THE AMAR
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Marsh Bulletin 5(1)(2010)43-55

MARSH
BULLETIN

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Distribution and source of Polycyclic Aromatic Hydrocarbons (PAHs) in surficial sediment from Shatt Al-Hilla River, IRAQ

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Abstract

The presence of organic pollutant in aquatic systems poses a serious threat to environmental health. Surface sediment collected from Shatt Al-Hilla (branch of Euphrates River, a few kilometers southern Al-Musayab town)/Iraq, in 1995 for studying levels, distribution and origin of some polycyclic aromatic hydrocarbon (PAHs). The concentration of naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, (Benz(a) anthracene + Chrysene) and Benzo(b) fluoranthene were measured in five stations. The total of these compounds ΣPAHs were ranged from 26.668 to 900.042 ng/g (dry weight). There were significant differences between various sites of the study area. The highest is in the area adjacent to high way traffic across the river and all studied PAHs resulted from pyrogenic and petrogenic origin.

1- Introduction

Polycyclic (or polynuclear) aromatic hydrocarbons (PAHs) are among the most carcinogenic, mutagenic and toxic contaminants found in aquatic systems (Kennish, 1992), occur in most urbanized, coastal areas of the world, as well as in fresh water and terrestrial systems. They accumulate in sediment and present a potentially serious hazard to the benthos. Many benthic species bioaccumulate PAHs at high levels and exposure to higher trophic levels may occur through the aquatic food chain. PAHs encompass abroad range of compounds with two or more benzene rings; side groups (substituted PAHs) also occur. In general, PAHs have low solubility in water, high melting points, and low vapor pressure. As solubility increases, melting and boiling points increase, and vapor pressure decreases with increasing molecular weight (MW). Due to their high hydrophobicity, PAHs are classified as non-polar narcotics. Like other narcotics, PAHs do not affect specific organs, organ systems or biochemical pathways. Rather, they cause a reversible disfunction called general narcosis.

Each of these sources produces a characteristic PAHs pattern (Benlahcen *et al*., 1997), and its distribution governed by chemical and physical properties (Brown *et al*., 1985). The origin of PAHs can be assessed by using molecular indices based on ratios of individual PAH concentration in sediment (Budzinski *et al*., 1997), (Baumard *et al*., 1998).

PAHs compound distribution were studied in surface sediment from Shatt Al-Arab river and their concentration ranged between (3.8-7.6) ng/g (Al-Saad, 1987) and in the sediment of Hor Al-Hammar, in Basrah the value of these compound ranged between (0.5-2) ng/g (Al-Saad and Al-Timari, 1989) and a study of these compound in the core sediment of Khour Al-Zubair in NW. Arabain Gulf show a high concentration of PAHs 40 ng/g dry weight which indicated that navigation, oil pollution and burning of fossil fuel could be the source of these compound (Al-Hamdi, 1989).

No data or information was available for evaluating PAHs contamination levels and their origins in Shatt-Al-Hilla river sediment, it was therefore necessary to study the distribution and origin of these compound.

2- Materials and Methods

Surficial sediments were collected during summer 1995 by Avan veen grab sampler at five sites from Shatt Al-Hilla River to determine the distribution of PAHs (Fig. 1). At each site, a composite sediment sample was collected, freeze dried, homogenized and stored in glass-jar and immediately frozen before analysis, then sub-sample of each composites were analyzed for PAHs compound by the procedure which is described by Farrington and Tripp (1975), total organic matter TOC% were done according to (Gaudette *et al*., 1974), while the grain size analysis according to (Folk, 1974) method.

