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ASSESSMENT OF POLYCYCLIC AROMATIC HYDROCARBONS (PAH) POLLUTANTS IN SEDIMENTS OF NORTH-WEST ARABIAN GULF AND SHATT AL-ARAB ESTUARY

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ABSTRACT

The persistance of aromatic hydrocarbons in the environment,their relative ease of isolation and measurement and their abundance in petroleum make them acceptable indicators of oil pollution monitoring. Polycyclic Aromatic Hydrocarbons (PAH) in sediment samples were analyzed from seven stations along Shatt Al-Arab estuary and North-West region of the Arabian Gulf by high resolution capillary gas chromatography.

PAH in sediment ranged from 8.42 to 70.56 ng/g dry weight. The PAH appeared divisible into two groups: Low molecular weight including Naphthalene Biphenyl, Acenaphthylene,Fluorene,Phenanthrene and Anthracene, and high molecular weight homologues group including Fluoranthene,Pyrene, Chrysene, Benzo(ghi)perylene and Benzo(a)Pyrene. The overall PAH distribution found in surface sediment layer was not unique to aquatic environment. The sources of PAH in Shatt Al-Arab estuary and North-West region of the Arabian Gulf were dominated by both pyrogenic and petrogenic input, but rarely by biogenic origin. The PAH concentrations in these sediment are governed by many transport processes, and were within the range of the other parts of the world.

INTRODUCTION

A major source of the entire PAH suite is most likely street runoff, which incorporates atmospheric dust, road-wear particles, and automotive oil and greases, all of which contribute Polycyclic Aromatic Hydrocarbons (PAH) derived from pyrolysis and combustion processes. Wakeham et al.,(1980) had shown a strong correspondance between the composition of PAH accumulation in surface sediment of several lakes and those present in street dust. In particles, the components derived from asphalt (and cement) particles contain an assembelage of PAH.
Low levels of PAH were found in sediments further away from their original sources too. This idea is supported by the fact that a long range atmospheric transport of anthropogenic compounds is well documanted (Al-Mudaffar et al.,1990). In addition, combustion-generated PAH naturally produce PAH (from grass and prairie fires) can be carried equally long distance. Accordingly the very low PAH in sediment is propably due to both natural and anthropogenic sources.
There are two transport models responsible for the wide distribution of PAH; i.e the resuspension and transport of contaminated sediments found near urban areas; and the long range airborn particulates.
A comparison by Grimalt et al.,(1992) for PAH distribution in an estuarine sediment and in local atmosphere indicated that a primary source of PAH to aquatic environment was anthropogenic combustion produce compounds emitted to the atmosphere and then washed to estuaries by freshwater runoff. Particulate combustion products transported atmospherically from various distinations settleing in watersheds which drain into the estuary, may be anthor source of contamination.
The relative abundance of the individual PAH are slightly altered by degradation during atmospheric transport to remote sites, but this removal processes is unimportant once the PAH delivered to sediment where microbial degradation take place (Leahy and Colwell, 1990).
Polycyclic Aromatic Hydrocarbons (PAH) are formed in different combustion processes from many kinds of organic materials and are widespread throughout the environment. The carcinogenic properties of certain PAH have long been recognized. PAH have been detected in the trace amounts in a wide variety of matrices, varying from exhaust gases,smoke,airborne particulates,surface and drinking waters and food-stuffs to soils and sediments.
Bottom sediments in aquatic systems represent reservoirs, or sink, for the accumulation of contaminants derived from both natural and anthropogenic sources.The deposition of biogenic particles,mineral grains and hydrous metal oxides-hydroxides in freshwater environments aids in removing dissolved contaminants but results in increased concentrations in bottom sediment. In the present work, the presistent of PAH were measured in sediment samples from Shatt Al-Arab estuary and North-West Arabian Gulf.

MATERIAL AND METHODS

Sediment samples were collected from seven stations (Fig.1) by a Van Veen grab sampler . Undistributed,triplicate samples were taken. After retrieval of the sampler, the water was allowed to drain off, avoiding disturbing the surface layer of the samples. As soon as the samples were retrieved, they were wrapped in aluminium foil or placed in a glass jar and immediately frozen to -20°C.

