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Sedimentary record of PAH in a tropical coastal lagoon from the Gulf of Mexico

Registro sedimentario de HAP en una laguna costera tropical del Golfo de México

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ABSTRACT

Sediment core samples were collected in Sontecomapan coastal lagoon, Veracruz; in the Gulf of Mexico on August 1992. The concentrations of 15 priority Polycyclic Aromatic Hydrocarbons (PAH) were analyzed by gas chromatography, using capillary columns of high resolution and flame ionization detection (GC-FID) to reconstruct a history of PAH contaminant input into the lagoon. The average values of PAH registered for core "A" (with fresh water influence) were from 9.76 µg/g; core "B" (in the zone where fresh and marine water mix) registered the highest concentrations with 16.80 µg/g; and core "C" (marine influence) demonstrated the lowest levels with 8.13 µg/g. Vertical profiles of PAH concentrations were characterized by a maximum at depth between 1-5 cm and by almost constant descent levels at depth of 6 to 15 cm. With regard to the hierarchical behavior of the individual compounds of PAH in all cores, in descending order, they were: Chrysene > Indeno(1,2,3-c,d)pyrene > Benzo(a)anthracene > Benzo(b)fluoranthene > Benzo(k)fluoranthene > Benzo(a)pyrene. The aromatics with 4 to 6 rings predominated in the concentrations of PAH, which suggests the origin of these compounds is due to the pyrolysis of organic material and fossil fuels. The higher aromatics predominated due to their higher persistence. PAH goes into system through motor boat activity, river discharges, by tidal action from the coast and from atmospheric transport.

Keywords: polycyclic aromatic hydrocarbons, sediment cores, coastal lagoon, Sontecomapan, Veracruz.

RESUMEN

Se colectaron núcleos de sedimento en la Laguna de Sontecomapan, Veracruz; en el Golfo de México en el mes de agosto de 1992. Se determinaron las concentraciones de 15 Hidrocarburos Aromáticos Policíclicos (HAP) prioritarios, los cuales fueron analizados por cromatografía de gases empleando columnas capilares y detector de ionización de flama (CG-DIF) con el propósito de reconstruir la historia de depositación de estos contaminantes en la laguna. El valor promedio de HAP registrado para el núcleo "A" (con influencia dulceacuícola) fue de 9.76 µg/g; para el núcleo "B" (en la zona de mezcla de agua marina y dulceacuícola) presentó las mayores concentraciones promedio con 16.80 µg/g; y el núcleo "C" (de influencia marina) mostró los niveles menores con 8.13 µg/g. Los perfiles verticales de las concentraciones de HAP estuvieron caracterizados por un máximo a profundidades entre 1-5 cm y casi por un descenso constante en los niveles a profundidades de 6-15 cm. Con respecto al desarrollo jerárquico de los HAP individuales en todos los núcleos, en orden descendente fueron: Criseno > Indeno(1,2,3-c,d)pireno > Benzo(a)antraceno > Benzo(b)fluoranteno > Benzo(k)fluoranteno > Benzo(a)pireno. El predominio de aromáticos conformados por 4 a 6 anillos bencénicos

en las concentraciones de HAP, sugiere que estos compuestos son de origen pirolítico, tanto de materia orgánica como de combustibles fósiles. La dominancia de los anillos bencénicos antes mencionados se debe a la gran persistencia de los mismos. Los HAP están ingresando al sistema a través de la actividad de las lanchas, las descargas de los ríos, la acción mareal de la costa y por transporte atmosférico.

Palabras clave: hidrocarburos aromáticos policíclicos, núcleos de sedimento, laguna costera, Sontecomapan, Veracruz.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAH) are made up of hydrogen and carbon organized in the form of two or more benzene rings fused to substitute groups possibly joined to one or more rings (Boehm, 1981). PAH are environmental pollutants that constitute a potential risk for public health and to other forms of life (Martel *et al.*, 1986). Some of them, such as benzo(a)pyrene, are powerful carcinogens, associated with the presence of some human cancers (Clanksky and Winsted, 1992).

Nowadays there is an increasing amount of literature about the levels of PAH in coastal systems around the world (Valette, 1993; Zhang *et al.*, 1993). However, there are few studies on estuary-lagoon systems related to the deposition history of PAH, by means of sediment core samples (Coakley *et al.*, 1993; Latimer and Quinn, 1996; Li *et al.*, 1998) and most of these studies have been carried out in areas that receive the direct influence of industrial and municipal discharges.

Moreover, specific literature about the presence and distribution of PAH in coastal and estuarine environments of tropical areas, as well as the effects of PAH on marine biota is less abundant. Such studies are necessary in order to understand the behavior, transport mechanisms, and bioacumulation of PAH in estuarine species.

Sontecomapan Lagoon, in Veracruz State is a highly productive coastal ecosystem bordered of mangrove forest, which has been affected during the last two decades by immoderate tree-felling, primarily for agricultural purposes, specially in "Los Tuxtlas" region (Angeles, 1997), where the most important activity is the tobacco industry, which uses the mangrove tree with the aim of building galleries to burn and to dry tobacco leaves. The PAH arise from natural forest and prairie fires, most of PAH in the environment are the result of the incomplete combustion of organic matter at high temperatures (Neff, 1979). On the other hand, PAH have the advantage of being more persistent than metals in environments of fluctuating salinity (Coakley *et al.*, 1993).

