DISTRIBUTION OF POLYCYCLIC AROMATIC HYDROCARBONS (PAH) IN SEDIMENTS OF SHATT AL – ARAB RIVER AND THEIR EFFECTS ON ENVIRONMENT[+]

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Abstract

The present work comprised the study of presence , origin , type , and distribution of polycyclic aromatic hydrocarbons (PAH) in sediments of Shatt Al – Arab river . A total of up to 70 samples of sediment were collected from seven stations along Shatt Al – Arab river for the period of November 2003 to April 2004 . The samples were extracted and concentrations of PAH were determined by high resolution capillary gas chromatography . The concentrations of PAH in sediments of Shatt Al – Arab river varied from 11.83 ng / g dry weight at station 3 to 77.86 ng / g dry weight at station 6 . The dominant PAH compounds were anthracene , fluoranthene , pyrene , perylene throughout the stations . There was a significant relationship between the concentration of PAH and total organic carbon (TOC) . The grain size analysis of these sediments indicated that distribution of PAH is related to the texture of the bottom deposit .

المستخلص

تضمن العمل الحالي دراسة وجود و اصل و نوع و توزيع الهيدروكاربونات الاروماتية متعددة الحلقات في رواسب نهر شط العرب .جمعت اكثر من ٧٠ عينة من الرواسب من سبعة محطات على طول نهر شط العرب لمدة ستة اشهر من تشرين الثاني ٢٠٠٣ الى نيسان ٢٠٠٤ . استخلصت الهيدروكاربونات الاروماتية متعددة الحلقات من هذه العينات و قيست بواسطة جهاز غاز الكروماتوغرافي المزود بالعمود الشعري ذات تقنية الفصل العالية . تراوح تركيز الهيدروكاربونات الاروماتية متعددة الحلقات في رواسب نهر شط العرب من ١١,٨٣ نانوغرام / غرام وزن جاف في محطة رقم ٣ الى ٧٧,٨٦ نانوغرام / غرام وزن جاف في محطة رقم ٦ وان المركبات الرئسية التي وجدت هي الانثراسين و الفلورانثين و البايرين و البرايلين . بينت بعض التحاليل الجيوكمياوية بان توزيع الهيدروكاربونات الاروماتية متعددة الحلقات تعتمد على حجم جزيئات الرواسب القاعية . فضلا عن وجود ارتباط معنوي بين تركيز الهيدروكاربونات الاروماتية متعددة الحلقات و كمية الكاربون العضوي الكلي .

Introduction

In recent years, the concern about the presence of polycyclic aromatic hydrocarbons(PAH) in air , soil , and water systems has increased , since this important class of chemicals is carcinogenic in experimental animals and a potential health risk to man [1] . A summary of the structure , toxicity , and genotoxicity of PAH commonly found in soil and aquatic ecosystems is given in Table (1) .

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Table (1) : Toxicilogical characteristic of selected PAH .

No.of Rings	Chemical	Toxicity	Carcinogenicity	Genotoxicity
2-Rings	Naphthalene	Algae,24h,50%,33ppm Fish,96h,TLm=1-2ppm Rat,LD_{50}=306–600ppm Rabbit,LD_{50}=800ppm	–	–
	1-,2–Methyl-naphthalene	Fish,48 h,LD_{50}=8–9ppm	–	–
3-Rings	Acenaphthene	ND	_,?	+Ames
	Anthracene	Mouse,LD_{50}=430ppm	_	_
	Fluorene	ND	_	_
	Phenanthrene	Mouse,LD_{50}=700ppm	_/?	-
4-Rings	Benz(a)anthracene	ND	+	+Ames +SCE +UDS
	Chrysene	Mouse,LD_{50}=320ppm	+	+Ames +SCE +CA
	7,12–Dimethyl–benz (a) anthracene	ND	+	+Ames
	Fluranthene	Mouse,LD_{50}=500ppm Rat,LD_{50}=2000ppm Rabbit,LD_{50}=3180ppm	+/?	+Ames
	Pyrene	Mouse,LD_{50}=514-678ppm	-,?	+/?Ames +UDS +SCE
5-Rings	Benzo(a)pyrene	Mouse,LD_{50}=250mg/kg Embryotoxic Teratogenic	+	+Ames +UDS +SCE +DA
	Dibenz(a,h)anthracene	ND	+	+Ames +*E.coli* +DNAdamage +CA
	3–Methyl-cholanthrene	ND	+	+Ames
	Perylene	ND	-,?	+Ames +CA
6-Rings	Indeno(1,2,3c,d)pyrene	ND	+	+Ames
7-Rings	Cronene	ND	+/-,?	+Ames