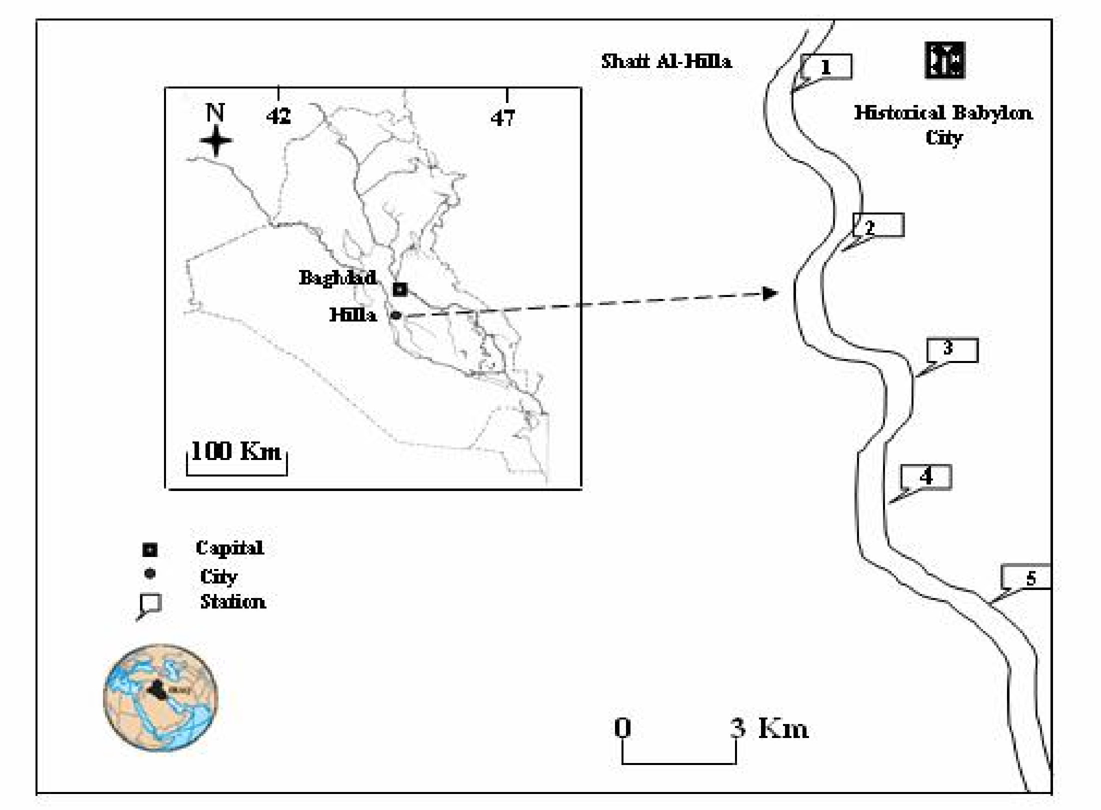

Figure (1): Sampling stations in Shatt Al-Hilla River, Iraq.

3- Results and Discussion

Sediment associated PAHs concentrations varied with sites in the individual compound, and in the total PAHs (Fig. 2, 3 and 4). The observed increases of PAHs concentration appears in site (2) could be due to the local anthropogenic combustion sources resulting from high way traffic and from automobile washing besides the presence of fuel station near the site. Between sixteen PAHs have been listed as priority pollutants and regulated by the USEPA (Prest, 2002; Akaishy *et al.*, 2004; Sarrazin, 2006), the PAHs compound which detected in Hilla sediment with genotoxicity and carcinogenicity effect were anthracene (N.D-2.382), Fluoranthene (5.373-282.922), Benz (a) Anthracene and Chrysene (3.215-148.511), Benzo (b) Fluroanthene (N.D-39.451) ng/g dry weight. The total PAHs ranged between 26.668 in site 5 to 900.042 ng/g in site 2. The PAHs which is detected in the five stations were : Acenaphthylene, Phenanthrene, Fluoranthene, Benz (a) anthracene and Chrysene while Naphthalene, Acenaphlene, Fluorene, Anthracene, Pyrene and Benzo (b)

Fluoranthene were detected in site 2 only. PAH with 2 to 5 ring appear in site 2 only. While in the other station PAHs with 2 and 3 ring appear only (Fig.5).From the total PAHs, Acenaphthylene form the greater ratio in site 3, 4 and 5 (68.66, 56.72 and 55.72 respectively) were Fluoranthene form the greater ratio in site 1 and 2 (44.525 and 31.434 respectively) (Fig.6).