Before analysis, sediment samples were freeze-dried, ground finely in agate mortar and seived through a 62µ metal (stainless stell) seive.

The extraction procedure was based upon that of Gutox and Saliot (1980). Sediment were soxhlet extracted with 150ml methanol:benzene (1:1) mixture for 24hours. At the end of this period, the extract was transferred to a storage flask and the sample was further extracted with a fresh solvent. The combined extracts were reduce in volume to ca 10ml in a rotary evaporater. It was then saponified for 2hours with a solution of 4N KOH in 1:1 methanol:benzene. After extracting the unsaponified matter with hexane, the extract was dried over anhydrous Na_2SO4, concentrated by a stream of N_2 . The concentrated extract was cleaned up by column chromatography on 5% deactivated florisil. The polycyclic aromatic hydrocarbons was eluted with benzene. The fraction then reduced to a suitable volume by a stream of pure N_2 prior to analysis by capillary gas chromatography.

Elemental sulfur was removed through treating the extract with deactivated copper.

A Perkin-Elmer Sigma 300 capillary gas chromatograph equipped with Flame Ionization Detector (FID) and splitless mode injection port used. Quantification of peaks and identification of hydrocarbons in chromatograms was acheived by Perkin-Elmer computing integrator model LC-100. The fused silica capillary column used was a Wall Coated Open Tubular (WCOT) 50mX0.25mm i.d. SE-30 (methylsilicone).

Helium was used as acarrier gas with a linear velocity 1.5ml/min. Operating temperatures for detector and injector were 350 and 320°C respectively. The column was operated under temperature programmed conditions from 70°C for 0 min to 300°C for 30 min with a rate of 4°C/min.

Total Organic Carbon (TOC) concentrations in sediments were determined by treating subsamples with phosphoric acids to remove carbonate, then dried at 60°C to a constant weight and combusted using a Perkin-Elmer model 240B Elemental Analyzer.

Most of the collected sediment samples consisted mainly of mud. These muddy samples were dried at 50°C for 48 hours. A 15g sub-sample from each dried sample, was wet seived by 230 mesh (diameter 63µ). The coarser grain (<63µ) were passed through the Sedigraph ET-5000 instrument, in order to obtain the grain size distribution in the silt and clay grades. The percentage of three size fractions was calculated according to Folk (1974) and Shepard (1954).