PAHs are mainly formed as products from the combustion of fossil fuels and also occur as natural constituents of unaltered fossil fuels . Due to their hydrophobic properties and limited water solubility , PAHs tend to adsorb to particulates and eventually migrate to the sediments in river , lake , estuarine , and marine waters . Industrial effluents from coal gasification and liquification processes , waste incineration , coke , carbon black , and other petroleum – derived products also add to the high input of PAHs in urban terrestrial and marine sediments [2 ,3] . PAH have been identified as genotoxic pollutants in freshwater and coastal sediments [4] . The concentration of PAHs in sediments depends upon the sites distance from industrialized region , anthropogenic activities , and the various PAHs transport mechanisms . PAHs enter the biosphere through various routes such as accidental discharges of fossil fuels , direct aerial fallout , chronic leakage industrial and sewage

discharges , and surface water runoff . A variety of processes including volatilization , adsorption , chemical oxidation , bioaccumulation , photo decomposition , leaching , and biodegradation are important mechanisms for environmental loss PAHs Figure (1) [5,6] .

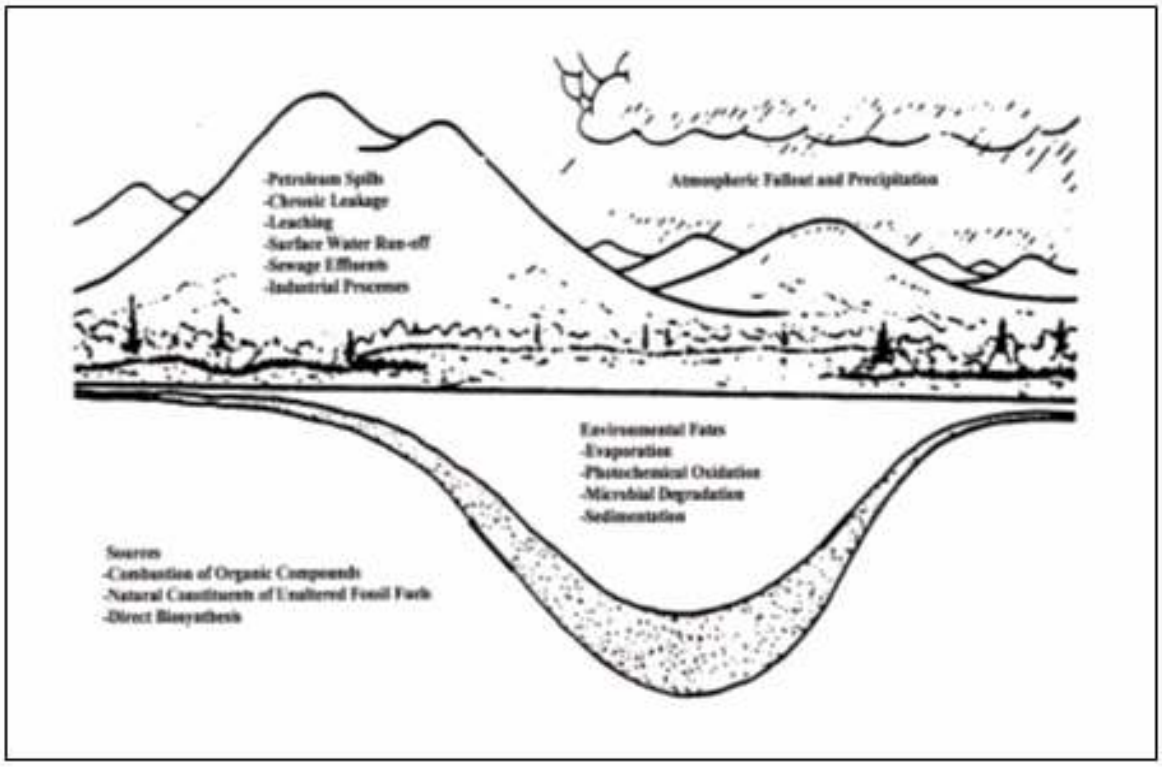

Figure (1) : Schematic represented sources and fates of PAH in the environment .

Shatt Al – Arab river , the area of concern in this report , receives the contamination by oil from different sources . Bedair and Al - Saad [5] reported that the oil refinery effluents , and losses during loading operations have been identified as the major sources of oil contamination in the waters of Shatt – Al Arab river . Therefore , a chronic input of hydrocarbons into the river sediments is to be expected . Thus , the present work was conducted to determine the regional distribution of PAH in sediments of Shatt Al – Arab river .