Thus, the principle objectives of this study were to evaluate the concentrations and vertical distribution of PAH in the sediment core samples and to show their trends and depositional history, as well as to research the correlation between those PAH with the percentage of organic carbon.

MATERIALS AND METHODS

Sontecomapan Lagoon is located in the South of the State Veracruz on the Gulf of Mexico, between 18°30' - 18°34' N and 94°54' - 95°02' W, it has an area of approximately 8.9 Km^2 and has been an important fishing town (Fig. 1). This study comprises one sampling time on August 1992 during rainy season. The temperature was evaluated using a cup thermometer (± 0.1°C), the salinity was measured using an "American Optical" refractometer (± 0.5 ups) and the pH was measured with a "Conductronic" field potentiometer (± 0.1 pH unites).

The sampling sites for cores were chosen using aerial photographs, which show transport of sediments and inputs for rivers as web as marine influence zones. Divers using a PVC hand-held corer during August of 1992 at locations through Sontecomapan lagoon collected three 0 to 35 cm sediment cores. These were frozen until analysis; X ray radiographs of each core was performed to check core integrity, then the cores were cut in sections using a round cutting. A total of twenty one samples were frozen (- 4°C) in glass jars previously cleansed and rinsed with bi-distilled acetone and dried over night for 200°C, then rinsed with hexane chromatographic grade. Samples were defrosted and dried during 48 h at 45°C in the laboratory and sieved through a 0.25 mm mesh.

Analytical procedures for extraction and purification of PAH were performed following the CARIPOL/IOCARIBE/UNESCO (Caribbean Pollution Programme. Intergovernmental Oceanographic Commission for Caribbean of UNESCO, 1986) method, according to UNEP (United Nations Environment Programme, 1992). Each set of samples (6) was accompanied by a complete blank and a spiked blank, and handled identically to the samples throughout the entire analytical procedures. 10 grams of dried sediment were Soxhlet extracted with methanol (100 mL) and KOH 5%, standard additions were added before extraction. The internal reference standard contained phenanthrene (200 µL). The saturated and

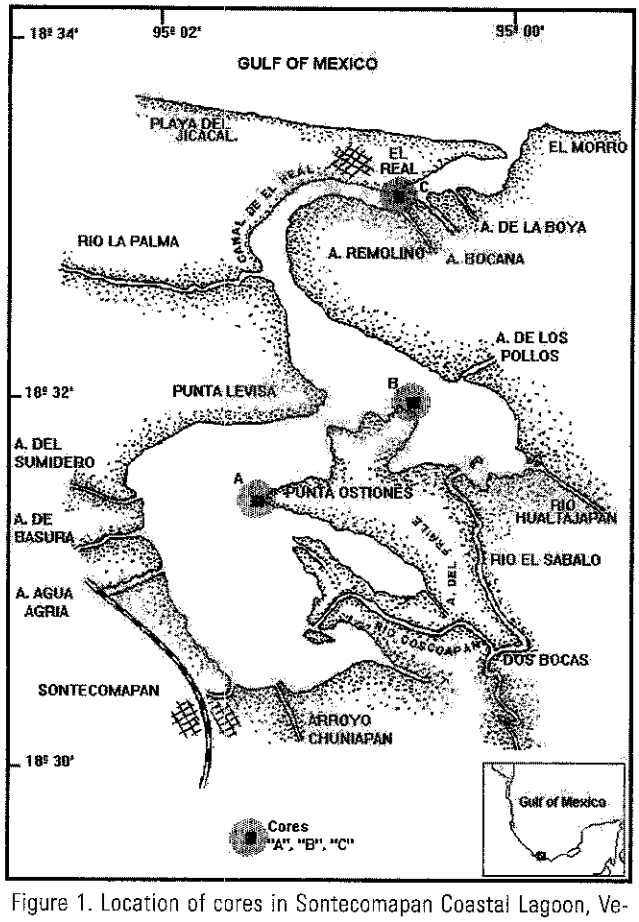

Figure 1. Location of cores in Sontecomapan Coastal Lagoon, Veracruz.

aromatic fractions were purified by adsorption chromatography using glass columns of 2.5 cm internal diameter and 25 cm length, packed with alumina and silica gel (5%) deactivated with water. Aliphatic hydrocarbons were eluted in the first fraction with n-hexane more n-hexane, and aromatics in the second fraction with n-hexane/methylene chloride mixture (7:3) and methylene chloride. The extracts containing fraction 1 (saturates) and fraction 2 (aromatics) were roto-evaporated up to 2 mL and analyzed by high resolution gas capillary chromatography with a flame ionization detector (GC-FID) and capillary column.

Identification and quantification of the aromatic fraction was performed using 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). Nitrogen was used as carrier gas (flow 1 mL/min). A standard with a mixture of 15 PAH (Chemical Service PPH-10M) was used as external reference. Detection limit for individual aromatic compounds was 0.01 mg/g and recovery yields were up to 95%.