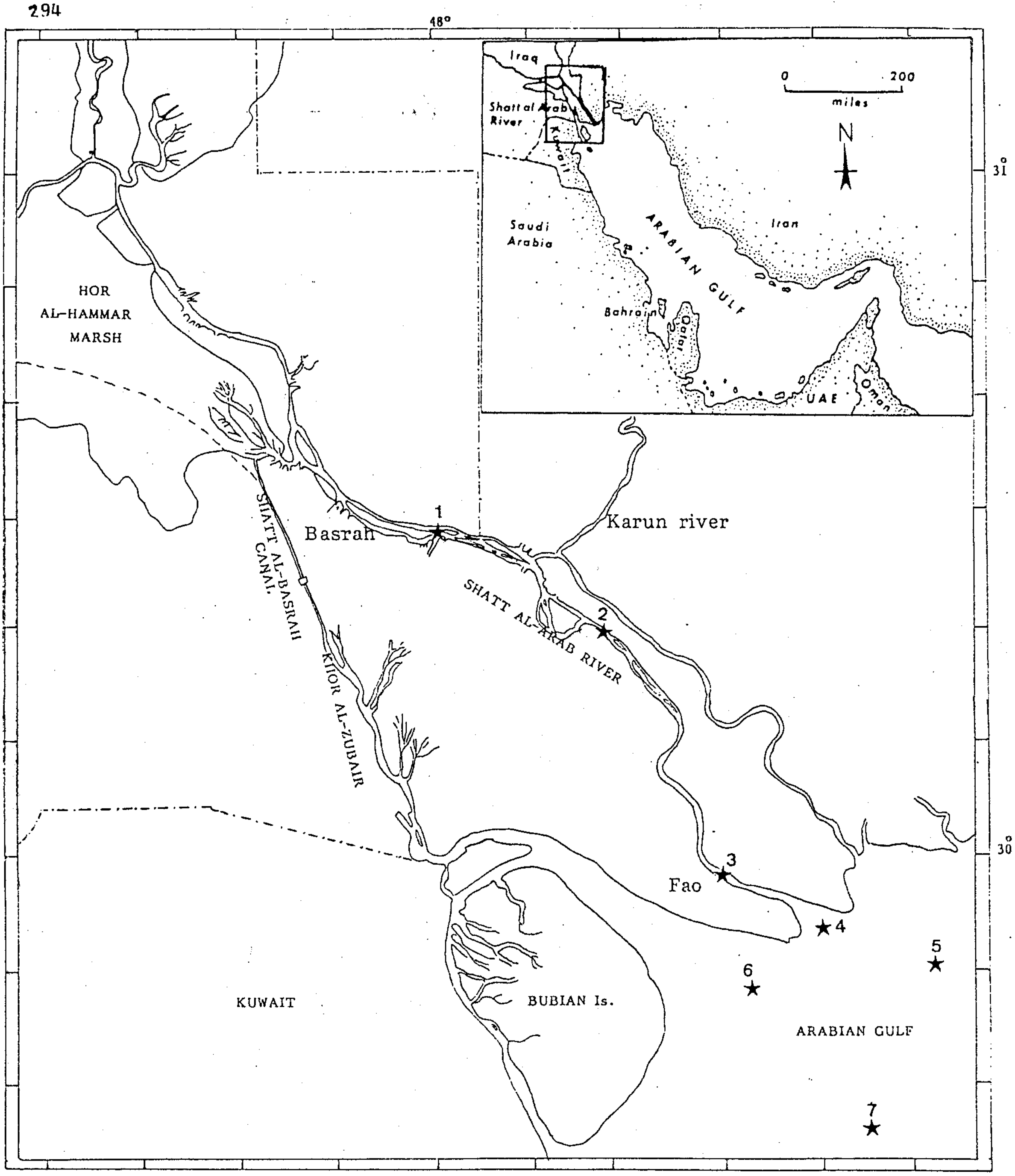

Fig.1) Map of Shatt Al-Arab estuary and North-West Arabian Gulf showing the position of stations

RESULTS AND DISCUSSION

The distribution of PAH in sediment samples from Shatt Al-Arab estuary and North West Arabian Gulf are summarized in Table 1. The total concentrations of PAH in sediments samples ranged from 8.42 ng/g at station 7 to 70.56 ng/g dry weight at station 2. The PAH appeared divisible into two groups: Low molecular weight PAH group including Naphthalene, Biphenyl, Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene and Anthracene and high molecular weight homologues group including Fluoranthene, Pyrene, Chrysene, B(ghi)P, and B(a)P. Comparison of some gas chromatograms of sediment samples against typical blank are shown in Fig. 2. Dominant PAH in sediment samples were B(ghi)P, Pyrene ,Anthracene, Fluoranthene and Acenaphthene. It was found that B(ghi)P occured more frequantly than any other PAH, while the irregular occurence of other PAH may have been caused by small localised input. Higher levels of PAH in the sediment compared to water probably due to the deposition of compounds adsorbed onto particulate matter. Concentration of PAH showed a sharp decline within few kilometers off station 2. The highest concentrations were found in Shatt Al-Arab river near a potential oil pollution sources, close to station 2(Abadan) and station 3(Fao). This could be due to oil spillage and engine exhaust from a number of small fishing boats moored nearby and also contamination by power boat activity.

The overall PAH distribution found in surface sediment layer of the Shatt Al-Arab and North-West Arabian Gulf is not unique to aquatic environment. Such a pattern is common in recently deposited sediment of marine and freshwater bodies. Lamparczyk et al.,(1990) summarized the result of analysis of numerous sediment samples from Baltic sea, suggested, a dominance of PAH with 3-5 rings. Brooks et al.,(1990) studing the PAH in Matagorda, Texas, found an average range between 29 to 112 ng/l, while it was as high as 490 to 1820 ng/l near a platform. John and Levy (1990) found that atmospheric inputs and direct discharge effluents were the major sources of PAH in sediment of Saguenary river, Quebec. Siron et al.,(1991) found low levels of PAH in sediments of Saint Lawrence estuary, confirming a slight pyrogenic contamination. Evan et al.,(1990) found that Fluoranthene was the dominant PAH in sediment of Derwent river in Derbyshire, U.K.,with road runoff and atmospheric fallout to be the main sources. Recently PAH generated during high temperature combustion such as that occur during the oil well fires in Kuwait were mainly of high molecular weight (> 4 aromatic ring) and many of which were carcinogenic (Fowler et al.,1993), while Readman et al.,(1996) found the concentartion of PAH in marine environment of the Arabian Gulf are comparatively low,with oil rather than combustion being the major source. Moreovere, based on the composition, it appears that PAH from the burning of wells in Kuwait had not resulted in any large-scale contamination of the coastel area in the Gulf (Readman et al.,1996). The concentration of PAH in Shatt