Materials and Methods

Sediment samples were collected between November 2003 and April 2004 from seven stations Figure (2) . A van veen grab sampler was employed . Undisturbed triplicate samples were taken . After retrieval of 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 .

Figure (2) : Map of sampling location

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

The extraction and clean – up procedure for the determination of PAH in sediment is based on [7]. The glass fiber filters were placed in pre – extracted cellulose thimble and soxhlet extracted with 150 ml methanol : benzene (1 : 1) mixture for 24 hours .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 reduced in volume to ca 10 ml in a rotary vacuum evaporator . It was then saponified for 2 hours with a solution of 4 N KOH in 1 : 1 methanol : benzene.After extracting the unsaponified matter with hexane, the extract was dried over anhydrous Na_2 SO_4 concentrated by a stream of N_2 . The elemental sulfur was removed from sediment extracts through treating the extracts with deactivated copper .The concentrated extract was then cleaned up by column chromatography. A column filled with 8 g each of 5 % water deactivated alumina(100-200 mesh) top and silica (100-200 mesh) bottom was used . The extract was then applied to the head of column and eluted with 50 ml of benzene to isolate the aromatic fraction . The fraction was reduced to suitable volume by a stream of pure N_2 prior to analysis by a Perkin - Elmer Sigma 300 capillary gas chromatography equipped with Flame Ionization Detector (FID) and splitless mode injection part was used .

Quantification of peaks and identification of hydrocarbons in chromatograms were achieved by Perkin - Elmer computing intgrator model LC - 100. The fused silica capillary column used was Wall Coated Open Tubular (WCOT) 50 m x 0.25 mm i .d SE - 30 (methylsilicone) (Perkin-Elmer) . Helium was used as a carrier gas with a linear velocity of 1.5 ml / minute .

Operating temperatures for detector and injector ware 350 and 320 º C respectively. The column was operated under temperature programmed conditions as : Initial temperature = 70 º C , initial time = 0 minute , final temperature = 300 º C , final time = 30 minute , rate = 4 º C / minute .

Total organic carbon (TOC) concentrations in sediments were determined by treating sub - samples with phosphoric acids to remove carbonate , then dried at 60 º

C to a constant weight and combusted using a Perkin – Elmer model 240 B Elemental analyzer [8] .

Grain size analysis of the sediment was carried out using the combined dry sieve and pipette method [9] .

Strenuous efforts ware made to minimize contamination of the samples , which would otherwise yield erroneous result . Throughout the procedure great care was taken to ensure that samples ware not being contaminated ; for example a voiding unnecessarily exposure of the samples , the solvent or the final extract to the atmosphere or other potential sources of contamination . However, procedural blanks consisting of all reagents and glassware used during the analysis , ware periodically determined . It was preferred to eliminate sources of contamination rather than adjusting or correcting that data actually obtained according to the blank value .

The standards of aromatic (polycyclic aromatic hydrocarbons) compound supplied by Supelico and Chrompack were used in capillary gas chromatography for calibration .

Results and Discussion

The distribution of petroleum hydrocarbons in surface sediment , is important to studies of oil contamination , and understanding temporal variations in the aquatic environment [10] .

The distribution of PAHs in the sediment samples of Shatt Al – Arab river and sedimentological data are represented in Table (2) .

Table (2) : Concentrations of PAH in sediments of Shatt Al – Arab river together with their sedimentological parameters .

Station	PAH concentration ng / g dry weight												Sediment type	% TOC
	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	Total		
1	1.53	0.21	0.31	0.13	0.21	3.20	0.33	0.86	0.41	0.33	7.01	14.53	Muddy sand	0.68
2	2.52	1.19	1.63	3.30	6.22	7.52	8.03	1.04	4.23	4.69	8.53	48.9	Sandy mud	0.65
3	1.53	1.11	0.50	1013	2.21	1.46	0.77	0.81	1.15	1.13	0.03	11.83	Mud	0.76
4	1.49	0.21	1.03	1.86	0.01	2.20	3.57	10.0	1.53	0.21	2.81	35.31	Sandy mud	0.84
5	0.89	0.08	0.47	4.69	0.73	3.17	0.21	0.31	0.31	0.26	4.35	15.49	Sandy mud	0.79
6	5.14	6.13	7.83	7.67	7.42	8.56	7.34	8.96	5.24	5.01	8.56	77.86	Sandy mud	0.77
7	0.36	5.17	4.40	3.70	5.93	6.52	7.24	5.03	5.63	4.25	5.66	53.84	Sandy mud	0.52

I = Naphthalene , II = Biphenyl , III = Acenphthylene , IV = Fluorene , V = Phenanthrene , VI = Anthracene , VII = Fluoranthene , VII = Pyrene , IX = Chrysen , X = Benzopyrene , XI = Perylene .

