

HYDROCARBONS IN SURFACE SHELF SEDIMENTS OF THE MEXICAN TROPICAL PACIFIC OCEAN

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ABSTRACT

Hydrocarbons from Mexican eastern tropical Pacific surface shelf sediments were measured in 37 stations to establish baseline concentrations and possible origins and transformations in the region. Aliphatic hydrocarbon concentrations ranged from 1.3 to 61.3 ppm and aromatic hydrocarbons varied from 1.3 to 272.5 ppm. The modal values for both fractions were within the concentration range of pristine environments. The n-alkane chains nC_{31} , nC_{29} , nC_{27} , nC_{18} and nC_{19} predominated among the aliphatic fraction. A few polycyclic aromatic hydrocarbons (PAH) of possible terrestrial origin were present. The relatively high nC_{18} and phytane concentrations, low pristane:phytane ratios, and the presence of PAHs, reflect the anoxic environment of deposition. Accumulation and preservation of organic matter over the shelf is feasible considering the environmental characteristics of the region.

RESUMEN

Las concentraciones de hidrocarburos en sedimentos superficiales de 37 estaciones del Pacífico tropical oriental mexicano fueron medidas para obtener sus niveles base y los posibles orígenes y transformaciones que estos compuestos sufrieron en la región. La concentración de hidrocarburos alifáticos presentó un intervalo de 1.3 a 61.3 ppm y los hidrocarburos aromáticos variaron de 1.3 a 272.5 ppm. Los valores modales de las dos fracciones se encontraron dentro de las concentraciones de ambientes libres de contaminación. Las cadenas de n-alcenos nC_{31} , nC_{29} , nC_{27} , nC_{18} y nC_{19} fueron predominantes en la fracción alifática. En contraste, se hallaron algunos hidrocarburos aromáticos policíclicos (HAP) de posible origen terrestre. Las concentraciones relativamente altas de nC_{18} y fitano, las proporciones bajas de pristano:fitano y la presencia de HAPs, son indicadores de un ambiente de depositación anóxico. La acumulación y la preservación de la materia orgánica en la plataforma continental son factibles si se consideran las características ambientales de la región.

INTRODUCTION

Hydrocarbons sources in sediments include direct inputs from the remains of organisms, in situ biogeochemical modifications of biological precursors, and petroleum-derived compounds deposited by natural phenomena (e.g., seeps), or by anthropogenic activity. A knowledge of the origin of sediment hydrocarbons is thus useful to trace potential petroleum sources, study the fluxes and transformations of biogenic compounds, and monitor anthropogenically-threatened environments.

In shelves with high oxygen demand, such as the Peru and Benguela upwelling regions, the environment of deposition favors organic matter preservation that results from a high rate of primary production in the euphotic zone, low benthic biomass (which inhibits bioturbation), and a predominance of fine-grained sediments (McCaffrey *et al.* 1989). The organic carbon content in sediments of these productive regions is high (up to 20 %) and it has been estimated that ca. 10 % of the organic matter produced by phytoplankton is deposited in the sediments (e.g., Jahnke *et al.* 1983, McCaffrey *et al.* 1989). These zones are thus good environmental settings for studies of organic matter diagenesis.

The eastern tropical Pacific Ocean (ETP) is characterized by an oxygen minimum layer (OML) which drives particular biological processes and chemical reactions including intense denitrification (e.g., Garfield *et al.* 1983), speciation of dissolved metals (Sawlan and Murray 1983), and water-column organic compound diagenesis (Wakeham 1987). The continental shelf of the Mexican ETP between 10°N and 20°N is a pristine region with scarce anthropogenic activity, relatively constant intra-annual environmental conditions, with terrestrial and autochthonous biological inputs, and large inter-annual climatic variations. This region can be used as frame for biological and geochemical studies, both from environmental constancy and global change perspectives. In this study, aliphatic and aromatic biogenic hydrocarbons from Mexican ETP continental shelf surface sediments were quantified and their possible sources and early diagenetic behavior are discussed.

Study Zone

The continental shelf of the Mexican states of Guerrero and Michoacán (between 16°N and 20°N) is steep and narrow with an average width of 12 km. The Sierra Madre del Sur runs parallel to the coastline and in some places falls directly to the sea; thus the rivers of the region have a short extension and areal drainage. Coastal lagoons are common features along the coastline. Some of these are seasonally open (Mandelli and Botello 1976). The continental shelf surface sediments form parallel bands with the coastline, and sands are found at depths < 30 m, while clays occur at 100 m depth (Márquez and Morales 1984). These sediments have reducing conditions and the thickness of its oxic layer (on the order of < 1 to 3 cm) diminishes towards the coast (Lynn and Bonatti 1965, Sawlan and Murray 1983).

