in the affinity of PAH's with matter that has a high organic carbon content, such as clay and silt. This non-affinity has been reported for marine sediments (Johnson *et al.* 1985; Readman *et al.* 1986), and in suspended estuarine particles (Herrman and Thomas 1984; Raoux and Garriges 1991; Coakley *et al.* 1993).

In relation to the nature of the PAH's determined, Pueblo Viejo Lagoon reflects both a petrogenic and an anthropogenic origin of PAH's. However in Tamiahua and

Table 1. Levels of PAH's, percentage of organic carbon and type of sediments in coastal lagoons northeast Gulf of Mexico.

	Pueblo Viejo Lagoon					Tamiahua Lagoon								Tampamachoco Lagoon				
COMPOUNDS	STATIONS					STATIONS								STATIONS				
µg/g	1	2	3	4	Total	1	2	4	5	6	7	8	Total	1	2	3	4	Total
Naphthalene	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Acenaphthylene	0.20	0.17	0.38	< 0.01	0.75	< 0.01	0.11	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.11	< 0.01	< 0.01	0.40	0.21	0.61
Acenaphthene	0.35	1.14	0.59	< 0.01	2.08	0.43	0.24	< 0.01	0.11	0.13	0.39	< 0.01	1.30	0.15	< 0.01	0.03	< 0.01	0.18
Fluorene	0.11	0.34	0.30	0.11	0.86	0.41	0.15	1.01	0.45	0.11	0.14	< 0.01	2.27	0.17	0.22	0.03	< 0.01	0.42
Phenanthrene	2.00	0.08	0.11	0.16	2.35	0.75	0.12	0.25	0.11	0.10	0.14	< 0.01	1.47	0.15	< 0.01	0.16	3.00	3.31
Anthracene	0.18	0.13	0.12	< 0.01	0.43	0.09	0.07	0.30	< 0.01	0.36	0.07	0.15	1.04	0.33	< 0.01	< 0.01	< 0.01	0.33
Fluoranthene	0.19	< 0.01	0.21	0.14	0.54	0.15	0.14	0.55	< 0.01	0.29	0.25	0.43	1.81	0.30	0.45	0.21	0.14	1.10
Pyrene	< 0.01	< 0.01	0.59	0.04	0.63	< 0.01	1.40	1.95	< 0.01	1.02	1.05	< 0.01	5.42	0.81	< 0.01	1.62	0.91	3.34
Benzo(a)anthracene	1.15	0.05	0.43	0.12	1.75	0.93	1.02	4.08	< 0.01	0.70	0.57	< 0.01	7.30	0.69	< 0.01	4.81	< 0.01	5.50
Chrysene	0.15	0.14	0.17	0.31	0.77	< 0.01	0.11	< 0.01	< 0.01	0.14	0.22	< 0.01	0.47	0.20	< 0.01	0.23	0.16	0.59
Benzo(b)fluoranthene	0.51	< 0.01	< 0.01	< 0.01	0.51	< 0.01	0.26	< 0.01	< 0.01	< 0.01	0.37	< 0.01	0.63	< 0.01	< 0.01	0.35	0.29	0.64
Benzo(k)fluoranthene	0.37	< 0.01	< 0.01	2.40	2.77	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.35	< 0.01	1.13	< 0.01	1.48
Benzo(a)pyrene	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.46	< 0.01	< 0.01	0.46	< 0.01	< 0.01	0.42	< 0.01	0.42
Indeno(1,2,3cd)pyrene	< 0.01	< 0.01	1.35	< 0.01	1.35	< 0.01	< 0.01	< 0.01	< 0.01	1.63	< 0.01	< 0.01	1.63	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Benzo(ghi)perylene	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
TOTAL PAH's	5.21	2.05	4.25	3.28	14.79	2.76	3.62	8.14	0.67	4.94	3.20	0.58	23.91	3.15	0.67	9.39	4.71	17.92
%Organic carbon	0.51	1.04	0.87	1.51	1.04	1.41	1.82	1.65	1.32	2.03	0.95	0.44	1.37	1.51	2.65	1.27	1.15	1.62
Type of sediments	sand	clay	silt	clay		clay	sand	sand	silt	clay	silt	silt		clay	clay	clay	silt	

Detection limit: 0.01 µg/g

Tampamachoco, the PAH's come from anthropogenic input, basically from pyrolysis of organic matter and fossil fuels. In Tampamachoco there is evidence that the pollution by PAH's is determined by proximity to direct inflows, independently of the type of sediment present. Finally, it was confirmed that Tampamachoco is the lagoon system that is currently showing ascending average PAH's levels (7.65 µg/g) within the State of Veracruz, Mexico.

Due to the importance of these lagoon systems for fishing and oysters farming, it should be remembered that some of the PAH's detected in the present study are listed by the EPA (the Environmental Protection Agency) and by the European Community as dangerous waste-products, and are among the 65 priority toxic contaminants (Sitting 1985; Wild and Jones 1995) jeopardizing the farming the of fish and shellfish in the area and thus, affecting the economy of a very important nucleus of fishermen.

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