In order to predict the possible sources of PAHs in Hilla river sediment, the ratio of individual PAHs Phenanthrene/Anthracene (Phen/Anth) with 3 ring-PAHs group, Fluoranthene/Pyrene (Flur/Py) with 4 ring PAHs and low molecular weight PAHs high molecular weight PAHs (LMW-PAHs/HMW-PAHs) were used. When the ratio of Flur/Pyr greater than one and Phen/Ant less than ten referred to the pyrogenic sources (Sirece *et al*., 1987; Sanders *et al*., 2002 and Zhu *et al*., 2004) the result of the present study range between (2.6-8.649) and (1.43-31.6) respectively it mean that the sources were pyrogenic and petrogenic and when the ratio of L:MW-PAHs/HMW-PAHs) is used it is known that when the ratio is <1 it referred to pyrogenic processes (Doong and Lin, 2004) so the last ratios in the present study ranged between (0.35-2.88) which mean that the sources were pyrogenic and peterogenic (Table-1, Fig.7).

TOC% in sediment ranged between 0.072 in site 4 to 0.302 in site 2 (Table-2, Fig.8) and the result showing the presence of a good correlation with total PAHs (r= 0.886).

Grain size analysis indicated that the clay percent ranged from 0.17 in site 1 to 5.6 in site 3, the percent of silt ranged from 23.81 in site 4 to 50.41 in site 1 and sand percent ranged from 49.41 in site 1 to 74.91 in site 4 (Fig.9, Table-2) there were no correlation between total PAHs with clay, silt and sand particle (r=-0.218, r=0.05303 and r=-7.95×10^{-3}) respectively the result indicate that the concentration of total PAHs in Shatt Al-Hilla sediment not dependent on grain size of sediment and this result suggested that the distribution and concentration of PAHs in studied sediment depend on direct inputs, rather than by the sediment type itself.