Oxygen concentrations at the OML are < 1 ml O₂ L⁻¹ which extend from 25°N to 9°N. Off the Mexican coast the thickness of

the OML is 1200 m with minimum oxygen concentrations between 300 and 500 m depth (Wyrski 1967, Garfield *et al.* 1983). This layer develops off the American coast where oceanic circulation does not penetrate (Wyrski 1967); its low oxygen content reflects a long residence time for the water mass (ca. 10 y, Wyrski 1967) and a high oxygen demand for organic matter oxidation (McCaffrey *et al.* 1989). Off the Mexican shelf Gallegos *et al.* (1984) detected the upper limit of the OML at 35-55 m depth under normal conditions; during an El Niño-Southern Oscillation (ENSO) episode, however, the upper limit was depressed to more than 100 m depth (Gallegos *et al.* 1984, De la Lanza and Galindo 1990).

Associated to this OML are a secondary nitrite maximum along with a particle maximum and high microbial activity layers (Garfield *et al.* 1983). The types of respiration in these waters include a combination of oxygen consumption, nitrate reduction and denitrification (Garfield *et al.* 1983).

MATERIALS AND METHODS

Surface sediment samples were collected on the continental shelf from Guerrero and Michoacán states during cruise DAMA-1 (June 1981) aboard R/V PUMA. A total of 37 stations were sampled between 18°21'N, 103°31'W and 16°15'N, 98°37'W, at depths of 30 to 100 m (Fig. 1), off bays, lagoons and rivers, in clusters of 3-6 stations.

Hydrocarbon analysis was performed following the method used by Botello and Macko (1980). Sediment samples were collected with a van Veen grab; ca. 500 g of the sediment were stored in glass jars and kept frozen until their analysis. In the laboratory, samples were thawed and oven-dried at 60°C for 24 h. The dried sediment was ground to a thin powder and 75 g were Soxhlet-extracted with methanol for 6 h, and then with benzene for 6 h (all reagents used were chromatography

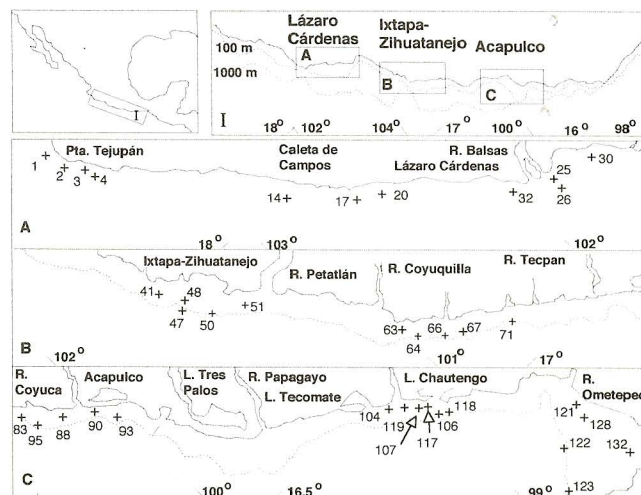


Fig. 1. Study zone and stations where surface sediments samples were collected. L, Lagoon; R, River

grade). The two fractions were mixed and concentrated by rotoevaporation. The mixture was saponified with 100 ml of 20 % KOH/methanol; the non saponified fraction was separated with 100 ml hexane and then with 100 ml benzene. Both fractions were mixed, rotoevaporated and then oven-dried at 60°C. This fraction was weighted analytically and includes hydrocarbons plus the non-saponifiable lipid fraction.

The aliphatic and aromatic hydrocarbons were purified with a 30 cm x 1 cm column chromatography using activated silica gel:alumina (4:1 v/v). The aliphatic fraction was recovered with 25 ml hexane and the aromatics with 25 ml benzene.

Samples were analyzed for individual components in a Hewlett Packard 4840 gas chromatograph (GC) equipped with flame ionization detector and a silica-gel column packed with OV-101. Furnace temperature was programmed from 60 to 260°C, with 6°C min⁻¹ temperature increase; nitrogen was used as carrier gas. The resulting chromatograms were compared with internal standards of n-alkanes, some monounsaturated alkenes, pristane and phytane for the aliphatic fraction; and monocyclic, dicyclic and polycyclic compounds for the aromatic fraction. Standards were analyzed before and after sample analysis to reconfirm the presence of aliphatic and aromatic compounds; recovery percentage for both fractions was over 90 %. Hydrocarbon concentrations are reported in micrograms per gram (ppm) of dry sediment and individual components are given in nanograms per gram (ng g⁻¹) of dry sediment. A one-way analysis of variance (ANOVA) was performed on chromatographic data by standard procedures (Steele and Torrie 1960), assuming that samples were normally-distributed around a sample mean.

RESULTS

Alkane fraction

Hydrocarbon concentrations for the aliphatic fraction are shown in figure 2. Alkane values varied from 1.3 to 61.3 ppm ($\bar{X} = 18.0 \pm 12.0$ ppm), with a modal value of 15 ppm.

Concentration distribution was skewed towards the lower values, since 46 % of the samples had 10-20 ppm while 95 % of the values occurred in the 0-30 ppm range.