Organic carbon determination 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 0.5N $Fe(NH_4)2(SO_4)\cdot 6H_2O$.

RESULTS AND DISCUSSION

Sontecomapan Lagoon is of the mixohaline type with an average salinity of 9.27 ups, and with average values of 16.95 ups in the northern zone. The lagoon connects with the sea by means of a channel of 137 m in width. The central area presents a mean salinity of 8.22 ups, and the southern zone has average salinity values of less than 4.23 ups, showing the importance of the fluvial input. The average water temperature (27.1°C) is closely related with the ambient temperature (26.9°C), due to the shallowness of the system. The mean depth is 1.67 m with a water transparency of 0.70 m and pH values were 7.5.

The sedimentation rate in the system is variable for each section of the lagoon, given that in the southeast zone it is greater than in the area influenced by the sea, which produces sandy sediment. Pérez-Rojas and Márquez, U.A.M.I., Personal communication indicates they measured that the sedimentation rate in the southern and central area of Sontecomapan Lagoon, during 1991, can be as much as 8 cm/year in rainy season, and 2cm/year in the dry season. This gives an average sedimentation rate of approximately 5cm/year. In addition, one study of Galvan *et al.*, (1999) concluded that the increment of sediment draw towards the lagoon is exponential, estimating the productive life of the system being of approximately ten years.

Olsen *et al.*, (1993) consider that the estuarine areas, frequently filled with fine grain sediments, are the appropriate areas for documenting the history of contamination based on sedimentary registers. In addition, the net rate of sedimentation in these areas varies from 0.5 to 5 cm/year (Olsen *et al.*, 1993; Latimer and Quinn,1996). Thus from the chronological point of view, the sediments of the system studied were considered to be relatively young, with an average of 7 years for the register of PAH. The average values of PAH registered for core "A" (with fresh water influence) were from 9.76 µg/g; core "B" (in the zone where fresh and marine water mix) registered the highest concentrations with 16.80 µg/g and core "C" (marine influence) demonstrated the lowest levels with 8.13 µg/g (Fig. 2).

According to the results obtained, in core "A", the greatest concentrations for total PAH was present in the lower

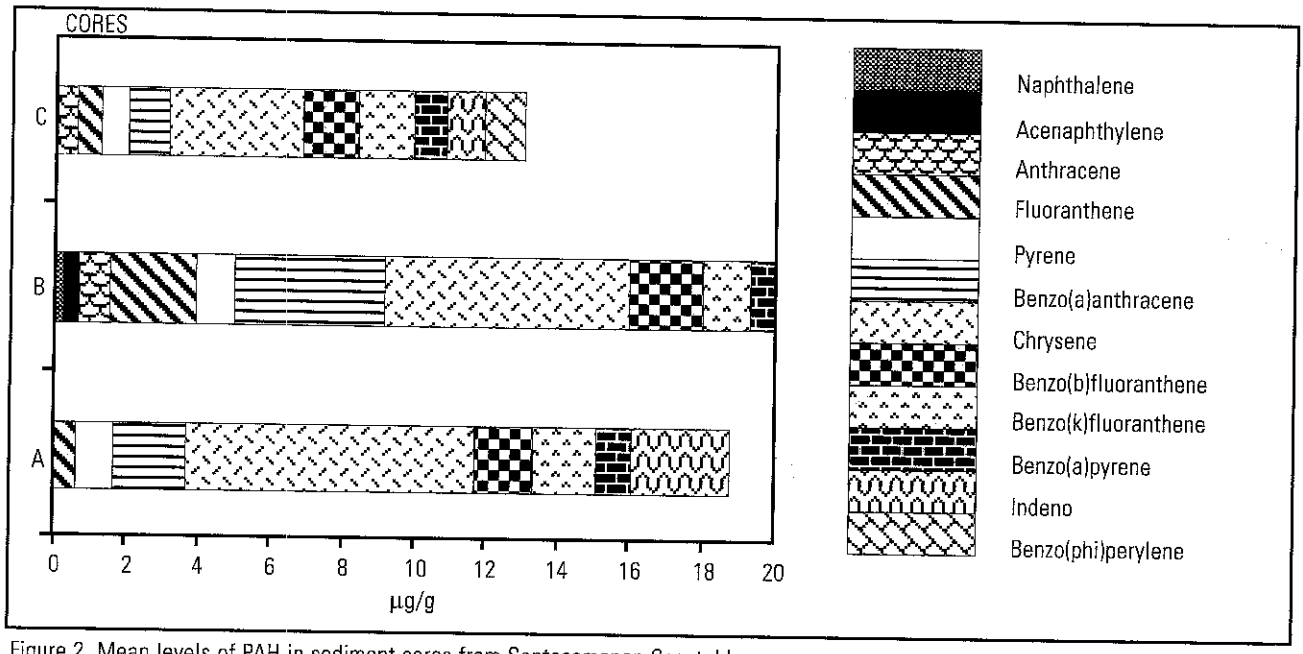

Figure 2. Mean levels of PAH in sediment cores from Sontecomapan Coastal Lagoon.

stratum (31-35 cm in depth) with 24.57 µg/g (Detection limit: <0.01- Maximum 16.09). The upper stratum (1-5 cm) has values of 10.83 µg/g (<0.01-3.47), and the lowest values were found between 11 and 15 cm, with 1.65 µg/g (<0.01-1.65) [Table 1]. The predominance of mean aromatic compounds, in descending order in core "A" were: Chrysene (8.05 µg/g), Indeno(1,2,3-c,d)pyrene (2.68), Benzo(a)anthracene (1.91), Benzo(k)fluoranthene (1.81) and Benzo(b)fluoranthene (1.63).