The PAHs appears divisible into two groups ; low molecular weight PAH incorporating naphthalene , biphenyl , acenphtaylene , fluorene , phenanthrene , and anthracene , and the high molecular weight homologues including fluoranthene , pyrene , chrysene , benzopyrene and perylene .Comparison of some gas chromatograms of sediment samples with typical blank establishes that this is not artifact of the analytical procedure nor can it be attributed to blending of the liquid phase during the programmed temperature analysis Figure (3) .

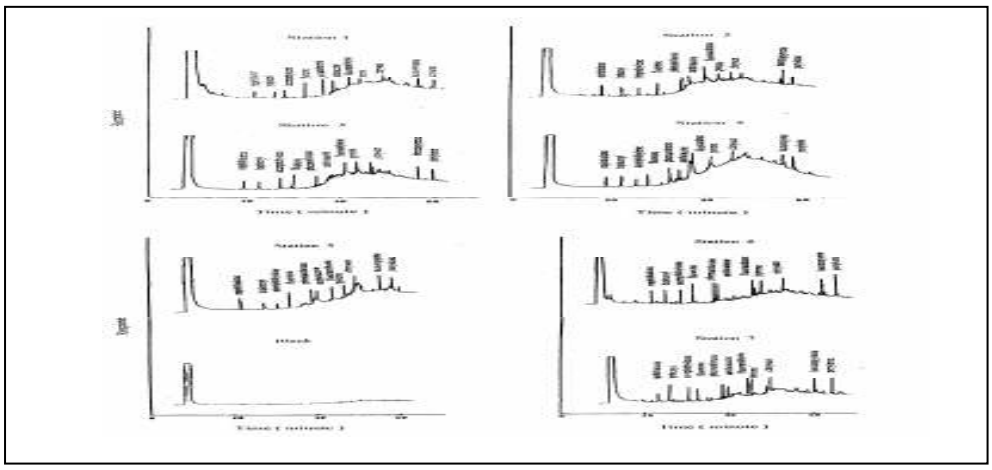

Figure (3) : FID gas chromatograms of PAH in sediments of Shatt Al – Arab river .

The overall PAH distribution found in sediment layer of Shatt Al – Arab river is not unique to aquatic environment . Such a pattern is common in recently deposited sediment of marine and freshwater bodies. Lamparczyk *et al* .[11] summarized the result of analysis of numerous sediment samples from Baltic Sea , suggested , a dominance PAH with 3 – 5 ring . Evan [12] found that Fluoranthene was the dominant PAHs in sediment of Derwent river in Derbyshire , U.K. The concentration of PAHs in sediment samples of Shatt Al – Arab river ranged from 11.83 ng / g dry weight at station 3 to 77.86 ng / g dry weight at station 6 . From the results presented here it is evident that all the sites are contaminated to some extent with PAHs . The concentrations of PAHs in Shatt Al–Arab river were within the range of other parts of worlds Table (3) [13–18] .

Table (3) : Concentrations of PAH in the waters of other sites of world .

Site and concentration	Reference
Usk river , U.K. (99.5 μ / g)	[13]
Marseille and Manaco (3.7 – 402 μ / g)	[14]
French Island portcros (3.4 – 58.4 μ / g)	[15]
Brisban river estuary , Australia (3.94 – 16.11 ng /g)	[16]
Kuwait (1.30 ng / g)	[17]
Saudia Arabia (5.7 – 175 ng / g)	[17]
Bahrain (3.3 – 7.9 ng / g)	[17]
UAE (4.01 – 6.1 ng / g)	[17]
Oman (1.9 – 5.7 ng / g)	[17]
NW. Arabian Gulf (6.88 – 39.85 ng / g)	[18]
Shatt Al – Arab river (11.83 - 77.86 ng / g)	Present study