Ten samples were selected for characterization, mostly near the coast or coastal lagoons where sediment hydrocarbons have been previously analyzed (Botello and Macko 1980). The concentration of n-alkanes are given in table I, and in figure 3 representative chromatograms for the aliphatic fraction are shown. N-alkanes predominated over a wide range of resolved peaks, and in most samples they were present in a range from nC₁₆ to nC₃₁ with concentrations that varied from undetected to 133 ng g⁻¹, and one exceptional value of 4732 ng g⁻¹. Most samples had nC₃₁ or nC₂₉ as the predominant n-alkane with a secondary maximum at nC₁₈ or nC₁₉. Low values were found between nC₂₀ to nC₂₈. Exceptions to this general pattern include stations 107 (range of nC₁₇ to nC₂₇, and one maximum at nC₁₈), and 20 (with a monotonic increase from nC₂₀ to nC₂₆).

An ANOVA using the n-alkane distribution as treatment and stations as replicates shows no statistical difference between the concentrations of the different n-alkane chains nor between stations (Table II), and suggests that these compounds originated from the same sources (e.g., the bimodal distribution of n-alkanes is representative of the region); alternatively, it may suggest that the environmental conditions over the shelf produce a similar n-alkane distribution.

Among the unidentified resolved peaks, some aliphatic hydrocarbons occurred in most or all samples (e.g., KI= 1863, 2141, 2241, 2434, 2272 and 2922; Fig. 3), however their relative concentrations were lower than those of most n-alkanes. On the other hand, no n-alkenes comparable to our standards were detected. The unresolved complex mixture (UCM: the area below the resolved peaks) was moderately large, and consists of those compounds that did not elute with this technique.

Odd-even relationships

The carbon preference index (CPI), which is a ratio of odd over even n-alkanes, was calculated between nC₁₈ and nC₃₀

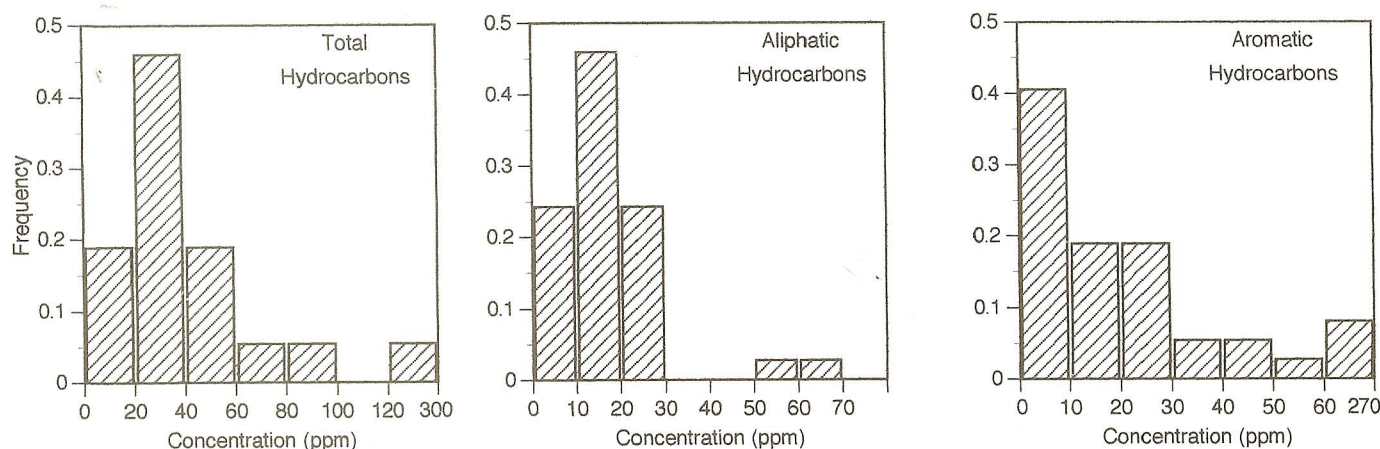


Fig. 2. Concentration histograms for the 3 analyzed hydrocarbons fractions from 37 Mexican Tropical Pacific surface shelf sediments samples. Note scale change in concentration axis for total and aromatic fractions

TABLE I. N-ALKANE, PRISTANE AND PHYTANE CONCENTRATIONS (ng g⁻¹), AND CPI RATIOS IN MEXICAN TROPICAL PACIFIC SURFACE SHELF SEDIMENTS

