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Polycyclic Aromatic Hydrocarbons (PAHs) in Sediment Samples From Euphrates River, Iraq

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International Journal of Marine Science 2016, Vol.6, No.2 doi: 10.5376/ijms.2016.06.0002

Received: 07 Dec., 2015

Accepted: 19 Feb., 2016

Published: 19 Feb., 2016

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Preferred citation for this article:

Al-Saad H.T., Ali S.T., Mahdi S, Alkafaji B.Y., and AL-Hello.A., 2016, Polycyclic Aromatic Hydrocarbons (PAHs) in Sediment Samples From Euphrates River, Iraq, International Journal of Marine Science, 6(2): 1-5 (doi: <u>10.5376/ijms.2016.06.0002</u>)

Abstract Sediment samples were collected from four selected sites along the Euphrates river near Al-Nassyira city south of Iraq during summer 2012 to winter 2013. Sixteen PAHs listed by USEPA as priority pollutants were detected. The total of PAHs ranged from 0.197 ng/g dry weight in summer at station 1 to 80.006 ng/g dry weight in winter at station 3. The LMW/HMW, Flouranthene/Pyrene and Phenanthrene/Anthracene ratio indicated that the source of PAHs was pyrogenic. Whereas BaA/(BaA+Chry) ratio indicated that the source of PAHs was pyrogenic and at least petrognic. The highest value of TOC % was 1.91% at station 3 in winter while the lowest value was 0.73% at station 1 in summer. The study shows that there is a significant correlation between TOC% and grain size in the sediment with concentration of PAH. The present study indicates that hydrocarbons exist in the study area, but its levels are in acceptable range.

Keywords PAHs; Sediment; Euphrates River; Pollution

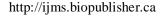
Introduction

Monitoring of some Polycyclic Aromatic Hydrocarbons (PAHs) compounds in the sediments gives a good information about their concentration, origin and distribution in the aquatic system. Polycyclic Aromatic Hydrocarbons (PAHs) with two to six rings are a class of organic contaminants mainly derived from incomplete combustion of organic matter, such as coal, fossil, fuel (M.B. et al., 2012) such as phenanthrene, fluorine, benzo [a] pyrene and pyrene as in car exhaust, while phenanthrene, fluorine and pyrine as in diesel vehicles exhaust (Azhai et al., 2011; Al-Hejuje et al., 2015). Numerous of these compounds are potential carcinogens (Al-saad, 1995). Study of the composition of hydrocarbon compounds in different marine sediments can provide much information about their sources and diagenetic processes and reflect the extent of anthropogenic pressures on the environment (Hostetter et al., 1999; Medeiros et al., 2005). Hydrocarbons generated by biological or diagenetic processes natural hydrocarbon baseline of an ecosystem (commendatore and esteves, 2004). Human activities like shipping and industrial, stromwater and domestic discharge are believed to be an important influence on hydrocarbons in aquatic sediment especially in coastal areas (Zheng and Richardson, 1999; Commendatore and Esteves, 2004). Ratio of LMW/HMW, Phenanthrene/Anthracene, Flouranthene/Pyrene and some index give an image about the sources of hydrocarbons compounds in the aquatic environment.

Study Area

The study area included 4 stations on Euphrates river in Al-Nassiryia city, and the first station was located at the entrance of the river to Al-Nassiryia city and far from the second station by 10 km which was located at convergence (junction) zone of hot water emerging from the thermal electric power station with the river. The third station was located at convergence zone stream discharging waste water, while the fourth station was located before the river left the city of Al-Nassiryia and far from the third station by 10 km (Figure 1).





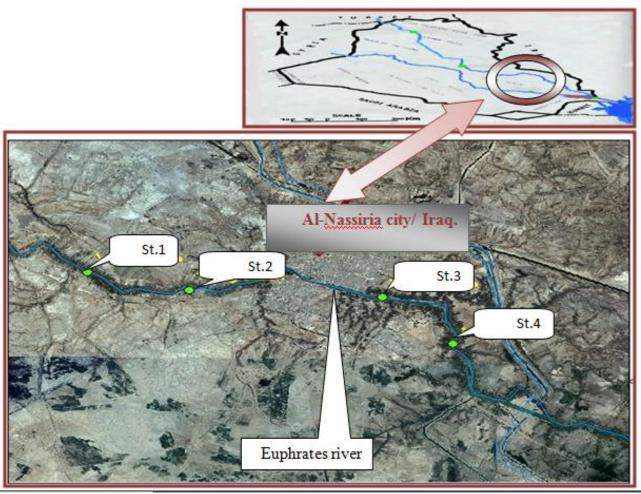


Figure 1 Study Area

Materials and Methods

Samples were collected from the above mentioned stations during summer 2012 to winter 2013. Sediment was collected by means of a Van Veen grab sampler. In lab sediment samples were dried in freeze dryer, ground finely in agate mortar and sieved through a 63 µM mesh metal sieve, stored in glasses containers until analysis. Fifty grams of sieved sediments were placed in cellulose thimble and soxhlet extracted according to method of Goutx and Saliot (1980), the sample was then analyzed in a Allegiant capillary gas chromatography (GC) in which the helium gas was used as a carrier gas with a linear velocity of 1.5 ml min⁻¹. The operating temperatures for detector and injector were 350 $^{\circ}$ and 320 $^{\circ}$, respectively. The silica capillary column was operated under initial, final and rate temperatures that programmed as follows: initial temperature was 60 °C for 4 min while final temperature was 280 $^{\circ}$ C for 30 min and rate was 4 $^{\circ}$ C/ min.

