Bull. Environ. Contam. Toxicol. (2001) 67:889–897

DOI: 10.1007/s00128-001-0205-9

Bulletin of Environmental Contamination and Toxicology

Polycyclic Aromatic Hydrocarbons in Sediments from Coastal Lagoons of Veracruz State, Gulf of Mexico

A. V. Botello,[1] L. G. Calva B,[2] G. Ponce V[1]

[1] Institute for Marine and Limnological Sciences, National Autonomous University of Mexico, Marine Pollution Laboratory, Post Office Box 70305, Mexico, D.F. C.P. 04510, Mexico
[2] Coastal Ecosystems Laboratory, Department of Hydrobiology AS-224, Metropolitan Autonomous University, Campus Iztapalapa, Mexico, D.F. C.P. 09340, Mexico

Received: 19 December 2000/Accepted: 24 September 2001

At present, marine pollution due to petroleum and its derivatives in Mexican coasts is one of the greatest ecological challenges, since Mexico is among the most important producers of crude oil, exporting to the USA, Canada, Latin America, Europe, and Asia about 2.8 millions of barrels per day.

Polycyclic aromatic hydrocarbons (PAHs) are among the by products of the oil industry that represent a potential risk to public health and other forms of life (Martel et al. 1986). Some of them, such as benzo(a)pyrene, are powerful carcinogens, associated to the ethology of some human cancers (Arcaro et al. 1999). Nowadays there is a great deal of literature about PAHs levels in coastal systems around the world (e.g. Botello et al. 1993; Valette, 1993); however, most of these studies have been carried out in areas that receive direct influence of industrial and municipal discharges, but very few work is devoted to tropical o subtropical systems with direct influence of oil industry.

It is important to mention that PAHs are associated with fine particles in the coastal waters, thus; their range, distribution pattern, and extension of their accumulation in tropical estuarine systems are extremely variable (Olsen et al. 1993). Recent studies indicate that PAHs are not only detected in urban centers, but also in rural and remote areas due to atmospheric transport (Valette, 1993).

In the coastal systems, during water mixing, particles of the contaminated sediments remain suspended in the water column, affecting bivalve organisms that feed through filtration (Eertman, et al. 1995), hence, the relevance of determining PAHs levels in sediments from coastal lagoons, since these sites are extremely important for the development and growth of organisms constituent of commercial fisheries; among them are oysters, mussels, and detritivorous crustaceans such as the shrimps and lobster.

This study was aimed to evaluate the concentrations, characterization and distribution of PAHs in sediment samples, and to search for a correlation between PAHs and the percentage of organic carbon and with the type of sediments from the tropical lagoons considered in this study.

Correspondence to: A. V. Botello

MATERIALS AND METHODS

The area considered (Fig1) includes the Salada, El Llano, La Mancha, and Mandinga lagoons, and is located in the state of Veracruz, at Central Coastal Plains of southern Gulf of Mexico. It is limited by the outer geographic coordinates of 18°30, 19°42' latitude, and 95°00', 96°27' longitude.

Surface sediments were collected between 1997 and 1999 from 20 sampling sites by means of a small stainless steel van Veen grab sampler (6 L) and 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 grade chromatographic. Samples were defrosted and dried during 48 h at 45°C in the laboratory and sifted through a 0.25-mm mesh.

Samples were collected during different periods of time: El Llano, Salada, and La Mancha lagoons during October (1997), February, May, and August(1998); and Mandinga lagoon in December (1998), February and May (1999).

Analytical procedures for extraction and purification of PAHs were performed following the CARIPOL/IOCARIBE/UNESCO (Caribbean Pollution Program. Intergovernmental Oceanographic Commission for Caribbean of UNESCO,1986) method, according to UNEP (United Nations Environment Programe,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 aromatic fractions were purified by adsorption chromatography using glass columns of 2.5 internal diameter and 25cm of length, packed with alumina and silica gel (5%) deactivated with water. Aliphatic hydrocarbons were eluted in the first fraction with 12 ml *n*-hexane more 12 ml *n*-hexane, and aromatics in the second 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).