Chain	Station									
	3	14	17	20	64	66	67	71	107	117
16	0.0	0.0	0.0	19.7	0.0	3.9	24.2	0.0	0.0	4.0
17	8.2	1.2	1.7	27.3	8.1	15.8	46.5	15.7	4.9	12.4
18	48.5	19.3	14.0	68.5	52.2	46.6	68.9	38.6	27.8	50.8
19	50.2	22.3	12.2	35.7	16.7	15.4	44.0	30.7	9.5	30.0
20	26.0	23.8	7.3	26.6	11.9	10.3	31.6	23.9	5.9	26.0
21	29.1	26.6	8.0	21.9	24.5	35.9	51.1	30.1	7.5	29.7
22	25.8	24.1	26.0	32.0	11.1	9.9	24.5	19.1	6.0	26.9
23	30.6	26.2	8.8	50.8	15.1	16.1	26.6	19.7	8.1	36.7
24	23.3	21.5	6.3	91.9	10.2	11.6	18.2	15.5	7.2	29.0
25	38.8	24.1	10.9	105.7	14.9	21.1	28.8	20.3	6.5	32.6
26	26.5	18.0	6.3	133.0	11.8	11.7	16.0	11.7	6.2	28.3
27	73.3	29.8	17.6	125.1	27.5	31.2	33.3	23.3	5.2	40.7
28	30.0	15.0	0.0	115.3	13.9	17.5	15.1	13.5	0.0	25.0
29	4723.5	72.2	55.1	94.1	79.0	120.9	91.8	50.7	0.0	80.4
30	30.5	0.0	0.0	76.3	15.5	14.5	17.3	6.3	0.0	14.2
31	238.6	64.2	50.8	56.6	111.8	110.9	104.4	56.9	0.0	60.6
pr ^a	3.5	0.0	0.0	14.7	3.0	8.0	13.9	3.0	1.6	3.7
ph ^b	10.7	2.6	0.7	16.1	4.0	8.3	15.8	10.0	4.2	10.7
CPI ^c	29.3	1.8	3.6	0.9	2.0	2.7	1.9	1.7	1.1	1.5

^apristane, ^bphytane, ^cCPI₁₈₋₃₀ = 0.5(($\Sigma_{\text{odd}}C_{19-29}/\Sigma_{\text{even}}C_{20-30}$) + ($\Sigma_{\text{odd}}C_{19-29}/\Sigma_{\text{even}}C_{18-28}$))

(Table I). CPI oscillated between 0.9 (station 20) and 29.3 (station 3). In most samples, the low CPI (≈ 1.0) reflects the almost constant concentrations between consecutive n-alkanes in the range nC₂₀ to nC₂₆, and the predominance of odd chains in the high molecular weight range (\geq nC₂₇). The high CPI for station 3 is due mostly to nC₂₉ which appeared in the ppm range, and in lesser degree to nC₃₁.

Odd-even preference (OEP) values give the ratio of odd over even n-alkanes between 5 consecutive molecules (Scalan and Smith 1970). This ratio is useful because it shows trends along the whole n-alkane range, in contrast to the CPI which averages all the molecules. In general the samples had OEP ≤ 1 in the low-weight range (nC₁₇-nC₁₉), similar values between nC₂₀ and nC₂₆, and ratios ≥ 2 for the chains \geq nC₂₇, especially for stations 3, 14 and 17 (Fig. 4).

An ANOVA performed on OEP ratios (Table II) shows that, in contrast to the non statistical differences found for the n-alkane distribution, OEP ratios varied significantly ($p < 0.01$) between chain-lengths but not between stations. This difference

can be explained by the relative importance of extremely high or low values, since any alkane appears in 5 consecutive OEP ratios (e.g., nC₂₉ is averaged from nC₂₇ to nC₃₁) and its relative concentration is weighted throughout this range.

Isoprenoids

The acyclic isoprenoids pristane and phytane were resolved in the chromatograms (Fig. 3). Pristane concentrations varied from undetected to 14.7 ng g⁻¹ and appeared in 80 % of the chromatograms; phytane occurred in all the samples and varied from 1.0 to 16.1 ng g⁻¹ (Table I). The correlation between both isoprenes was 0.86, and the pristane:phytane ratio ranged between 0.3 and 1.0.

Aromatic hydrocarbons

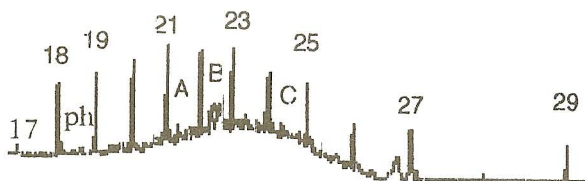
Aromatic hydrocarbon concentrations varied from 1.3 to 272.5 ppm, ($\bar{X} = 27.5 \pm 46.2$ ppm); 45 % of the values fell between 0 and 10 ppm while 78 % ranged between 0 and 30 ppm, again showing a skewness towards the lower

TABLE II. ANALYSIS OF VARIANCE FOR N-ALKANE CONCENTRATIONS AND OEP RATIOS

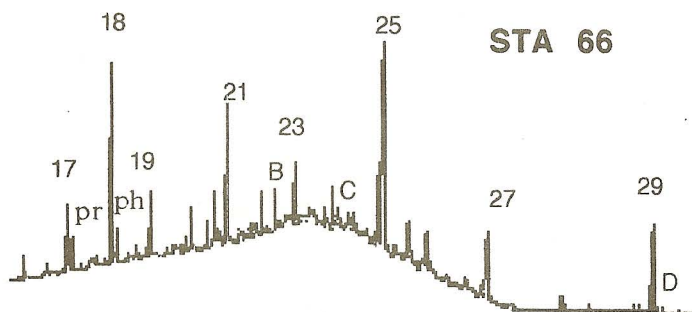
Source of variation	D.F. ^a	M.S. ^b	F	p ^c
n-alkanes ^d	15	165,126.83	1.17	0.303
stations	9	156,828.30	1.11	0.360
error	135	141,116.30		
OEP ^e	11	171.42	2.83	0.003*
stations	9	95.99	1.59	0.129
error	99	60.54		