In core "B", the upper layer, between 1-5 cm in depth, showed 41.52 µg/g (<0.01-25.57) of total PAH, followed by the stratum between 16-20 cm with 32.09 µg/g (<0.01-12.27). The lowest results were registered in the stratum between 21 and 25 cm in depth, with 3.34 µg/g (<0.01-2.98) [Table 2]. In core "B", the greatest average concentration was again of Indeno(1,2,3-c,d)pyrene (6.78 µg/g) followed by Chrysene (6.84), Benzo(a)anthracene (4.14), Benzo(a)pyrene (2.68) and Fluoranthene (2.42).

In core "C", the highest values of total PAH were registered between 1-5 cm in depth, with 15.22 µg/g (<0.01-3.56)), and between 11-15 cm there was a concentration of 14.35

Table 1. Levels of total PAH for core "A" from Sontecomapan Lagoon.

Compound (µg/g dry weight)	Depth (cm) 1-5	6-10	11-15	16-20	21-25	26-30	31-35	Mean	S.D.
Fluoranthene	<0.01	0.45	<0.01	0.52	0.95	0.93	0.22	0.61	0.32
Pyrene	<0.01	0.66	<0.01	<0.01	<0.01	0.71	1.88	1.08	0.69
Benzo(a)anthracene	2.84	0.97	<0.01	0.68	0.92	2.39	3.65	1.91	1.22
Chrysene	<0.01	<0.01	<0.01	<0.01	<0.01	2.02	14.07	8.05	8.5
Benzo(b)fluoranthene	1.65	0.28	<0.01	<0.01	3.84	0.41	1.99	1.63	1.44
Benzo(k)fluoranthene	1.35	0.69	<0.01	4.07	<0.01	1.22	1.70	1.81	1.32
Benzo(a)pyrene	1.52	0.64	<0.01	<0.01	<0.01	0.65	1.06	0.97	0.41
Indeno(1,2,3-cd)pyrene	3.47	1.48	1.65	4.40	2.42	<0.01	<0.01	2.68	1.24
[Total PAH]	10.83	5.17	1.65	9.67	8.13	8.33	24.57		
Mean	2.17	0.74	1.65	2.42	2.03	1.19	3.51		
S.D.	0.93	0.39	0	2.10	1.39	0.74	4.77		
% O.C.	4.48	1.47	2.08	2.82	5.04	2.95	0.90	2.82	1.51

* Naphthalene, Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene and Benzo(ghi)perylene = <0.01 µg/g.

Table 2. Levels oftotal PAH for core "B" from Sontecomapan Lagoon.

Compound	Depth (cm)								
(µg/g dry weight)	1-5	6-10	11-15	16-20	21-25	26-30	31-35	Mean	S.D.
Naphthalene	<0.01	<0.01	<0.01	0.27	<0.01	0.22	0.18	0.22	0.04
Acenaphthylene	<0.01	<0.01	<0.01	<0.01	<0.01	0.31	<0.01	0.31	0
Anthracene	2.58	<0.01	0.78	0.33	<0.01	0.46	0.33	0.90	0.96
Fluoranthene	6.20	<0.01	0.13	0.93	<0.01	3.80	1.02	2.42	2.53
Pyrene	<0.01	0.30	<0.01	2.52	<0.01	<0.01	0.88	1.23	1.15
Benzo(a)anthracene	<0.01	<0.01	<0.01	5.55	<0.01	2.72	<0.01	4.14	2.00
Chrysene	<0.01	0.46	<0.01	12.27	<0.01	<0.01	7.80	6.84	5.96
Benzo(b)fluoranthene	<0.01	<0.01	<0.01	2.61	<0.01	<0.01	1.44	2.03	0.82
Benzo(k)fluoranthene	0.42	1.26	1.83	3.30	0.36	0.21	2.06	1.35	1.13
Benzo(a)pyrene	6.75	<0.01	0.57	1.69	<0.01	3.01	1.37	2.68	2.44
Indeno(1,2,3-cd)pyrene	25.57	3.16	1.22	2.62	2.98	5.13	<0.01	6.78	9.29
[Total PAH]	41.52	5.18	4.53	32.09	3.34	15.86	15.08		
Mean	8.30	1.30	0.91	3.21	1.67	1.98	1.89		
S.D.	9.99	1.31	0.64	3.54	1.85	1.93	2.46		
% O.C.	5.68	2.00	2.86	5.81	5.20	6.39	3.83	4.54	1.66

* Acenaphthene, Fluorene, Phenanthrene = <0.01 µg/g.