Quantification and identification of the aromatic fraction was made by means of a Hewlett Pack-ard 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 PAHs (Chemical Service PPH-10M) was used as external reference . Detection limit for individual aromatic compounds was 0.01 µg/g and recovery yields were up to 95%.

Sediment composition (sand, silt, and clay content) was measured by wet sieving and pipette analysis (Folk, 1974). The percentage of organic carbon was

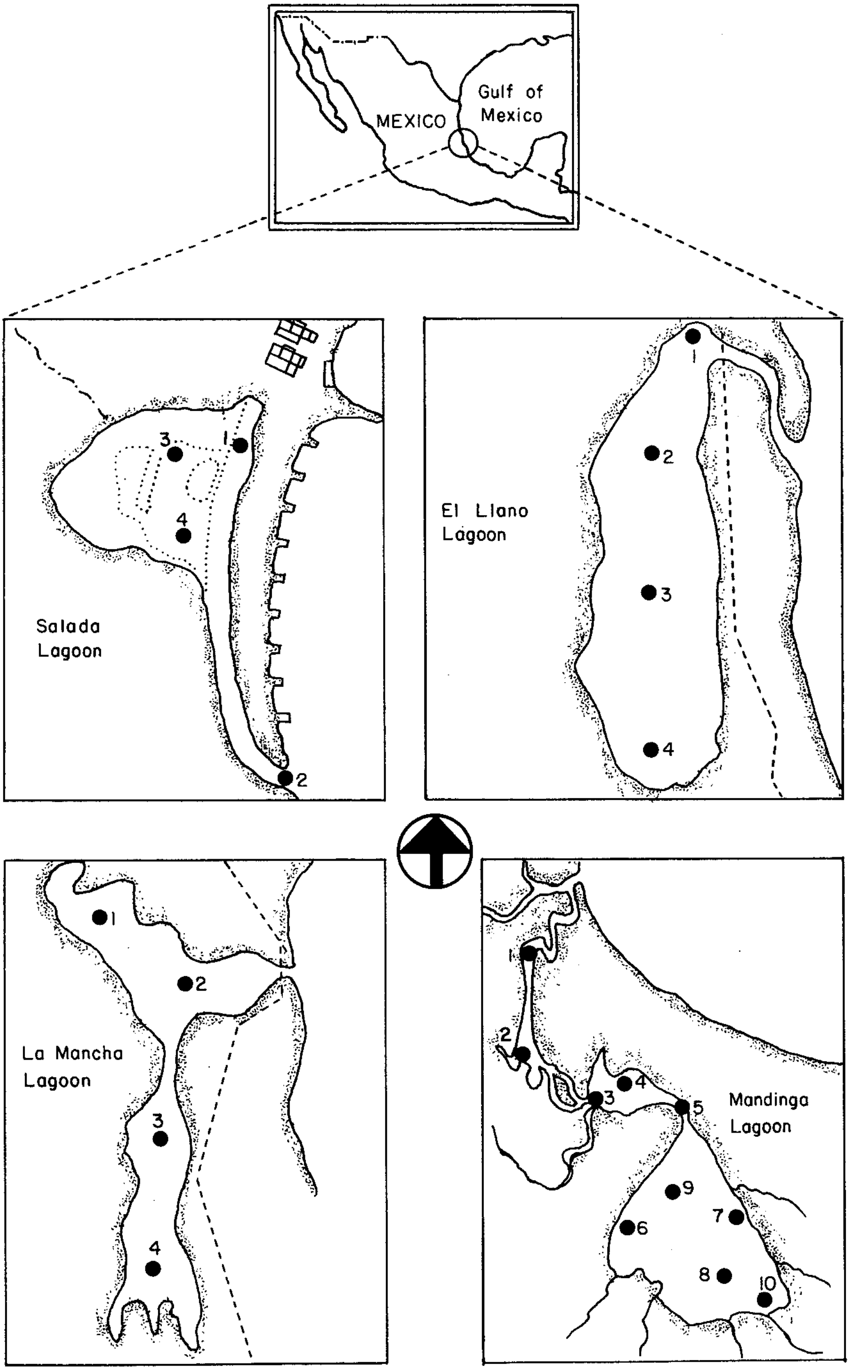

Figure I. Location of sampling sites.