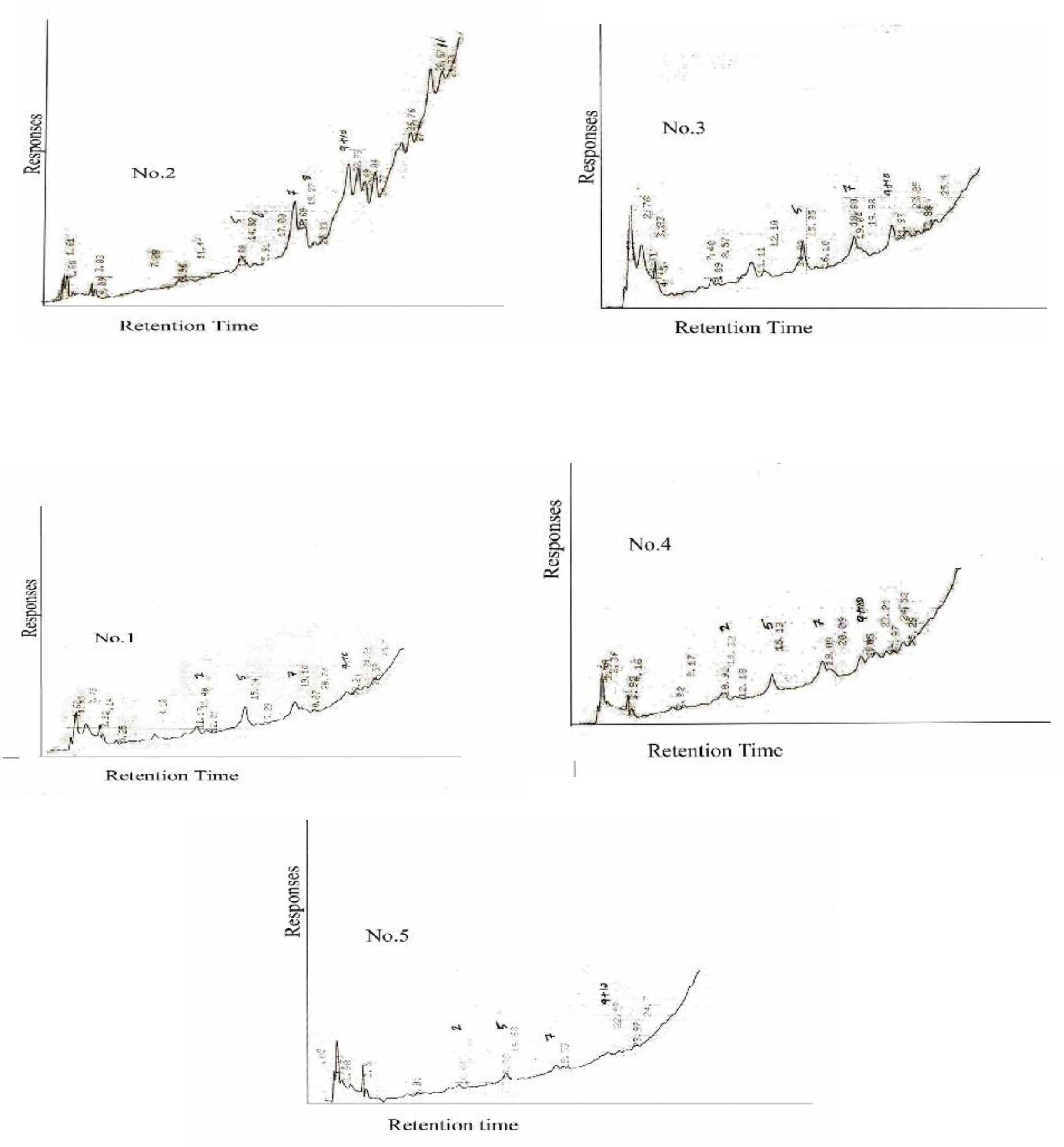

Figure (2): PAHs chromatogram of the sediment extract from Shatt Al-Hilla River, Iraq.