Total organic carbon TOC concentration in sediment was determined according to burning method (Ball, 1964).

Tow grams of sediments dried and (sieved < 63 mm) were put in pre-weighted crucible and burned at 550° C for 48 hrs. The difference in mass of crucible and sediment sample before and after burning was calculated as TOC. Mean grain size analysis of the sediment was carried out using the combined dry sieve and pipet techniques according to Folk (1974) method. The grain size (silt, sand and clay) was determined as percentage of sediments.

Results and Discussion

All samples were analyzed for 16 USEPA priority PAHs, including naphthalene (NaP), acenaphthene(Ace), acenaphthylene (Any), fluorine (Fl), phenanthrene (Phe), anthracene(An), fluoranthene (Fla), pyrene (Pyr),



benz[a]anthracene (BaA), chrysene(Chr), benzo [b]fluoranthene (BbF), benzo [K]fluoranthene (BKF), benzo[a]pyrene(BaP), indeno[1,2,3p-cd]pyrene (IcdP), dibenz[a,h]anthracene (dBA), and benzo[g,h,i]perylene (BPe), also measured and quantified according to the respective peak areas. The sources of PAHs to aquatic sediment are pyrogenic from combustion processes and small contribution of petrogenic source and enter the sediments from runoff and atmospheric deposition (Chen, 2001). The lowest value of (0.001ng/g) dry weight was recorded for benzo (g, h, i) perylene in summer while the highest value of (7.123 ng/g) dry weight for carbazol in winter (Table 1, 2). Some individual PAHs showed significant differences among sites. It was found that variation in the concentrations of PAHs among sites may be due to additional input source (Maskaoui et al., 2002) and the proximity of site from the source. The highest concentration recorded was obtained in winter (7.123 ng/g) dry weight while the lowest concentration recorded in summer were (0.001 ng/g) dry weight. This may be related with the climatic condition of Iraq and the effect of photo oxidation, volatilization and high degradation during the hot season (Al-Saad, 1987; Al-Hamdi, 1989; and Al-Timari, 2000). The highest concentrations were recorded at station 3 and 2 due to effluents discharged from domestic sewage treatment unit and electric power station which are located at the river bank. Although the high concentrations of PAHs in sediment, but it lie within acceptable range. The highest concentration of total PAHs were 80.006 ng/g dry weight at station 3 in winter. The lowest concentration of total PAHs were 0.197 ng/g dry weight at station 1 in summer. The highest value TOC% were 1.91% at station 3 in winter while the lowest value were 0.73% at station 1 in summer (Table3). The present results referred to significant positive correlation between TOC% and total PAHs in the sediment (r=0.81, P<0.01) which may be due to hydrophobicity nature of PAHs and their affinity to organic material or due to the fraction of TOC in the sediment (Al-Saad, 1983; Zakaria et al., 2002; Maskaoui et al., 2002). The sediment texture were mixed from (sand, clay and silt) where value was (22.4%, 86.4%, 9.3%) at station 1 while (6.58%, 80.2%, 10.2%) at station 2 while (5.71%, 77.03%, 17.25%) at station 3 and (2.33%, 26.05%, 71.61%) at station 4 respectively (Figure 2-5).

Compounds	Winter			
r	S1	S2	S 3	S4
Naphthalene	0.010	4.046	5.257	0.320
Indole	0.040	3.210	4.220	0.260
Acenaphthylene	0.003	2.363	3.010	0.020
Acanaphthene	0.020	1.350	2.260	0.035
fluorine	0.008	3.327	4.406	0.012
Phenanthrene	0.028	2.674	3.546	0.036
Anthracene	0.043	2.093	5.586	0.053
Fluoronthene	0.043	4.231	4.140	0.350
Pyrene	0.035	4.301	5.241	0.042
Carbazol	0.039	5.563	7.123	0.041
Benz(a)anthracene	0.026	3.408	6.083	0.027
Chrysene	0.007	3.238	4.627	0.042
B(b) fluoronthene	0.004	2.298	4.547	0.040
B(k) fluoronthene	0.031	2.825	3.547	0.033
Benzo(a)pyrene	0.041	3.537	5.773	0.109
indeno(1,2,3-cd)pyrene	0.003	2.652	3.039	0.110
dibenzo(a,h)anthracene	0.010	4.267	4.039	0.160
benzo(g,h,i)perylene	0.002	2.963	3.562	0.006
Total	0.393	58.346	80.006	1.696
fluoranthen/pyren	1.229	0.984	0.790	8.333
Phen/Ant	0.651	1.278	0.635	0.679
LMW-PAHs/HMW-PAHs	0.631	0.485	0.547	0.767
Ant/(Ant+Phen)	0.606	0.439	0.612	0.596
BaA/(BaA+Chry)	0.854	0.522	0.555	0.722
Flt/(Flt+py)	0.551	0.496	0.441	0.893
InP/(InP+BghiP)	0.231	0.383	0.429	0.407