determined by the method of Gaudette et al. (1974), in which exothermic heating and oxidation with K_2CrO_7 and concentrated H_2SO_4 was followed by titration of the excess dichromate with 0.5 N $Fe(NH_4)2(SO_4).6H_2O$.

To test for significant differences between group means, Analysis of Variance (F) was used when data were homoscedastic (Levene's test 95%) and Kruskal-Wallis test (H) when heteroscedasticity was detected even after log transformation. To describe the possible association between variables, a non-parametric correlation of Sperman (Zar, 1996) was determined.

RESULTS AND DISCUSSION

Table 1 shows the mean levels and relative abundance by groups (2-3 and 4-5 rings) of PAHs, as well as the percentage of organic carbon and the type of sediments obtained from all sampling sites in different climatic seasons (dry and rainy).

Salada Lagoon system neighbors with the Nuclear Power Plant of Laguna Verde (NPLV), sediments are typically sandy with an organic carbon content from 0.8 to 3.4%. The highest PAHs concentration was obtained in August 1998 (9.48 µg/g). At the other sampling periods, average levels ranged from 0.15 µg/g in October 1997 to 2.01 µg/g in May 1998.

Regarding individual distribution of PAHs, stations 2 and 4 presented the highest mean concentrations with 7.3 and 11.6 µg/g, respectively, whereas station 3 yielded the lowest concentration (1.1 µg/g). The mean Total PAHs in this system was 3.35µg/g.

Specific analysis of total PAHs revealed the following concentrations in decreasing order: benzo(a)anthracene > benzo(b)fluoranthene > pyrene > benzo(k)fluoranthene > fluoranthene.

Since this lagoon is the closest one to the Nuclear Power Plant, it was also performed gas chromatography analyses of the fuels used for its operation, i.e., diesel and lubricant.

Results revealed that lubricant presents 11 of the 15 PAHs contained in the mixture of reference standards, predominating benzo(k)fluoranthene, acenaphthene, chrysene, and benzo(a)anthracene, with a total sum of approximately 177 µg/g. Diesel revealed 7 PAHs, predominating chrysene and benzo(a)anthracene with a total sum of approximately 62 µg/g. Therefore, the presence and distribution of PAHs in Salada Lagoon seems to be produced by direct chronic inflows from Nuclear Power Plant, independently that their sediments are predominantly conformed by sands (68.7 – 90.2%).

Table 1. Mean Levels of PAHs, percentage of organic carbon and type of sediments in Salada, Llano, Mancha and Mandinga Lagoons (μg/g).