^a Degrees of freedom, ^b Mean square, ^c Probability of error in rejecting null hypothesis, ^d N-alkanes in the range nC₁₆-nC₃₁, ^e OEP ratios in the range nC₁₇-nC₂₈ (= C_i), where: OEP = ((C_{i-2}+6C_i+C_{i+2})/(4C_{i-1}+4C_{i+1}))⁻¹⁽ⁱ⁻¹⁾. * Highly significant ($p < 0.01$)

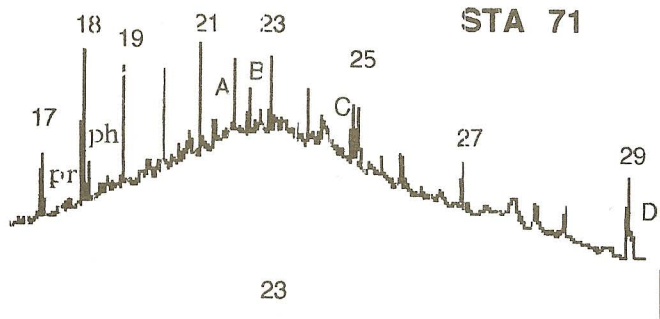
STA 14



STA 66



STA 71



STA 117

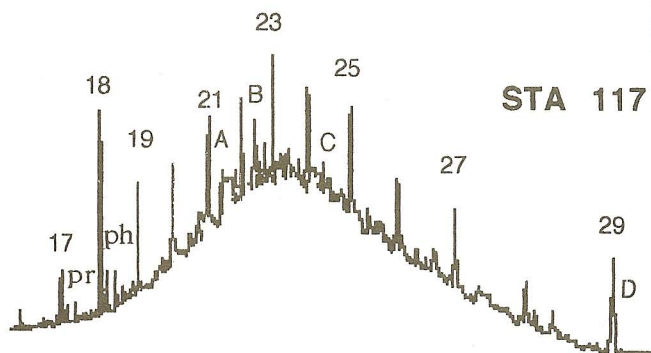


Fig. 3. Chromatograms for Mexican Tropical Pacific surface sediment aliphatic hydrocarbons. Numbers above peaks denote n-alkane carbon chains. pr: pristane, ph: phytane, A: KI = 2141, B: KI = 2241, C: KI = 2434, D: KI = 2922

concentration range (Fig. 2).

The chromatograms for this fraction (Fig. 5) show a few aromatics grouped together in a narrow range of retention times between pyrene ($R_t = 25.4$) and nonadecil ($R_t = 41.2$) standards. No low-molecular weight aromatics were detected in the chromatograms. All but one sample had compounds with similar retention times, with relative maxima at $R_t = 38.1$ (ca. 50 % of the total area of the resolved peaks). The UCM was relatively low and probably reflects the small variety of compounds present in this fraction.

DISCUSSION

N-alkanes

Total (aliphatic plus aromatic) hydrocarbon concentrations in the study zone fall within the interval of 20-200 ppm for pristine shelf and ocean basin surface sediments (Tissot and Welte 1978). These values are much lower than those for petroleum-polluted sediments which may vary between 100 and 12,000 ppm (Tissot and Welte 1978). In general, coastal zones with terrestrial input have relatively high hydrocarbon concentrations, in contrast to pelagic regions where inputs are mainly derived from marine organisms and where an oxygenated environment favors organic matter degradation (Tissot and Welte 1978).

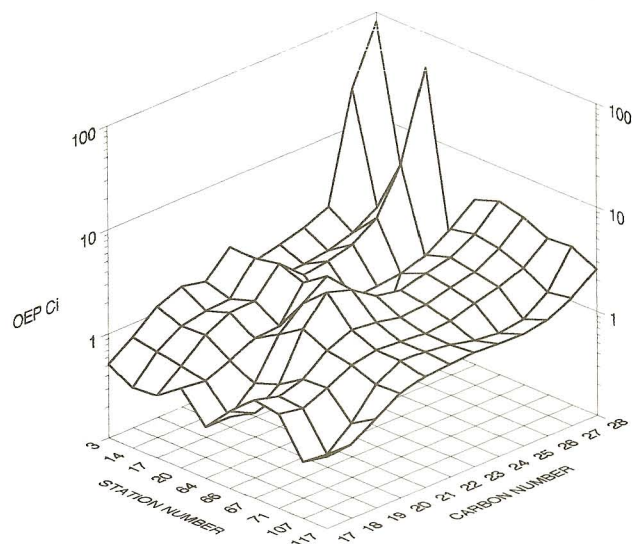


Fig. 4. Average OEP ratios in the range C_{17} to C_{28} for each station. Note log scale on vertical axis. C_i : n-alkane chain of i carbon atoms

Measurements of n-alkanes from 3 ETP coastal lagoons suggest that the relatively high concentrations at Mitla Lagoon (2.6-37.8 ppm) reflect its isolation and eutrophication state (Botello and Macko 1980). In contrast, Chautengo (1.8-4.1 ppm) and Superior-Inferior Lagoon (with 1.0-1.8 ppm) interchange freely with the adjacent shelf and are highly dynamic. Although their n-alkane values are ± 10 times lower than those from the shelf (modal values of 1.5 and 15 ppm, respectively), similar concentrations were found at the mouths and shelf; it thus seems that negligible amounts of sediment hydrocarbons are exported from the ETP lagoons to the adjacent continental shelf.