Table- 1-

Concentrations of Polycyclic Aromatic Hydrocarbons (PAH) in Sediment (ng/g) of Shatt Al-Arab river and North-West Arabian Gulf

Summer 1993	Station						
Compounds	1	2	3	4	5	6	7
Naphthalene	—	1.75	0.15	1.40	—	—	—
Biphenyl	2.36	3.39	2.58	2.63	2.23	—	1.25
Acenaphthylene	—	5.04	3.07	1.46	—	—	—
Acenaphthene	2.42	6.70	2.04	1.06	4.09	3.26	2.16
Fluorene	4.26	3.99	3.47	2.08	—	0.20	0.97
Phenantherene	1.81	8.40	1.49	—	—	—	—
Anthracene	6.58	10.03	7.22	2.43	4.48	4.45	2.84
Fluoranthene	—	3.02	—	—	—	—	—
Pyrene	1.28	2.25	2.77	4.58	1.85	3.56	1.24
Chrysene	0.98	2.55	1.18	1.46	—	—	0.09
Benzo(ghi)perylene	1.63	13.39	10.84	6.16	3.50	4.83	1.63
Benzo(a)pyrene	0.81	10.05	—	2.18	3.01	—	0.07
TOTAL	22.13	70.56	34.81	26.16	19.16	16.30	10.25
Summer 1994							
Naphthalene	—	1.09	—	—	—	—	—
Biphenyl	—	3.13	1.89	1.43	—	—	—
Acenaphthylene	—	5.56	3.80	2.56	—	—	—
Acenaphthene	2.58	4.28	5.35	3.18	2.27	2.81	1.85
Fluorene	5.62	7.74	3.15	5.72	1.83	2.16	2.28
Phenanthrene	4.36	10.20	1.46	—	3.65	0.18	0.13
Anthracene	1.50	19.12	2.57	—	—	2.23	2.17
Fluoranthene	0.75	4.27	1.16	2.16	—	—	—
Pyrene	0.84	3.85	2.02	2.37	2.68	1.63	0.29
Chrysene	0.63	2.74	0.99	0.97	—	—	0.35
Benzo(ghi)perylene	1.28	3.68	9.15	4.18	4.19	3.73	1.26
Benzo(a)pyrene	0.82	1.72	—	—	1.01	—	0.09
TOTAL	18.38	67.41	31.54	22.57	15.63	12.74	8.42

— = Not detected.