	Salada				**Llano**				**Mancha**				**Mandinga**							
	Stations				Stations				Stations				Stations							
	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	5	6	7	8
1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.1	0.1	0.0	0.1	ND	0.3	ND	0.2
3	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.1	0.5	0.1	0.2	ND	0.2	0.2	0.1
4	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.1	ND	ND	ND	ND	ND	ND	ND
5	ND	ND	ND	0.1	ND	0.1	0.1	ND	ND	0.3	0.1	0.1	0.1	0.2	0.1	0.1	ND	0.7	ND	0.1
6	0.3	0.3	ND	0.4	0.3	0.1	0.1	ND	0.2	0.2	0.1	0.2	0.2	0.2	0.1	0.4	0.2	0.3	0.2	0.1
7	0.2	0.4	ND	0.5	0.2	0.4	0.1	ND	0.3	0.3	0.3	0.8	0.1	0.1	0.2	0.2	0.2	0.8	0.6	0.4
8	1.7	0.8	0.1	0.9	3.2	1.2	0.1	0.3	0.6	0.6	1.4	1.9	ND	0.1	0.2	0.2	0.1	0.1	0.6	0.1
9	2.7	3.0	0.1	6.1	3.9	2.2	0.1	0.2	1.0	0.7	2.2	2.9	0.2	0.3	0.2	0.5	0.3	1.4	0.4	0.4
10	ND	ND	0.1	ND	1.1	ND	0.1	ND	ND	0.7	3.0	ND	0.6	0.1	0.9	1.1	0.6	9.0	0.2	0.0
11	0.7	1.24	0.3	1.7	1.6	0.9	0.1	0.2	0.5	0.4	0.7	0.8	0.3	0.6	0.4	0.8	1.0	2.0	0.4	0.9
12	0.7	0.87	0.5	0.9	1.3	0.7	ND	0.2	0.4	0.3	1.0	0.6	0.1	0.1	0.1	0.6	0.1	0.3	0.3	0.2
13	0.4	0.61	0.1	0.9	0.8	0.5	ND	ND	ND	0.4	0.5	0.5	0.3	0.7	0.4	0.7	0.7	1.5	0.7	0.9
14	ND	ND	ND	ND	ND	ND	ND	ND	0.9	ND	1.7	ND	0.1	0.6	0.3	0.5	0.6	0.9	0.6	0.5
15	ND	ND	ND	ND	ND	ND	ND	ND	0.2	ND	0.4	ND	0.1	0.3	0.2	0.2	0.1	0.6	0.3	0.2
16	6.6	7.3	1.1	11.6	12.4	6.1	0.6	0.9	4.0	3.8	11.3	7.8	2.2	3.9	3.2	5.4	3.9	18.2	4.5	4.1
17	0.8	3.2	0.4	0.1	6.0	2.0	0.4	0.5	2.5	2.5	7.5	5.1	0.8	2.4	1.6	2.8	2.1	12.3	2.9	2.7
18	0.9	2.1	0.5	0.2	7.9	3.9	0.2	0.6	2.0	1.7	6.6	6.8	1.3	2.1	1.1	1.0	2.6	10.7	2.4	2.1
19	4.2	4.4	ND	4	2.0	1.8	21.3	ND	5.0	12.6	1.5	4.3	24.0	27.8	9.8	14.1	5.6	8.2	10.0	13.2
20	95.8	95.6	100	95.9	98.0	98.2	78.7	100	95.0	87.4	98.5	95.7	76.0	72.2	90.2	85.9	94.4	91.8	90.0	86.8
21	2.0	1.6	1.6	1.5	1.9	1.9	1.6	1.4	3.7	3.5	3.8	4.7	1.6	0.9	0.8	1.6	1.5	1.5	1.6	na
22	8.7	0.2	0.9	1.6	0.1	0.6	52.94	0.4	0.1	0.4	2.6	0.2	na	na	na	na	na	na	na	na
23	68.7	87.3	88.2	90.2	89.6	18.6	12.5	10.8	11.3	9.0	89.0	22.6	100	50.2	52.2	51.2	19.4	49.3	14.2	0.7
24	19.6	0.1	0.2	0.3	ND	ND	7.4	44.0	53.69	10.91	5.7	13.5	ND	25.1	28.65	18.76	28.9	19.2	6.1	13.12
25	3.0	12.3	10.8	7.8	10.35	80.83	27.19	44.9	34.9	79.69	2.7	63.69	ND	24.67	19.17	30.08	51.7	31.5	79.69	86.15

1=Naphthalene, 2=Acenaphthylene, 3=Acenaphthene, 4=Fluorene, 5=Phenantrene, 6=Anthracene, 7=Fluoranthene, 8=Pyrene, 9=Benzo(a)anthracene, 10=Chrysene, 11=Benzo(b)fluoranthene, 12=Benzo(k)fluoranthene, 13=Benzo(a)pyrene, 14=Indene(1,2,3.cd)pyrene, 15=Benzo(ghi)perylene, 16=Total PAHs, 17=Mean PAHs,18=Std.Deviation, 19=PAHs 2-3 bencenic rings (relative abundance), 20=PAHs 4-6 bencenic rings (relative abundance), 21=Organic carbon %, 22=Gravel, 23=Sand, 24=Silt, 25=Clay, ND: < detection limit 0.01 μg/g, na: non analysed