µg/g (<0.01-10.58). The lower values were found in the stratum from 21-25cm, with 1.16 µg/g (<0.01-0.46) [Table 3.].

As with the sediment core samples "A" and "B", in core "C", Chrysene was the dominant compound (3.78 µg/g), accompanied by Benzo(k)fluoranthene (1.61), Benzo(b)fluoranthene (1.49), Indeno(1,2,3-c,d)pyrene (1.08) and lastly Benzo(a)anthracene (1.05) (Fig. 3).

The results above demonstrate that the sedimentation in the areas were taken was similar from which cores "A", "B" and "C" and in fact, the correlations of different specific compounds indicates that between core "A" and "B" it was r = 0.73, between "A" and "C" r = 0.95 and between "B" and "C" r = 0.60 with a meaning of (p = <0.05). It should be noted that the entry of these organic compounds into the sediments has been uni-

Table 3. Levels of total PAH for core "C" from Sontecomapan Lagoon.

Compound	Depth (cm)							
(µg/g dry weight)	1-5	6-10	11-15	16-20	21-25	26-30	Mean	S.D.
Anthracene	1.22	0.37	0.47	0.66	0.24	0.10	0.51	0.39
Fluoranthene	2.16	0.51	0.49	0.16	0.05	<0.01	0.68	0.85
Pyrene	1.58	<0.01	0.12	<0.01	<0.01	<0.01	0.85	1.03
Benzo(a)anthracene	0.75	1.66	1.47	0.61	0.46	1.37	1.05	0.50
Chrysene	3.56	1.63	10.58	<0.01	0.04	3.07	3.78	4.04
Benzo(b)fluoranthene	1.49	<0.01	<0.01	<0.01	<0.01	<0.01	1.49	0
Benzo(k)fluoranthene	2.18	2.31	1.22	0.56	<0.01	1.76	1.61	0.72
Benzo(a)pyrene	0.73	<0.01	<0.01	<0.01	0.37	1.56	0.89	0.61
Indeno(1,2,3-cd)pyrene	1.55	<0.01	<0.01	<0.01	<0.01	0.61	1.08	0.66
Benzo(ghi)perylene	<0.01	<0.01	<0.01	<0.01	<0.01	1.02	1.02	0
[Total PAH]	15.22	6.48	14.35	2.09	1.16	9.49		
Mean	1.69	1.30	2.39	0.52	0.23	1.36		
S.D.	0.87	0.83	4.04	0.23	0.19	0.95		
% O.C.	2.64	2.21	2.63	0.78	1.14	0.78	1.7	0.89

* Naphthalene, Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene = <0.01 µg/g.