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Table 2 Concentration of PAHs in sediment in summer 2012

Communeda						
Compounds	summer					
	S1	S2	S 3	S4		
Naphthalene	0.005	2.023	2.629	0.160		
Indole	0.020	1.605	2.110	0.130		
Acenaphthylene	0.002	1.182	1.505	0.010		
Acanaphthene	0.010	0.675	1.130	0.018		
Fluorine	0.004	1.664	2.203	0.006		
Phenanthrene	0.014	1.337	1.773	0.018		
Anthracene	0.022	1.047	2.793	0.027		
Fluoronthene	0.022	2.116	2.070	0.175		
Pyrene	0.018	2.151	2.621	0.021		
Carbazol	0.020	2.782	3.562	0.021		
Benz(a)anthracene	0.013	1.704	3.042	0.014		
Chrysene	0.004	1.619	2.314	0.021		
B(b) fluoronthene	0.002	1.149	2.274	0.020		
B(k) fluoronthene	0.016	1.413	1.774	0.017		
Benzo(a)pyrene	0.021	1.769	2.887	0.055		
indeno(1,2,3-cd)pyrene	0.002	1.326	1.520	0.055		
dibenzo(a,h)anthracene	0.005	2.134	2.020	0.080		
benzo(g,h,i)perylene	0.001	1.482	1.781	0.003		
Total	0.197	29.173	40.003	0.848		
fluoranthen/pyren	1.229	0.984	0.790	8.333		
Phen/Ant	0.651	1.278	0.635	0.679		
LMW-PAHs/HMW-PAHs	0.631	0.485	0.547	0.767		
Ant/(Ant+Phen)	0.606	0.439	0.612	0.596		
BaA/(BaA+Chry)	0.854	0.522	0.555	0.722		
Flt/(Flt+py)	0.551	0.496	0.441	0.893		
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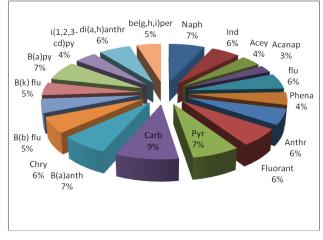


Figure 2 The PAHs compounds percentage in sediments samples during the studied periods

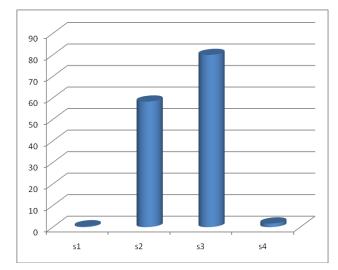


Figure 3 Total of PAHs in stations during winter 2013



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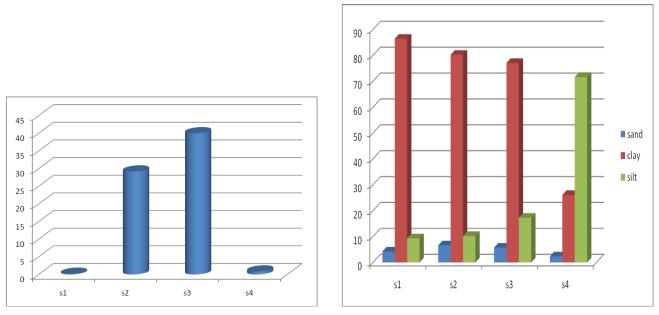


Figure 4 Total of PAHs stations during summer 2012

Figure 5 Percentage of sediment texture in study area

In the present study, the mean ratio of Phen/Ant, Flur/Py and LMW-PAHs/HMW-PAHs can provide a useful information for explanation of the origin of PAHs in the sediment. The mean ratio of Phen/Ant (0.651, 1.278, 0.635, 0.679) at station 1, 2, 3, 4 in winter respectively Phen/Ant<10 refer to pyrogenic Flur/py (1.229, 8.333) at station 1, 4 respectively Flur/py >1 refer to pyrogenic while (0.984, 0.790) at station 2, 3 respectively refer to petrognic products runoff, effluents discharged from domestic sewage treatment unit and electric power. The results prove the sources pyrogenic and least petrognic. As a conclusion the ratios of Flouranthene/pyrene, Phenanthrene/Anthracene, Benzo (a) pyrene/Benzo (ghi) perylene and LMW-PAHs /HMW-PAHs, refer to origin from different sources including pyrogenic, petrognic and urban air. The total higher concentration PAHs was at station 3, 2 in winter while the lowest concentration PAHs at station 1, 4 in summer. Strong correlation was recorded for PAHs in sediment with TOC% due to affinity to organic materials.

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