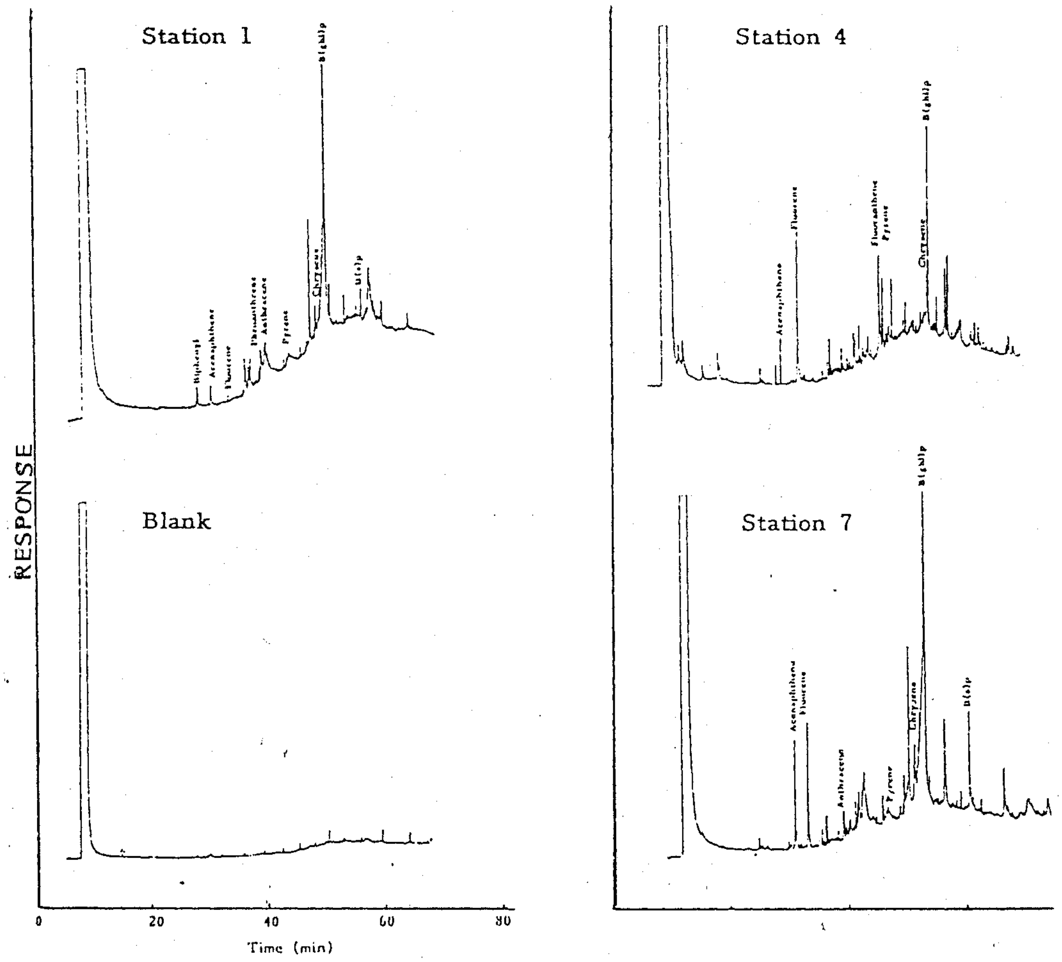

Fig.2.- Representative capillary gas chromatograms (GC/FID) of PAH in sediment samples from different stations with a typical blank

Al-Arab estuary and North-West region of the Arabian Gulf were also within the range of the other parts of the world (Table 2), and less than the concentrations obtain for the same area by Al-Saad (1987). This area have remained relatively undistributed by human activities for several years due to the circumstances of Iraq-Iranian war (1980-1988).

The sources of PAH in Shatt Al-Arab estuary and North-West Arabian Gulf were dominated by both pyrogenic and petrogenic input, but rarely of biogenic origin. In the present study, the source of PAH in station 2 is relatively heavy, but the concentration detected in sediment were rather low, which could be due to higher rate of microbial degradation at this station. This was in agreement with the results reviewed by Leahy and Colwell (1990) on the biodegradation activity in sediments, emphasising the fact that exposure of petroleum contaminated sediments to oil products accelerated the rate of PAH mineralization and the turn-over time, for upto 10 to 400 times than that in sediment of a pristine freshwater stream.

The Total Organic Carbon (TOC) content, can be considered as a measure of bulk organic matter possibely acting as a source of diagentic PAH. According to Lee et al.,(1978) and Grimalt and Albaiges (1990) PAH present in sediment are mainly bound to organic matter adsorbed onto the particles. The finer the grain size of the particles, the large is the surface area for such interactions, with a corresponding increased adsorption ability of the sediments. From Table 3 the relationships between the sediment type, the TOC percentage and the total concentrations of PAH was found by performing regression analysis of these variables. The correlation obtained between TOC% and total PAH was r= 0.871 and 0.949 for summer 1993 and 1994 respectively. Moreovere, higher concentration of PAH were associated with silt-clay than sandy particles. Thus it may concluded that the settlement of the silt and clay particles enriched by organic matter prevailed along the estuary. The same conclusion was reached by Al-Saad and Al-Timari (1989) in the sediment from the marshes of Iraq, Marcomini et al., (1986) in sediments of Adriatic sea, and Larsen et al., (1986) in the sediments of the Gulf of Maine (U.S.A).