The bimodal n-alkane distribution in our samples consisted of a primary maximum centered between nC_{27} and nC_{31} and a secondary peak at nC_{18} or nC_{19} . This bimodal distribution is typical of continental shelves of all latitudes including the Arctic (Shaw *et al.* 1979), temperate (Keizer *et al.* 1978, Simoneit 1977),

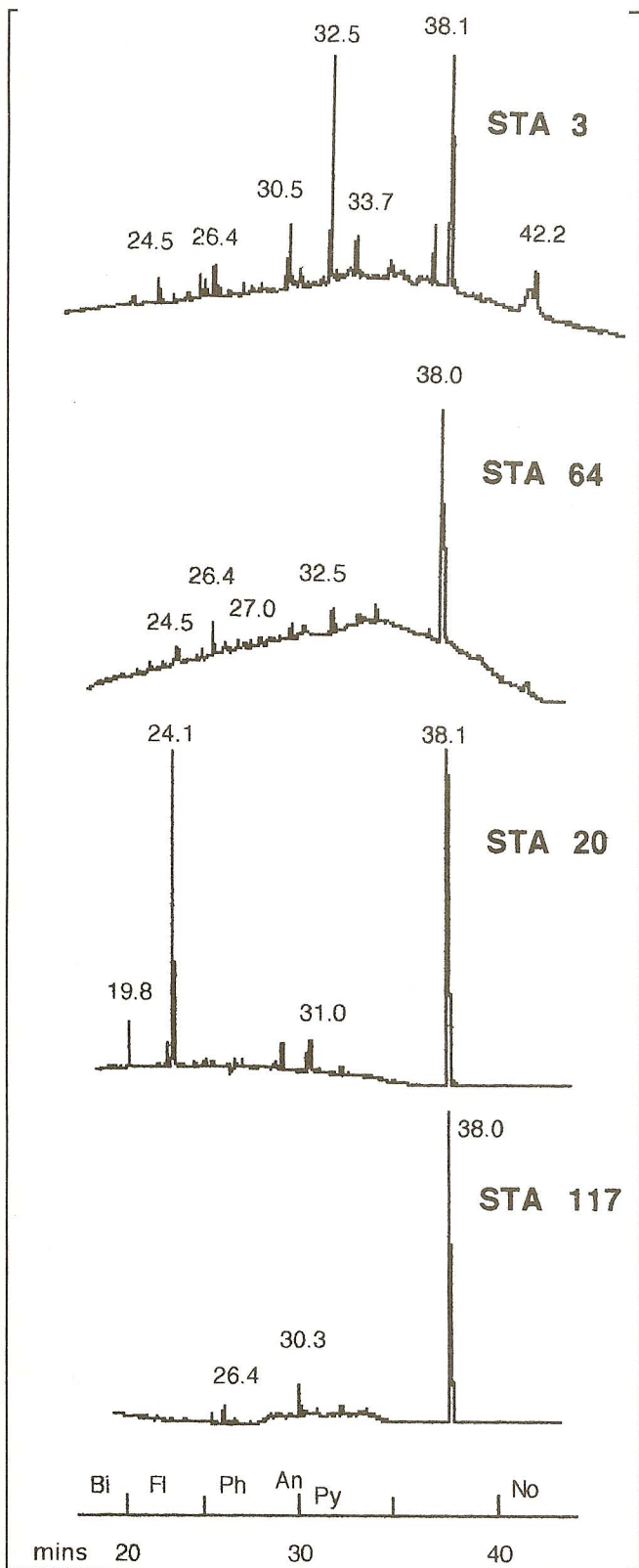


Fig. 5. Chromatograms for Mexican Tropical Pacific surface sediment aromatic hydrocarbons. Numbers above peaks denote retention times (Rt). Scale bars show Rt of standard compounds. Bi: biphenyl (Rt = 16.9), Fl: fluorene (21.3), Ph: phenanthrene (25.4), An: androstane (29.9), Py: pyrene (31.4), No: nonadecyl (41.2)

and tropical regions (Gearing *et al.* 1976, Volkman *et al.* 1983). This distribution results from a simultaneous terrestrial and marine organic matter input (Simoneit 1977, Brassell *et al.* 1978). The higher concentrations of long chains relative to short ones reflect the predominance of terrestrial n-alkane contribution (Tissot and Welte 1978, Volkman *et al.* 1983). Although most individual alkanes occurred in the ng g⁻¹ range, the ppm value for nC₂₉ at station 3 is similar to reported shelf concentrations near the coast (e.g., Farrington *et al.* 1977) where high contribution from terrestrial plant hydrocarbons may occur.