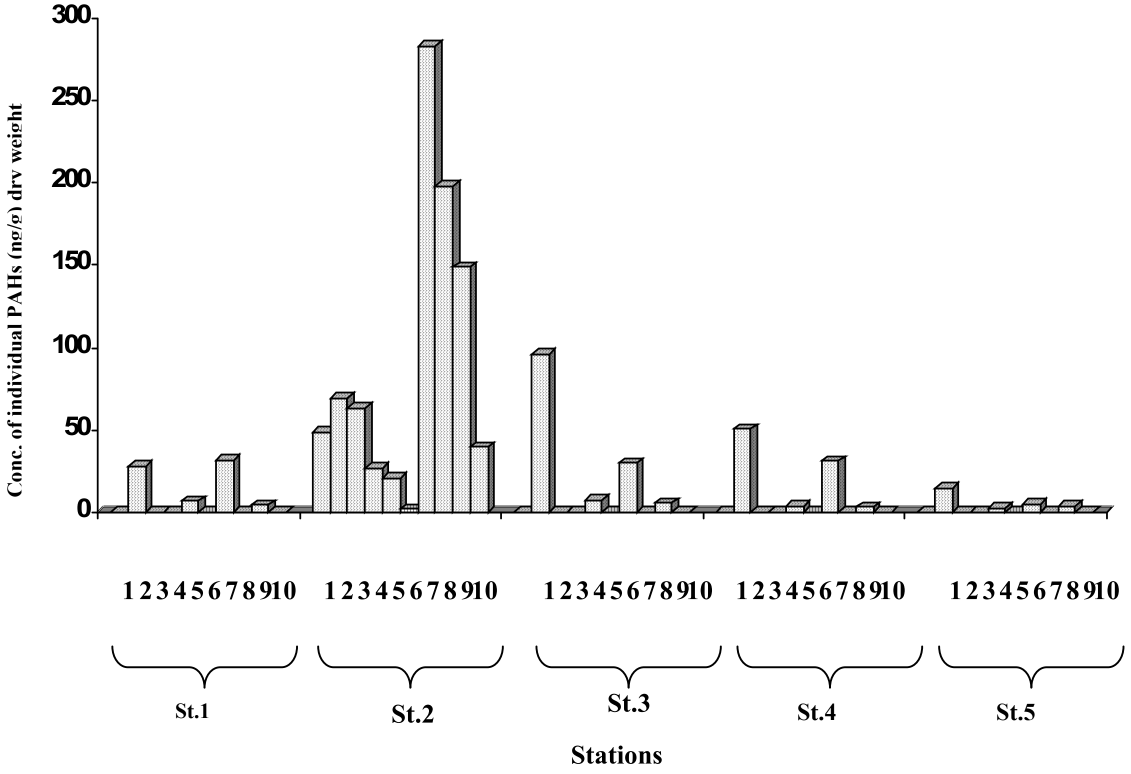

Figure (3): Compositional pattern of individual PAHs in the sediment of Shatt Al-Hilla river (1, 2,3,4,5,6,7,8,9 and 10) represent the individual PAHs (Naphthalene, Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, (Benz(a) anthracene + Chrysene and Benzo(b) fluoranthene), respectively.

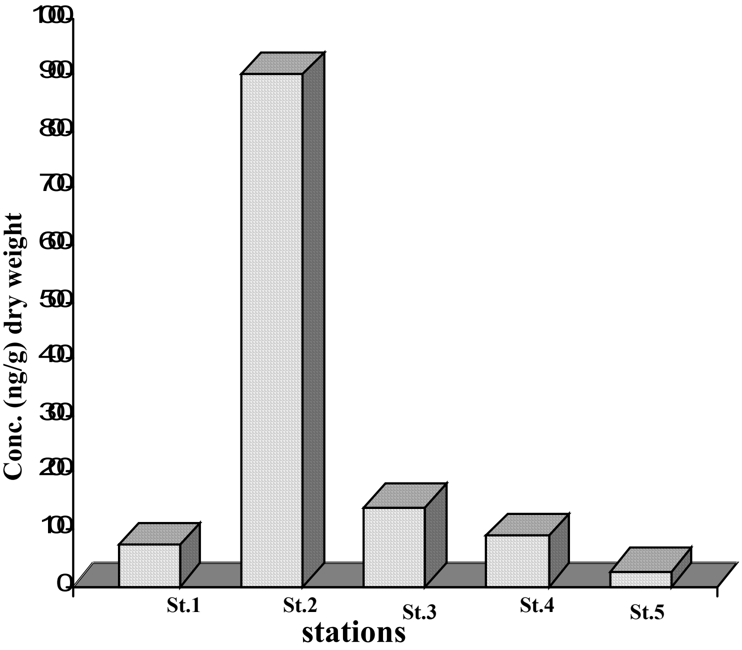

Figure (4): Total PAHs in sediment of Shatt Al-Hilla river (ng/g) dry weight.