Sediments from Salada, El Llano, and La Mancha lagoons revealed no acenaphthene, whereas Mandinga lagoon showed mean concentrations below 0.5 µg/g; probably because it is a very volatile PAHs, constituted by only two bencenic rings, affected by photo-oxidation, chemical oxidation, winds, tides, and microbial metabolic processes (Neff, 1979).

From all sites evaluated, Salada lagoon was the only one with a positive correlation between anthracene and clays ($r=0.5$, $p > 0.05$), however negative correlations were present between PAHs of 4-5 bencene rings and gravels (benzo(a)anthracene $r=-0.61$, $p=0.12$; benzo(b)fluoranthene $r=-0.58$, $p=0.2$; benzo(k)fluoranthene $r=-0.56$, $p=0.25$; and benzo(a)pyrene $r=-0.58$, $p=0.2$). PAHs distribution in Salada lagoon was similar to that reported by Botello and Calva (1998) for the Tampamachoco Lagoon where pollution by PAHs is determined by direct inflows from the nearby Thermal-Power Plant, independently from the type of sediments, however PAHs persistence increases with increasing molecular weight (Witt, 1995).

In contrast to other estuarine systems, El Llano lagoon recorded one of the highest mean PAHs levels at stations 1 (12.4 µg/g) and 2 (6.1 µg/g), which are placed near the mouth of the lagoon. These levels in its northern region are probably caused by the discharges of Actopan river. Another relevant fact is that several accidents of diesel and oil transporting vehicles had occurred in the surroundings of the system, causing important spills that were most probably transported towards the coastal zone and could have been deposited into the lagoon either by rain, run-off and winds.

Although station 3 is also subjected to riverine influences, its levels were lower (0.6µg/g), since gravel is the prevailing type of sediment in the region. Individual PAHs pattern was in decreasing order: benzo(a)anthracene > pyrene > benzo(b)fluoranthene > benzo(k)fluoranthene > fluoranthene.

Benzo(a)anthracene, pyrene, and fluoranthene can be found in municipal effluents and household discharges, as well as in emissions from pit-coal ovens, motorized vehicles, either gasoline or diesel, oil and gas refineries, and burning of grasslands, a common practice in the areas around these lagoons for agricultural and cattle raising purposes.

In La Mancha lagoon the highest mean concentration of PAHs was found in the rainy season, accompanied by organic matter supplies that contribute to a larger adsorption of PAHs which are precipitated and stored at the bottom within the sediments. By the same token, the location and the prevailing environmental conditions, such as minimal currents, large terrigenous supplies, and shallowness favored PAHs accumulation.

Stations 3 and 4 revealed the highest mean concentration with 11.3 and 7.8 µg/g, respectively. Station 2, located at the mouth of the lagoon yielded the lowest values (3.8 µg/g). A gas pipeline (from Petroleos Mexicanos, PEMEX) runs across this region along the coastal line; hence, the area has been influenced by the use of machinery and the maneuvers to ground the gas pipeline, dumping fuel and other wastes into the system.

In general, the most striking compounds were in decreasing order: benzo(a)anthracene > pyrene > benzo(b)fluoranthene > benzo(k)fluorantene > chrysene.

For Mandinga Lagoon, the station 6 located in the southern region of the system, yielded the highest PAH levels in all samplings, and also this station presented the major mean levels (18.2 g/g). Several streams, such as Caño Salazar, Palma Sola and Principal discharge their effluents in this area, which is, therefore, constituted by clayish-muddy sediments that would favor PAHs adsorption. Station 4 with 5.4 µg/g is located in the central portion of the lagoon, which is very shallow, reaching barely an average of 0.8 m depth; in contrast, station 1 near the mouth presented the lowest levels (2.2 µg/g), probably due to the fact that sediments there are sandy and the area is influenced by the discharge of Jamapa river.