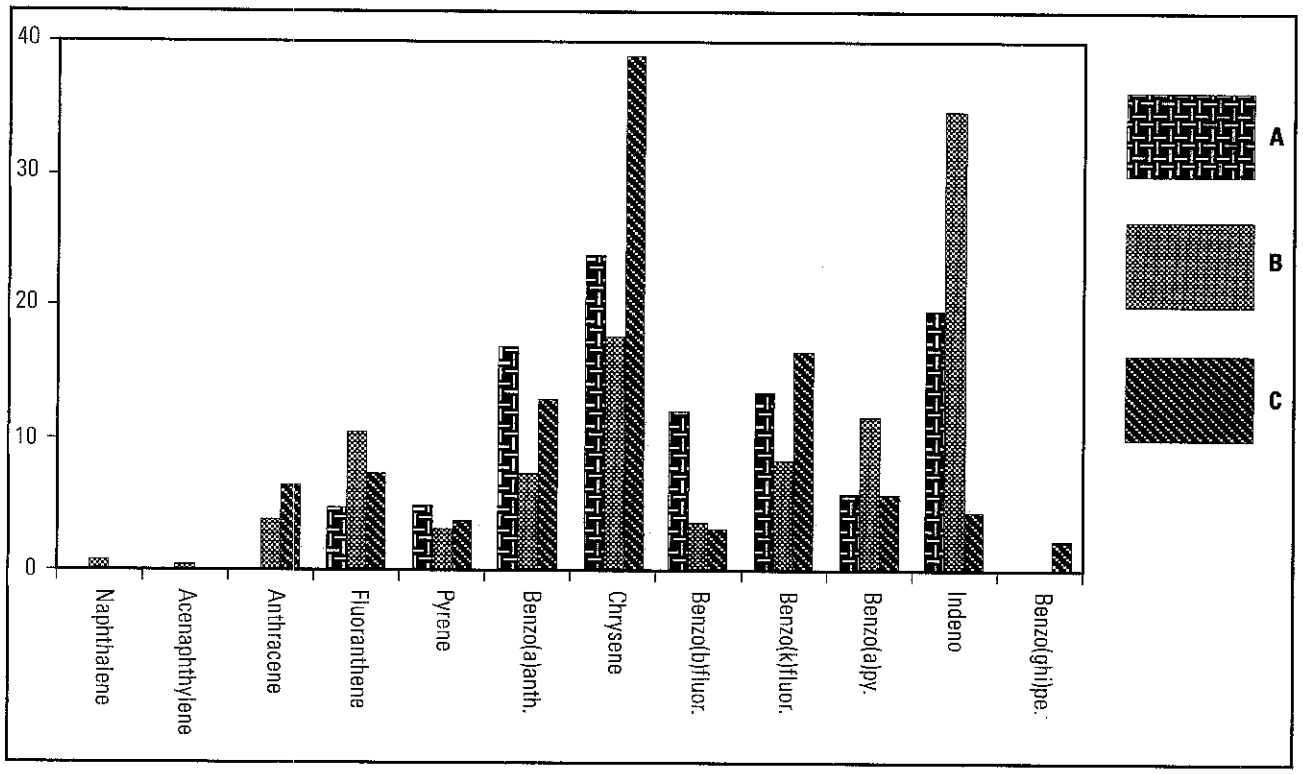

Figure 3. Percentage of PAH in sediment cores from Sontecomapan Coastal Lagoon.

form in composition. Similar to the date reported by Calva and Botello (1999), who carried out a study of the superficial sediments at 10 stations established through the length of the lagoon, a similar behavior was observed with regard to the predominance of aromatic compounds between the sediment core samples and these stations, except that at the surface stations no Indeno(1,2,3-c,d)pyrene was detected.

With regard to the dominance of PAH in the cores the compounds of 4 benzene rings prevail in mean concentrations from 11.30 µg/g in core "B", 8.0 µg/g for core "A", and 6.07 µg/g for core "C" respectively. In addition to in core "B" prevailed compounds conformed by five benzene rings with 7.72 µg/g. This evidence that the central zone is an area of deposition and storage of PAH, due to the fact that this is where high concentrations of compounds with high molecular weights remain. These contaminants are produced by the combustion of fossil hydrocarbons, or by wood on land, subsequently transported and deposited beyond the coast (Steinhauer and Boehm, 1992). The PAH with 2-3 benzene rings are degradable in estuarine and fresh water ecosystems. Only the PAH with high molecular weights, such as Benzo(a)pyrene, remain for long periods, even in ecosystems that are microbiologically adapted to the presence of aromatic hydrocarbons (Riser,1992).

From the results mentioned above, it can be deduced that from the upper stratum of the sediment core samples (up to 5 cm in depth) there was an accumulation of PAH, given that from this stratum there are anoxic conditions that favor their concentration in the sediments, and that PAH of lower molecular weight (of 2 and 3 rings) remain.

PAH eventually undergo partial or complete oxidation, this is the reason why the range of degradation of hydrocarbons is less, by diminishing the potential of the reduction of oxygen. Thus hydrocarbons can remain in anoxic sediments for long periods of time, and remain indefinitely as environmental pollutants (Atlas, 1981 in Riser, 1992). Bernard *et al.*, (1996) assert that anoxic conditions and high levels of organic carbon are preferential for uptake and conservation of PAH. Apart from Naphthalene and Phenanthrene which are relatively rapidly degradable, PAH of high molecular weight are especially resistant and persistent in the environment for a very long time (Pitter and Chudoba, 1990).

On the other hand, the presence of raised values found in sediment at a depth of 5 cm from the bottom of the sediment in cores "A" and "B", and at a depth of 10 cm in core "C"", indicates that an introduction of hydrocarbons into the system brought by the input of the rivers that flow into the lagoon exists because of the spillage of oils, lubricants and gasoline used by the launches, and by pyrolysis of the surrounding vegetation, or even by atmospheric transport. In addition to consider that in the surrounding of Sontecomapan lagoon the

most important activity is the tobacco industry, which uses the mangrove with the aim of building galleries and burn it to dry tobacco leaves (Angeles, 1997). These is important because PAH arise from natural forest and prairie fires most of PAH in the environment are derived during the incomplete combustion of organic matter at high temperatures (Neff, 1979).

As a comparison, in Saguenay Fjord, Canada, the concentration of pollutants rose as a function of the depth in the sediments (Martel *et al.*, 1986). Similarly in three New Jersey rivers, the PAH levels were much greater in the deep layers of the sediments, and were low in the upper layers, indicative of the fact that in these places the input of PAH has diminished considerably (Huntley *et al.*, 1993). This is not the behavior in Sontecomapan Lagoon, on the contrary, there is recent input of PAH to the sediment and due to the dynamic of the system the PAH were tend to accumulate in the lagoon's central zone.

The concentrations in cores "A" and "B" are explained by the fact that, particularly in this area of the lagoon a delta is being formed. Rivers and streams coming from the southern zone flow into this delta favoring particle transport and as a consequence the xenobiotics, subsequent deposit in the sediments. In the central area (core "B"), the accumulation of PAH in the sediments is probably facilitated because of the fact that it is mixing zone, between sea and fresh water, with a salinity between 1 and 26 ups. This can bring about changes in water density, favoring the flocculation of PAH compounds. While flocculated sediments tend to sink and accumulate in the lagoon, dispersed particles tend to remain in suspension and to be carried towards the sea (Davis, 1985). The processes involved in the circulation of estuarine waters are probably the most important factors in the transport and deposition of sediments in estuary-lagoon areas (Nelson, 1972).