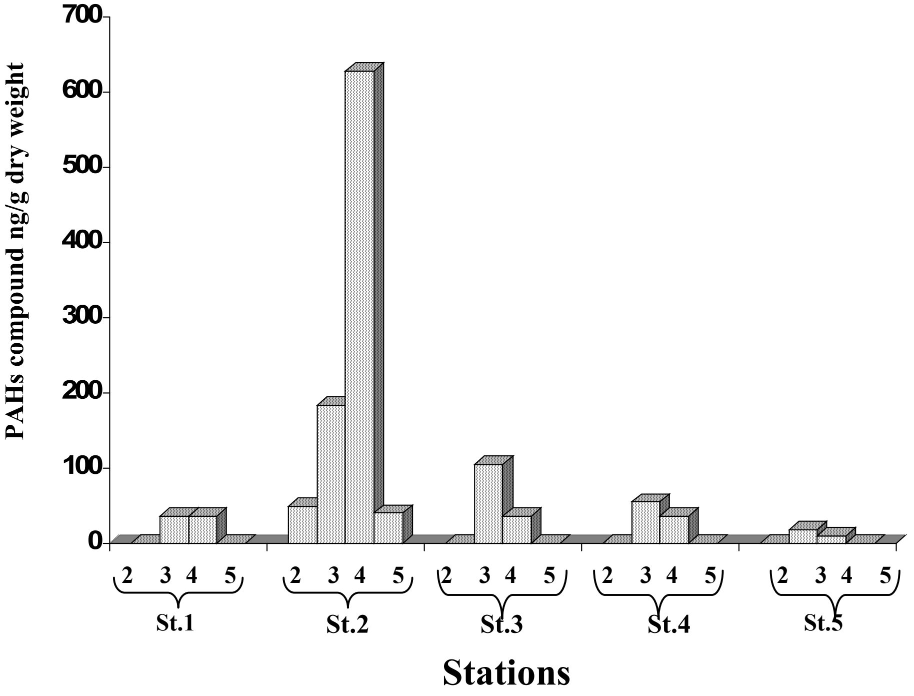

Figure (5): Rings number (2, 3, 4 and 5) of PAHs compound in Shatt Al-Hilla River sediment.