Among the most relevant PAHs found in this system were: chrysene > benzo(b)fluoranthene > benzo(a)pyrene > Indene(1,2,3-c,d)pyrene > benzo(a)anthracene.

The statistical results shown that differences in total concentration of PAHs during dry and rainy seasons were no significatives ($p=<0.05$), as well as the differences related with spatial distribution of PAHs. This is probably due to the shallowness and size of these lagoons, which are very small compared with others systems in the Gulf of Mexico.

Also it was not possible to establish a direct correlation between the organic carbon (C.O.%) and the PAHs determined in the sediments of each lagoon. This demonstrates that the PAHs concentrations are independent of the percentages of organic carbon present in the lagoons. This contradicts the sorption theory, which is sustained in the affinity of PAHs with sediments having a high organic carbon content, such as clay and silt. This non-affinity has been reported for marine sediments (Readman et al. 1986), and in suspended estuarine particles (Raoux and Garriges 1993; Coakley et al. 1993, Botello and Calva, 1998).

Comparison of the present results to those from other coastal systems along the Gulf of Mexico revealed that Mandinga lagoon is an area with high PAHs inputs mainly of pyrogenic origin, coming from the inflows of the rivers crossing industrial areas, oil and gasoline spills from fishing and tourism boats, the burning of surrounding vegetation and atmospheric transport. Its mean levels are comparable to those of Tampamachoco lagoon (7.65 µg/g) located north of Veracruz state, and also affected by urban discharges and industrial complexes (Botello and Calva, 1998).

The presence of compounds made up primarily of 4 and 5 benzene rings, proves the hypothesis that the origin of the PAHs determined in all these lagoons is mainly anthropogenic. Besides the presence of 2-ring aromatic compounds in Mandinga lagoon confirms recent petrogenic inputs, as pointed out by Cranwell and Koul (1989); Steinhauer and Boehm (1992); Raoux et al. (1999) and Gogou et al. (2000).

The levels of PAHs determined in the present work are higher compared with those reported for Florida coasts in a Mussel Watch study (1986-1991) by Miles and Delfino (1999),those from the Baltic Sea (Witt,1995) and from Prince William Sound in Alaska (Short et al. 1999). Noteworthy are the high benzo(a)pyrene concentrations found in the sediments of Mandinga lagoon, since oyster culture and production is commercially relevant in this lagoon, and this compound has been demonstrated to be carcinogenic and mutagenic even for humans (Shchekaturina et al. 1995).

Finally, the presence and levels of PAHs determined in this study, can be considered as an ecological risk for the estuarine organisms living 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.

Acknowledgments. We thank M. Castillo and anonymous reviewers of manuscript for their helpful comments and suggestions. We thank Alicia Durán for her help drawing the map.

REFERENCES

Arcaro KF, O'Keefe PW, Yang YI, Clayton W, Gierthy JF (1999) Antiestrogenicity of environmental pahs in human breast cancer cells. Toxicology 133: 115-127

Botello AV, Calva LGB (1998) Polycyclic aromatic hydrocarbons in sediments from Pueblo Viejo, Tamiahua and Tampamachoco lagoons in the southern Gulf of Mexico. Bull Environ Contam Toxicol 60:96-103

Botello AV, Ponce VG, Díaz G (1993) Hidrocarburos aromáticos policíclicos (HAP) en áreas del Golfo de México. Hidrobiológica 3:1-15

Calva LGB, Botello AV (1999) Polycyclic aromatic hydrocarbons in sediments from Sontecomapan Lagoon, Veracruz, Mexico. Hidrobiológica 9:45-52

CARIPOL/IOCARIBE/UNESCO (1986) Manual CARIPOL para el análisis de hidrocarburos del petróleo en sedimentos y organismos marinos. Programa CARIPOL II. Puerto Morelos Q Roo México, p 25