As regards core "C", from the northern area, which has predominantly marine influence, it seems the 5 ring benzene compounds were not accumulating in the same way as is happening in the central and southern areas. Here the limiting factor is the type of sediment, which is sandy, as a result of which there is less adsorption of PAH. At the same time, in the part near the mouth of the lagoon, the tides and currents were not favorable towards the accumulation of organic carbon and PAH, such that in protected areas with silty-clay sediment the reverse happens. Nevertheless, when pollutants remain trapped in the sediments, a re-suspension of these can happen, giving as a result the dissolution of hydrocarbons in the column of water (Kennish, 1992).

Organic carbon contents ranged from 0.9% to 5.04% in core "A"; 2% to 6.39% for core "B" and 0.78% to 2.64% for core "C". Higher values corresponded to coastal areas on the Gulf of Mexico receiving fluvial discharges and in this system does due too immoderate tree-feeling cause erosion.

With regard to the correlations between the PAH and the percentage of organic carbon present in the sediment core samples, core "C" demonstrates a good correlation ($r = 0.74$) and the same for the core "B" ($r = 0.6$), nevertheless in core "A" no correlation was established ($r = 0.28$). On the contrary, with regard to the correlations between the depths of the sediments and the PAH concentrations, core "A" presented a positive correlation ($r = 0.58$), whilst the correlations were inverse both in core "B" and core "C", $r = -0.3$ and $r = -0.51$ respectively; all values were significant ($p = <0.05$).

On comparing the general results and the percentage of PAH by benzene rings, it was concluded that the origin of the pollution being generated in Sontecomapan Lagoon is anthropogenic, basically from the pyrolysis of organic materials and fossil combustibles, with a predominance of 4 and 5 benzene ring compounds (Gogou *et al.*, 2000).

Indeno(1,2,3-c,d)pyrene and Benzo(ghi)perylene are typical PAH, generated by the combustion of petroleum Zhang *et al.*, (1993). Is important to point out the presence of Benzo(ghi)perylene, conformed by 6 benzene rings, which was found exclusively in core "C", with a concentration of 1.02 µg/g in the deepest stratum (31-35 cm). According to Guzzela and De Paolis (1994) Benzo(ghi)perylene is present in high concentrations in anaerobic sediments. Contradictory to what Zhang *et al.*, (1993) reports regarding remote sites receives relatively fewer PAH of high molecular weight such as Indeno(1,2,3-c,d)pyrene.

It is clear that some PAH (like Benzo(ghi)perylene) coming from the coast, are penetrating the lagoon system, confirmed by the fact that the greatest average concentrations of dissolved hydrocarbons were detected in the area around the mouth of the lagoon, with 10.17 µg/L, and by the observation of patches of tar all along the external bar of the lagoon. This is as a consequence of the fact that PEMEX (Mexican's Oil Company) has oil-drilling platforms in the Gulf of Mexico, with an intense traffic of ships and oil-tankers circulating in the region.

Botello and Villanueva (1992) refer to the fact that the exploitation of off-shore oil is particularly important in the Gulf of Mexico, where a large number of off-shore drilling platforms operate. Furthermore, at approximately 80 km to the south of Sontecomapan Lagoon, the rivers Coatzacoalcos and Tonalá flow into the sea, and along their banks are the Latin America's largest petrochemical complexes.

An important event to be taken into consideration is the oil-spill from the well Ixtoc I, occurred in 1979 in the south of

Table 4. Range of PAH (µg/g dry weight) in sediment cores from the literature.

Site	Reference	Range
Belt Sea, Germany	Witt & Trost, 1999	0.01 - 19.0
Richardson Bay, USA	Pereire *et al.*, 1999	0.04 - 6.30
St. Pablo Bay, USA	Pereire *et al.*, 1999	0.04 - 1.30
Milwaukee Harbor Estuary, USA	Li *et al.*, 1998	25.0 - 200.0
Lagoons of Caribbean Island of Guadalupe	Bernard *et al.*, 1996	0.1 - 1.66
Lago de Valencia, Venezuela	Bifano *et al.*, 1996	13.0 - 23.40
Green Bay, USA	Zhang *et al.*, 1993	0.30 - 8.50
Upper Estuary of St. Lawrence River, Canada	Huntley *et al.*, 1993	0.44 - 1.05
Elizabeth & Arthur Kill Rivers, USA	Huntley *et al.*, 1993	<0.01 - 16.0
Sontecomapan Coastal Lagoon, Mexico	This study	<0.01 - 41.52

the Gulf of Mexico which was dispersed during 9 months in a northwest direction. Boehm and Fiest (1980) reported concentrations of 30 to 150 µg/g in sediments contaminated by hydrocarbons. Botello and Macko (1982) reported concentrations of 12 to 88 µg/g of total hydrocarbons, in 9 coastal lagoons and 2 rivers along the length of the Gulf of Mexico, attributing the presence of high concentrations of these contaminants to the oil-spill from Ixtoc I. However, the PAH detected in Sontecomapan bear no relation to the Ixtoc I oil-spill, given that the API (1978), Phenanthrene is one of the principle components of crude oil, yet none was detected in any of the strata of the sediment core samples from the system in this study, mainly due to PAH are of pyrolytic origin.