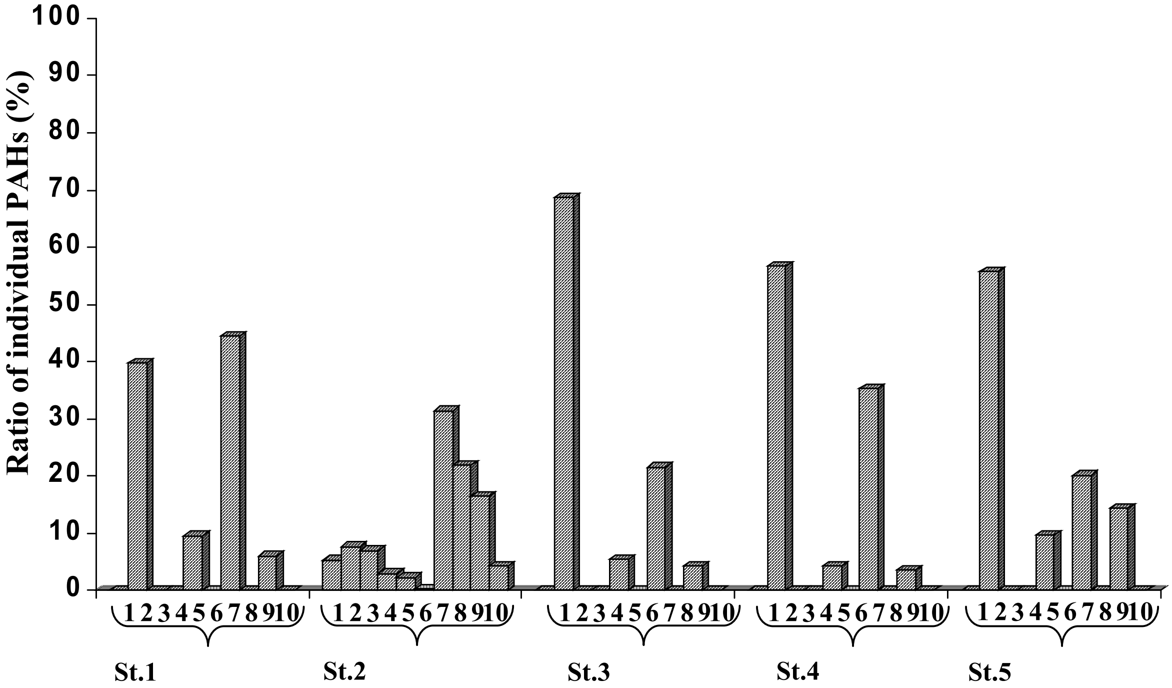

Figure (6): The ratio of individual PAHs in the sediment of Shatt Al-Hilla River (1, 2,3,4,5,6,7,8,9 and10) represent the individual PAHs (Naphthalene, Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, (Benz(a) anthracene + Chrysene and Benzo(b) fluoranthene), respectively.

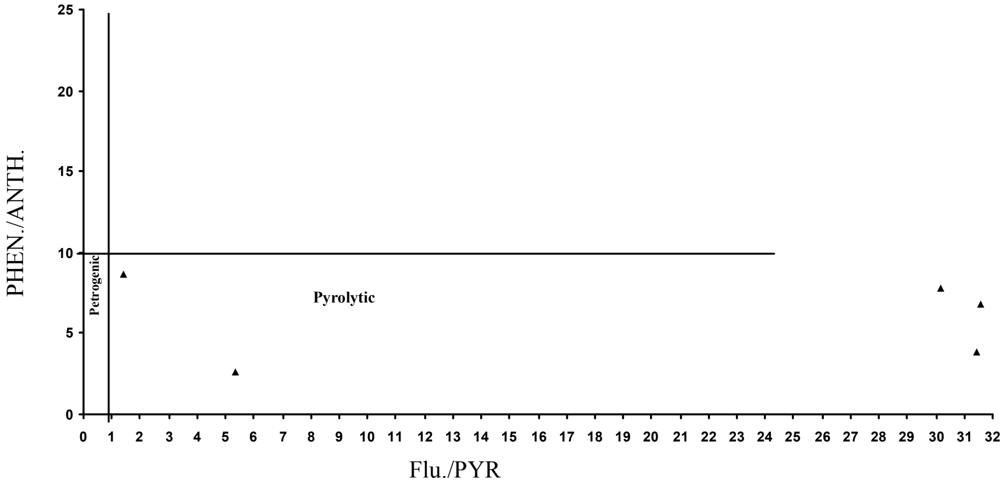

Figure (7): Plot of isomeric ratios phenanthrene vs anthracene (PHEN/ANTH) vs fluoranthene vs pyrene (Fu/PYR) for Shatt Al-Hilla River surficial sediment-Iraq.

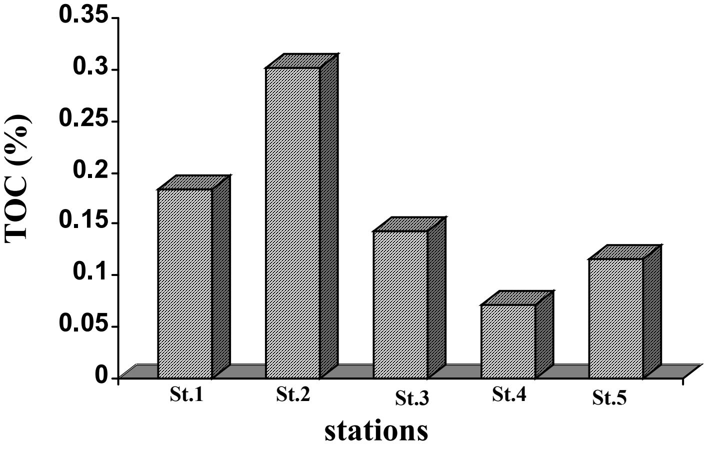

Figure (8): TOC % in sediment of Shatt Al-Hilla river (ng/g) dry weight.