As a conclusion, the PAH concentrations in Shatt Al-Arab estuary and North-West region of the Arabian Gulf sediments are governed by four transport processes:

1- Aeoline transport of fossile fuel, grass fire and combustion products followed by deposition on the surface water and subsequent sedimentation

2- Riverine transport of combined PAH source (e.g. stromwater runoff, municipal sewage effluents, oil spillage from ports and industrial inputs) in estuary system.

3- Direct introduction of wate material via ship and leisure boats and fishing boats.

4- Resuspension of materials reaching coastel aquatic sediment via aeoline transport and deposition in setting areas.

Table-2-

Comparison of values of PAH in sediment of Shatt Al-Arab estuary and North-West Arabian Gulf with other values in the world

Location	**Concentration (ng/g)**	**References**
Usk River (U.K.)	99.5*	Eglinton et al.,(1975)
Marseille & Monaco	3.7-402*	Milles et al.,(1982)
French Island port cros	3.4-58.4*	Barnier et al.,(1986)
Elizabeth River (U.S.A)	140.0	Bieri et al.,(1986)
Shatt Al-Arab & NW Arabian Gulf	0.20-76.25	Al-Saad (1987)
Euphrates River	0.59-2.07	Al-Saad & Al-Timari(1989)
Brisban River Estuary (Australia)	3.94-16.11	Kayal & Connell (1989)
Bay of Bascay (Espain)	507.5-895	Canton & Grimalt (1992)
Kuwait	1.30	Fowler et al.,(1993)
Saudia Arabia	5.7-175	Fowler et al.,(1993)
Bahrain	3.3-7.9	Fowler et al.,(1993)
UAE	4.01-6.1	Fowler et al.,(1993)
Oman	1.9-5.7	Fowler et al.,(1993)
NW Arabian Gulf	6.88-39.85	Al-Hamdi (1989)
Shatt Al-Arab & NW Arabian Gulf	8.42-70.56	Present study

* = Concentration in (μg/g)

Table-3-

Sediment type analysis of Shatt Al-Arab estuary and North-West Arabian Gulf with Total Organic Carbon (TOC%)

Station	Sediment type			Texetural	TOC%	
	Sand%	Silt%	Clay%		Summer 1993	Summer 1994
1	3.008	40.736	56.225	Silty clay	0.64	0.50
2	3.834	44.236	51.929	Silty clay	0.85	0.82
3	6.736	44.776	48.497	Silty clay	0.72	0.62
4	0.708	47.660	51.631	Silty clay	0.69	0.59
5	39.192	30.404	30.404	Sand-silt-clay	0.52	0.48
6	6.828	54.971	38.200	Clayey silt	0.44	0.40
7	3.904	42.282	53.811	Silty clay	0.38	0.34

تقدير الملوثات الاروماتية المتعددة الانوية في رواسب شمال غرب الخليج العربي ومصب شط العرب

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المستخلص

ان وجود المركبات الاروماتية في البيئة ، ولسهولة فصلها وقياسها من النفط تجعلها دليل مقبول لمراقبة التلوث النفطي ، فقد تم قياس هذه المركبات من سبعة مناطق مختارة على طول مصب شط العرب وشمال غرب الخليج العربي باستخدام تقنية الغاز الكروموتوغرافي المزود بالعمود الشعري . تراوحت تراكيز المركبات من ٤٢ ر ٨ الى ٥٦ ر ٧٠ نانوغرام بالغرام كوزن جاف . لوحظت بان هذه المركبات تقسم الى مجموعتين : مجموعة ذات الاوزان الجزيئية الواطئة تتضمن النفثالين ، البايفينال ، الاسنفثين ، الفلورين ، الفينانثرين والانثراسين . والمجموعة الثانية ذات الاوزان الجزيئية العالية التي تتضمن الفلونثين ، البايرين ، الكرايسين والبنزو (كاي) بريلين والبنزو (اي) بايرين . لوحظ بان جميع المركبات الاروماتية في الرواسب السطحية هي ليست متناظرة وان مصادرها متنوعة وان قيمها تقع ضمن القيم الاخرى من العالم .