Coakley J, Nagy E, Serodes J (1993) Spatial and vertical trends in sediment-phase contaminants in the upper estuary of the St. Lawrence river. Estuaries 16:653-669

Eertman RH, Groenink CL, Sandee B, Hummel H (1995) Response of the blue mussel *Mytilus edulis* L. following exposure to PAH's or contaminated sediment. Mar Environ Res 39:169-173

Folk RL (1974) Petrology of sedimentary rocks. Hemphill Publishing Company, Austin, Texas, p 182

Gaudette H, Fligh W, Toner L, Folger D (1974) An inexpensive titration method for the determination of organic carbon in recent sediments. J Sediment Petrol 44:249-253

Gogou A, Bouloubassi I, Stephanou EG (2000) Marine organic geochemistry of the Eastern Mediterranean: 1. Aliphatic and polyaromatic hydrocarbons in Cretan Sea surficial sediments. Mar Chem 68:265-282

Martel L, Gagnon J, Masse R, Leclerc A, Tremblay L (1986) Polycyclic aromatic hydrocarbons in sediments from the Saguenay Fjord, Canada. Bull Environ Contam Toxicol 37:133-140

Miles CJ, Delfino JJ (1999) Priority pollutant polycyclic aromatic hydrocarbons in florida sediments. Bull Environ Contam Toxicol 63:226-234

Neff J (1979) Polycyclic aromatic hydrocarbons in the aquatic environment. Sources, fates and biological effects.Applied Science Publishers Ltd, London, p 262

Olsen CR, Larsen IL, Mulholland PJ, Von Damm KL, Grebmeier JM, Schaffner LC, Díaz RJ, Nichols MM (1993) The Concept of an equilibrium surface applied to particle sources and contaminant distribution in estuarine sediments. Estuaries 16:683-696

Raoux C, Bayona JM, Miquel JC, Teyssie JL, Fowler SW, Albaigés J (1999) Particulate fluxes of aliphatic and aromatic hydrocarbons in near-shore waters to the northwestern mediterranean sea, and the effect of continental runoff. Est Coast Shelf Sci 48:605-616

Raoux CY, Garrigues P (1993) Mechanism model of polycyclic aromatic hydrocarbons contamination of marine coastal sediments from the Mediterranean Sea. Polycycl Arom Comp Suppl Vol 3:443-450

Readman JW, Mantoura RF, Lleqellyn CA Preston MR, Reeves AD (1986) The use of pollutant and biogenic markers as source discriminants of organic inputs to estuarine sediments. Intern J Environ Anal Chem 27:29-54

Shchekaturina TL, Khesina AL, Mironov OG, Krivosheeva G (1995) Carcinogenic polycyclic aromatic hydrocarbons in mussels from the Black Sea. Mar Pollut Bull 30:38-40

Short JW, Kvenvolden KA, Carlson PR, Hostettler FD, Rosenbauer RJ, Wright BA (1999) natural hydrocarbon background in benthic sediments of Prince William Sound, Alaska: Oil vs Coal. Environ Sci Technol 33:34-42

Steinhauer MS, Boehm PD (1992) The composition and distribution of saturated and aromatic hydrocarbons in nearshore sediments, river sediments, and coastal peat of the alaskan Beaufort Sea: Implications for detecting anthropogenic hydrocarbon inputs. Mar Environ Res 33:223-253

UNEP (United Nations Environment Programme) (1992) Determination of petroleum hydrocarbons in sediments. Reference methods for marine pollution studies N° 20, p 75

Valette, NS (1993) The use of sediment cores to reconstruct historical trends in contamination of estuarine and coastal sediments. Estuaries 16:577-588

Witt, G (1995) Polycyclic aromatic hydrocarbons in water and sediment of the Baltic Sea. Mar Pollut Bull 31:237-248

Zar JH (1996) *Biostatistical Analysis* 3rd ed Prentice Hall New Jersey p 662