The highest concentrations were found in Shatt Al – Arab river near potential oil pollutant sources , close to stations 2 (Nahran – omar) , 4 (Basrah) , 6 (Abadan) , 7(Al–Fao). This suggests that PAHs has originated from at lest two different sources , from refineries and port areas , and probable from natural seep due to tank shipping operations . Similar conclusions were reached by [19,20].The sources of PAHs to aquatic environment have been the subject of a number of investigations . Al - Saad

[20] reported that the sources of PAHs in Shatt Al – Arab river were dominated by both pyrogenic and petrogenic input , but rarely of biogenic origin . Stephanou [21] showed that some of PAHs could have biogenic origin . Kyckick and Bidleman [3] indicated that a primary source of PAHs to aquatic environment was anthropogenic combustion produced compounds emitted to the atmosphere and then washed to estuaries by freshwater runoff . LaFlame and Hites [22] showed PAHs enter the environment from a multiplicity of sources which include : direct aerial fallout , chronic leakage of industrial or sewage effluents , accidental discharges during the transport , use and disposal of petroleum products , or from natural sources such as oil seeps and surface water run – off from forest and prairie fire sites .

There are many factors that affect the distribution of PAHsin aquatic environment including Shatt Al – Arab river , such as volatilization , mixing , flushing , adsorption , chemical oxidation , photo – decomposition , sedimentation , and biodegradation . These factors collectively reduce the concentration of PAHs compounds . Lee *et al* . [23] in their experiments on the fate of some PAHs in a control ecosystem indicated the aromatic hydrocarbons in shallow marine water may have residence time in the order of a few days for low molecular weight aromatics , the results of experiments suggested that microbial degradation and volatilization were the primary removal processes . In contrast the concentrations of higher molecular weight aromatics were shown to be effected primarily by sedimentation and photo – chemical oxidation .

The total organic carbon (TOC) content , can be considered as a measure of bulk organic matter possibly acting as a source of diagentic PAHs . According to Grimalt and Albaiges [24] PAHs 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 sediment .

In the present study , the relationships between the sediment type , the TOC percentage and total concentrations of PAH was found by performing regression analysis of these variables . The correlation obtained between TOC % and total PAH was (r = 0.80) . The same conclusion was reached by Al – Saad and Al – Timari [25] in sediments from the marshes of Iraq , in sediments of Adriatic Sea [26] , and in sediments of the Gulf of Maine , U.S.A [27] .

Conclusions and Recommendations

The observed PAH assemblage can be divided into two major groups with respect to their molecular weight . The concentration of PAH in sediments of Shatt Al – Arab river are governed by, aeoline transport of fossile fuel , grass fire , combustion products , riverine transport of combined PAH sources including (stromwater , runoff municipal sewage effluent , oil spillage from ports and industrial inputs) , and direct introduction of ships and boats waste materials . In general the concentrations of PAH were within other values in the world . The higher concentrations of PAH may not always be an indicator of pollution they may be of natural origin , it could be synthesis by organisms [28] and also some PAH identified from sensitized photo – oxidation of gasoline and possibly other light distillate compounds [29] . There are many factors affecting the distribution of PAHs in Shatt Al – Arab river , such as volatilization , mixing , flushing , adsorption , chemical oxidation , photo – decomposition , sedimentation , and biodegradation . These factors collectively

reduce the concentration of PAH compounds from upstream to downstream . The sediments are likely to act as a sink for hydrocarbons . TOC and sediment type plays a role in the distribution of hydrocarbons . In areas subject to chronic input of petroleum to water , analysis of sediments provides means of identifying input sources , types of hydrocarbons present in the stream , and approximate average concentrations of hydrocarbons in waters . Petroleum projects in waters system should emphasize analysis of an indicator such as sediments . Refinery outfalls and losses during loading operations appear to be the major sources of chronic contamination in Shatt Al – Arab river . Similar sources are probably important in many aquatic ecosystems throughout the world . Every possible effort should be made to minimize petroleum input into aquatic environments . Outfall licenses should be strictly enforced and should be amended to specify permissible levels on the basis of the most toxic fractions of petroleum released into the environment . Aromatic hydrocarbons exhibit the most pronounced acute physiological effects on aquatic organisms [1] and should be carefully monitored in aquatic outfalls . Oil pollution associated with boating activities could be controled by enforcing stringent regulations on oil discharge and providing pump out stations similar or superior to the facilities for tanker ballast water treatment . The next stop in Shatt Al - Arab river hydrocarbon program is to provide data on whether levels of petroleum contamination are high enough to exhibit toxic effects on aquatic fauna and flora. A monitoring project using sediments in problem areas for later analysis has already commenced .

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