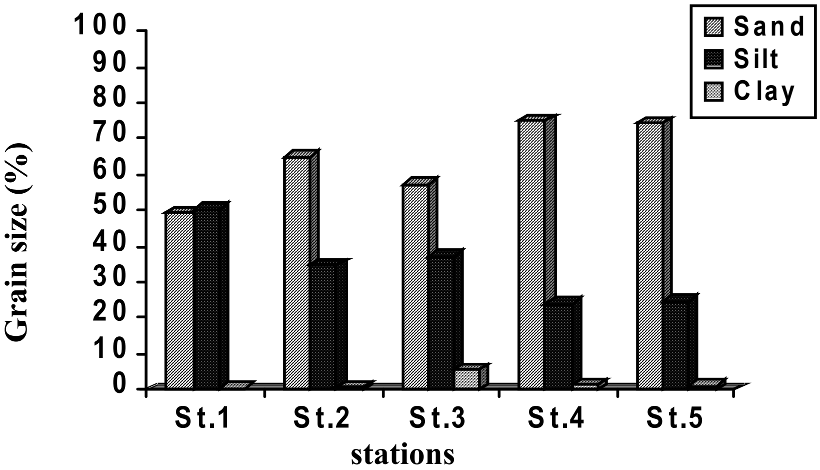

Figure (9): Grain size distribution of sediment from Shatt Al-Hilla River.

Table (1): Ratios of individual PAHs and low molecular weight to high molecular weigh and the sources of PAHs in Shatt Al-Hilla River sediment.

Ratio Site	Phen/Ant	Flur/Py	LMW-PAHs/HMW-PAHs	Sources
S.1	6.811	31.596	0.977	Pyrolytic+Petrogenic
S.2	8.649	1.431	0.346	Pyrolytic+Petrogenic
S.3	7.776	30.164	2.875	Pyrolytic
S.4	3.847	31.451	1.5668	Pyrolytic
S.5	2.600	5.373	1.896	Pyrolytic

Table (2): Total organic carbon percent, grain size distribution, name of sediment and total PAHs compound in Shatt Al-Hilla River sediment.

Station	TOC%	Sand%	Silt%	Clay%	Description	ΣPAH
1	0.183	49.41	50.41	0.172	Silt loam	70.962
2	0.302	64.88	34.62	0.500	Sandy loam	900.042
3	0.144	57.25	37.14	5.600	Sandy loam	139.981
4	0.072	74.91	23.81	1.250	Loam sand	88.982
5	0.116	74.31	24.67	1.025	Loam sand	26.668
Range	0.072-0.302	49.41-74.91	23.81-50.41	0.172-5.600	—	26.668-900.042

Acknowledgment

The Author wish to thank Dr.Taha K. for collecting field samples.

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أصل وتوزيع الهيدروكربونات الأروماتية متعددة الحلقات (PAHs) في الرواسب السطحية لنهر الحلة، العراق

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الخلاصة

يعد تواجد الملوثات العضوية في البيئة المائية خطراً حقيقياً للسلامة البيئية. جمعت عينات من الرواسب السطحية لنهر الحلة (أحد أفرع نهر الفرات الذي يبعد عدة كيلومترات جنوب مدينة المسيب، العراق) خلال عام 1995 ، لدراسة مستوى وتوزيع وأصل بعض الهيدروكربونات الأروماتية متعددة الحلقات (PAHs). قدر تركيز مركبات (النفثالين، أسينافثالين، أسينافثين، الفلورين، الفينانثرين، الأنثراسين، الفلورانثين، البايرين، البنزو – أ – أنثراسين + الكرايسين والبنزو – ب – فلورانثين) في خمسة مواقع. تراوح المجموع الكلي للمركبات من 26.668 إلى 900.042 نانوغرام/غرام وزن جاف. لوحظت اختلافات معنوية بين مواقع الدراسة الحالية المختلفة. قد يعود سبب ارتفاع بعض المركبات إلى قرب مواقع جمع العينات من المرور السريع عبر النهر كما أن أصل هذه المركبات ناجم عن pyrogenic و Petrogenic.