In the area of marine influence in the Sontecomapan system, the PAH found in largest concentrations in the deepest layer were Chrysene, Benzo(k)fluoranthene, Benzo(a)pyrene, Benzo(a)anthracene, Benzo(ghi)perylene and Indeno(1,2,3-c,d)pyrene, which are basically associated with pyrogenic sources. Teal *et al.*, (1992) established at 20 years and in temperate swamp a greater persistence of PAH of medium molecular weight in sediments polluted with petroleum and Corredor *et al.*, (1990) also confirmed this for tropical mangrove swamps.

Based on a study of the mean benzene rings, in the sediment core samples the following were found (Fig. 4):

Core "A": 4 > 6 -> 5 > 3;
Core "B": 4 > 5 > 3 > 2; and
Core "C": 4 > 5 > 3 > 6.

The presence of compounds made up primarily of 4, 5 and 6 benzene rings, proves the hypothesis that the origin of the PAH in the lagoon is anthropogenic, deriving from the pyrolysis of organic matter and fossil fuels, and rules out an association of the PAH with the 1979 Ixtoc I oil-spill. In the same

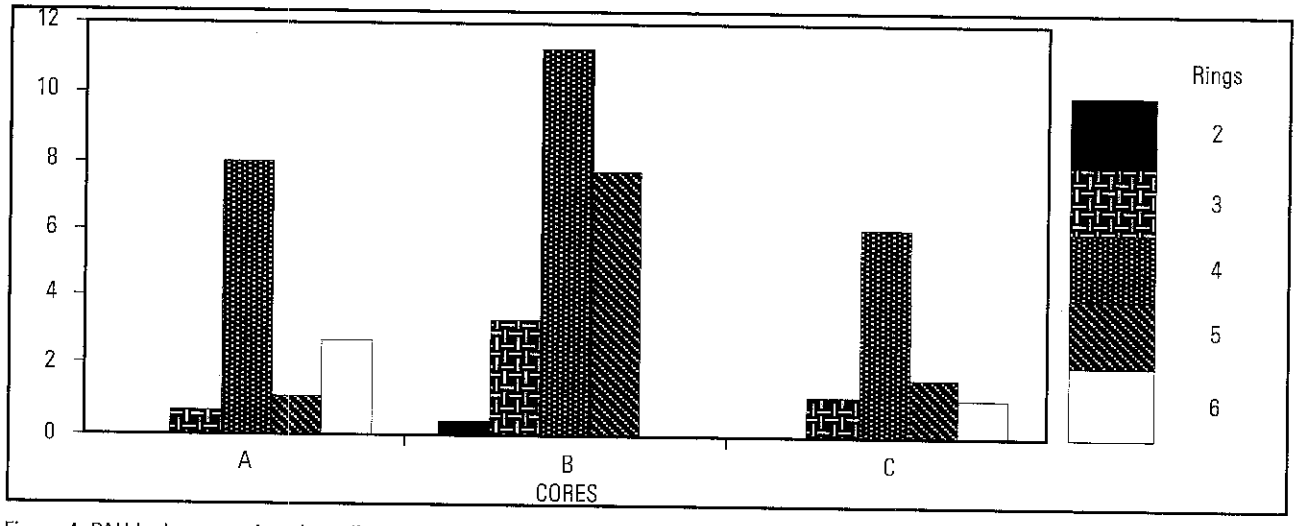

Figure 4. PAH by bencene rings in sediment cores.

form the acquirement of the radio $\Sigma<3/\Sigma>4$ benzene rings allows to appreciate the source of contamination. Hence, a ratio $\Sigma<3/\Sigma>4$ of 0.07 was obtained for core "A"; 0.27 for core "B" and 0.18 for "C", indicating that the contamination by PAH was due to combustion processes.

The previous results can be confirmed by using the Fluoranthene/Pyrene ratios showing the following results: for core "B" Fluo/Pyr = 1.97, for core "C" 0.8 and 0.56 for core "A", on the other hand the marine zone PAH showed pyrolitic origin associated with urban aerosols.

The conclusion is that Sontecomapan lagoon has been receiving additions of PAH for several years, and particularly in recent times. The greatest PAH concentration was found in the central and southeastern areas of the system, without forgetting that the northern zone also showed high concentrations of these pollutants. In addition to sediments associated PAH have undergone distinctly different depositional processes in each area.

The levels of PAH determined in the present work are higher compared to those reported for other systems, except to Milwaukee Harbor Estuary (Table 4), which confirms that Sontecomapan Lagoon is in fact receiving inadvertent additions of PAH.

Finally, according to Long *et al.* (1995) proposal, the presence and levels of PAH determined in this study, can be considered like moderately and highly toxic with ecological risk for the estuarine organisms in these tropical coastal lagoons and even more, their presence jeopardize the reproductive success for oysters and shrimps due to their ecophysiological effects on larvae and juvenile stages of these important species.

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