In contrast to its higher homologues, the origin of short chain n-alkanes (\leq nC₂₁) in the study zone is uncertain. It has been proposed that reducing environments promote fatty acid and alcohol hydrogenation and dehydration, while oxidizing conditions favor decarboxilation of fatty acids (Welte and Waples 1973). High values of nC₁₈ have been measured in reducing recent and ancient sediments. In NE Pacific sediments, the predominance of nC₁₆ and nC₁₈ alkanes may result from the reduction of n-fatty acids (Simoneit 1977); likewise, the presence of these hydrocarbons in Persian Gulf sediments may result from fatty acid and alcohol hydrogenation in reducing microenvironments (Welte and Ebhardt 1968).

Wakeham and Canuel (1988) found that saturated and monounsaturated chains of 18 and 16 carbons were predominant in alcohols and fatty acids from waxes and triacylglycerols of suspended and particulate matter in the ETP, and suggested a zooplanktonic origin for them. It is thus possible that nC₁₈ in ETP shelf sediments is produced by reduction of deposited stearic acid (e.g., from zooplankton) due to the prevalent reducing conditions in this region. Alternatively, the nC₁₈ and nC₁₉ hydrocarbons can result from certain bacteria. Han and Calvin (1969) found high concentrations of nC₁₈ and/or nC₁₉ (among other alkanes) in aerobic and anaerobic heterotrophic bacteria, in photosynthetic bacteria and in yeasts. The fatty acid cis-vaccenic acid (C_{18:1}ω₇), along with C₁₅ and C₁₇ isomers have also been attributed to bacteria (Volkman *et al.* 1980). Bacterial organic compound contribution in sediments from anoxic regions can be considerable: the sulfur-oxidizing bacterium *Thioploca*, for example, contributes with up to 80 % of the biomass in Peru OML sediments (McCaffrey *et al.* 1989).

N-alkanes < nC₁₆ were absent in all samples. These hydrocarbons are common to phytoplankton (Blumer *et al.* 1971) and their absence may reflect a low contribution from these organisms to the sediments or preferential metabolism by zooplankton or bacteria (Brassell *et al.* 1978).

Pristane is relatively common in recent sediments: Keizer *et al.* (1978) found an average of 6 ng g⁻¹ pristane in Nova Scotia shelf sediments, and Aizenshtat *et al.* (1973) detected up to 665 ng g⁻¹ pristane in deep Gulf of Mexico sediments. Zooplankton and certain bacteria are known to contain measurable concentrations of pristane (Han and Calvin 1969, Dydik *et al.* 1978), and these can be likely sources for this compound in the study zone. Phytane, on the contrary, is used as petroleum indicator since it is not detected in organisms; however, it has been reported to occur in highly reducing environments probably

as a breakdown product in chlorophyll's phytol reduction (Simoneit 1977, Welte and Waples 1973, Dydik *et al.* 1978). In ETP shelf sediments the relatively high concentrations of phytane can result as a breakdown product from phytol under anoxic conditions; phytane was significantly correlated with nC_{18} ($r = 0.89$) suggesting a common diagenetic origin for both compounds.

Aromatic hydrocarbons

Aromatic hydrocarbon concentrations were highly variable (1.3–272.5 ppm); values above 50 ppm, however fall within the range of non-polluted sediments with terrestrial influence. Aromatic hydrocarbons at Gulf of Tehuantepec sediments (south of the study zone) are similar to our aromatic hydrocarbon data with a range from 1.5 to 67.7 ppm (IMP 1984). Aromatic values for both ETP continental shelf sites are lower than those for polluted regions (e.g., > 1000 ppm, Tissot and Welte 1978).

Although identification of hydrocarbons from the aromatic fraction was not possible with GC alone, the position of the largest resolved peaks (Fig. 5) suggests that these were polycyclic aromatic hydrocarbons (PAHs). These peaks eluted between the 9,10-dihydrofluoranthene and nonadecil. Chromatograms for riverine and oceanic sediments and for kerogen combustion (Laflamme and Hites 1978, Tissier and Salot 1983) show that within this range anthracene, methylphenanthrene and fluorene occur. Phenanthrene is a tricyclic aromatic similar in structure to abietic acid from resins; and dihydroabietic acid, 1-methyl phenanthrene and retene are terrigenous indicators (Simoneit 1977).

ETP shelf vs. lagoon alkanes

Shelf and coastal lagoon hydrocarbon parameters for Mexican ETP are compared in table III. The ratios for nC_{17} : nC_{18} and pristane:phytane in shelf sediments are mostly < 1.0. In ETP lagoons these ratios are higher. OEP values are also higher as a result of odd chain predominance over even chains.

Most Mexican ETP lagoons are shallow and are seasonally or permanently open and their hydrodynamic conditions prevent totally anoxic situations. Even Mitla Lagoon, which is permanently closed, is oxygenated by the action of the wind and anoxic conditions are only found at its deeper parts (Mandelli and Botello 1976). In contrast, the adjacent shelf sediments are quasi-permanently anoxic as a result of the presence of the OML (Wyrski 1967, Gallegos *et al.* 1984), although this layer deepens and recedes offshore under ENSO conditions (De la Lanza and Galindo 1990).

The coastal lagoons show maxima at nC_{17} , nC_{19} and nC_{18} among the short chain n-alkanes, and nC_{29} and nC_{31} in the long-chain fraction (Botello and Macko 1980), which is similar to the adjacent shelf distribution. Both systems also have similar pristane: nC_{17} and phytane: nC_{18} ratios (Table III). The compared n-alkane ratios and concentrations suggest that both environments receive hydrocarbon inputs from similar sources. However the particular environment of deposition for each system leads to different organic compound degradation pathways.

TABLE III. HYDROCARBON PARAMETERS FOR MEXICAN TROPICAL PACIFIC SHELF AND COASTAL LAGOON SURFACE SEDIMENTS

Parameter	Shelf ^a	Lagoons ^b
n-alkane concentration	1.3-61.3 (15) ^c	1.0-37.8 (1.5)
n-alkane range	nC_{16} - nC_{31}	nC_{14} - nC_{33}
Long-chain maxima	nC_{31} , nC_{29}	nC_{31} , nC_{29} , nC_{33}
Short-chain maxima	nC_{18} , nC_{19}	nC_{17} , nC_{18} , nC_{19}
OEP	0.9-18.1 (1.5) ^d	1.5-5.0 (1.5, 4.5)
Pristane:phytane	0-4.1 (0.5)	3.9-7.9 (7.5)
Pristane: nC_{17}	0-0.54 (0.25)	0.17-1.48 (0.25)
Phytane: nC_{18}	0.05-0.26 (0.25)	0.02-0.82 (0.35)
nC_{17} : nC_{18}	0-7.5 (0.25)	0.6-7.7 (5.5)

^a Average of 10 samples

^b Average of 11 samples from 3 lagoons (from Botello and Macko 1980)

^c Modal values in parentheses

^d Average odd-even preference in the range nC_{17} to nC_{28}

Hydrocarbon diagenesis in ETP shelf sediments

Organic matter accumulation in sediments and its transformation by diagenetic reactions depend on the environment of deposition, the quantity and origin of organic matter, and the environment of accumulation (Aizenshtat *et al.* 1973, Tissot and Welte 1978). Accumulation is highest in shallow, productive, anoxic and low-energy environments.

The environment of deposition in the ETP is anaerobic both in the water column and sediments, and is thus favorable for organic matter preservation. The presence of low oxygen concentrations in the water column favors denitrification and inefficient organic matter degradation (Garfield *et al.* 1983). Likewise, ETP shelf sediments are predominantly anoxic and the depth of its oxic zone decreases as the coast is approached (Lynn and Bonatti 1965, Jahnke *et al.* 1982). These anaerobic sediments favor reduction reactions of the short chain n-alkane and preservation of longer ones.

Two potential sources of n-alkanes over the shelf are water column primary production and terrestrial vegetation input. Primary productivity in the region is on the order of 75 g C m⁻² y⁻¹ and increases nearshore (Owen and Zeitzschel 1970, King 1986). In turn, terrestrial influence should also be important since the steep Sierra Madre falls directly into the narrow shelf.

The low pristane:phytane ratios (≤ 1) likely result from the reduction of the chlorophyll's phytol chain to phytane (Dydik *et al.* 1978). This ratio is lowest in the southernmost stations, where OML conditions are intensified (Wyrski 1967), and upwelling from the adjacent Gulf of Tehuantepec enhances high productivity rates (Garfield *et al.* 1983). The ratio increases at ETP coastal lagoons (Botello and Macko 1980) since the environment of accumulation is less reducing. The significant correlation between phytane and nC_{18} in the study zone can be indicative of a single source for these two molecules; for example certain bacteria have high phytane and nC_{18} concentrations (Han and Calvin 1969). Alternatively

this ratio can indicate similar diagenetic modifications for the phytol chain and n-fatty acids. The lack of typical phytoplankton n-alkanes (except for nC_{16}) at all stations may reflect intense bacterial activity on the more degradable short chain hydrocarbons (Brassell *et al.* 1978).

In summary baseline concentrations of aliphatics were ≤ 60 ppm and aromatics were < 275 ppm in ETP surface shelf sediments. Qualitatively the data suggest that the widespread OML of the region favors organic matter preservation and reductive reactions in the sediments. Hydrocarbon inputs to this narrow shelf consist of terrestrial and benthic or degraded planktonic sources. The region is further characterized by the predominance of even numbered short chain ($\leq nC_{21}$) n-alkanes, and pristane:phytane ratios ≤ 1 which reflect the region's reducing environment of deposition.

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