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ASSESSMENT OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHS) IN WATER AND SEDIMENTS AT SOUTH PART OF AL-HAMMAR MARSH, SOUTHERN IRAQ

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ABSTRACT

Water and sediment samples were collected during 2018 from five stations which are Lusan-Harer, Al-Musahab, Al-Mutaka, Al-Nakara and Al-Burka from south part of Al-Hammar Marsh, to estimate sixteen of polycyclic aromatic hydrocarbons (PAHs) by using capillary gas chromatography. The results of summation polycyclic aromatic hydrocarbons (PAHs) ranged 42.859-331.875 ng/L in water samples, while in sediment ranged 342.82-434.438ng/g. The study exhibited two pattern of sources petrogenic and pyrogenic with predominate the petrogenic source. Moreover, the pollution in sediments is within moderate pollution.

KEY WORD: PAHs, Water, Sediment, Al-Hammar marsh, Gas chromatography.

INTRODUCTION

One of a serious problems that received much attention globally is pollution with hydrocarbons which contaminated the sediment and aquatic environment, these compounds which have origins from crude oil and its derivations such as diesel, gasoline, lubricating oil and others were recorded highly toxic, mutagenic and carcinogenic in nature (Zhou *et al.*, 2008; Zhang *et al.*, 2015; Kuppusamy *et al.*, 2020).

The increasing of human civilization caused several perturbation in the natural balance of environment this effect is a result of consuming the petroleum hydrocarbons as essential demand of modern life (Megharaj *et al.*, 2000).

Hydrocarbon compounds are one of big group that belong to chemical compounds which consisted from carbon and hydrogen as the skeleton with some hetero atoms such as oxygen, nitrogen, chloride, sulfur and so on. The hydrocarbon compounds can be classified into three main groups: aliphatic, alicyclic and aromatic compounds (Reeves, 2000; Al-Saad *et al.*, 2017).

USEPA has mentioned there are sixteen of polycyclic aromatic hydrocarbons (PAHs) as main significance this importance come from their toxic, carcinogenic or teratogenic (Yan *et al.*, 2004; Al-Kanany *et al.*, 2017), these polycyclic hydrocarbons can be classified into two kinds: the low molecular which have two to three fused rings with their solubility in water and volatile, so they are sensitive to degradation processes, while the high molecular which have more than four fused rings with less soluble, less volatile and more lipophilic than low molecular (Al-Talal *et al.*, 2019). In 2010, IARC classified eight compounds from PAHs which have more than four fused rings (high molecular weight) as carcinogenic, since these compounds are known for resisting to degradation by microorganisms. Moreover, their ability to accumulation in sediments, aquatic plants, and aquatic organisms such as mussels and fish (Bakhtiari *et al.*, 2009).

Nevertheless, the main sources of polycyclic aromatic hydrocarbons in ecosystem came from human activities which included industrial sewage, domestic waste, municipal and urban runoff. In addition, the oil production and accidents that

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related with it such as tanker operation, refineries, oil spillage accidents as well as uncompleted combustion of fossil fuels. Besides, some of the natural processes can contribute to enter polyaromic hydrocarbon into environment these processes like volcanic eruption and forest fire (Al-Saad and Al-Timari, 1989; Jazza *et al.*, 2015; Peng *et al.*, 2016).

Generally, PAH compounds are low soluble in water and decreasing their solubility with increasing their molecular weights, so the study of sediment and suspended particles can give an excellent image about numerous types of pollutants because it was recognized reservoir of these pollutants specially hydrophobic of them which come from water column and organic composition, these trace organic composition have stability in sediment as comparison with other environmental compartments such as water, air, as well as organism. On the other hand, some different processes such as physical, chemical, and biological processes are effected on organic compounds in aquatic system because they have ability to exchange sedimentary composition that due to increase the dispersion of organic pollutants (Grimalt *et al.*, 1992; Al-Timari *et al.*, 1997; Al-Saad *et al.*, 2009).

This study focuses a light on the origins and concentrations of polycyclic aromatic hydrocarbons and compared these results with others previous

studies to evaluate the levels of pollution in water and sediments at five chosen sites during 2018 in Al-Hammer Marsh Southern Iraq.

Description of area study

Marshes in Southern Iraq were regarded as one of ancient and famous swamps in the Middle East and Western Asia besides their economic and environmental importance required by their nature. Marshes have unique ecosystem of biodiversity, so they are respected as (Eden, Paradises in Earth) (UNEP, 2006). Border of three big cities in the south of Iraq which are Nasiriyah in the west, Amarah in the northeast and Basrah in the south were formed triangular area and which may reach 20.000 Km² from enormous shallow water and lakes, these marshes were composed as a result of overflow the two great Rivers, Euphrates and Tigris.

Finally, marshes play the major role in ecosystem by their conservation of biodiversity from aquatic plants and animals which inhabited in this rich environment (Bedair *et al.*, 2006; Saleh *et al.*, 2020).

MATERIALS AND METHODS

Water and sediment samples were taken from five stations which are: Lusan Harer, Al-Musahab, Al-Multaka, Al-Nkara and Al-Burka, in south part of Al-Hammer Marsh, Southern Iraq during 2018 (Fig.



Fig. 1. The study area (Saleh *et al.*, 2020)

1), water samples were collected (5 Liter) at least from depth 15-25 cm under the surface water or wherever it was possible by using dark glass bottles and added 20 mL from CCl_4 to preserve the sample, while sediment samples collected by using a van veengrap sampler, the samples were wrapped in aluminum foil and placed in ice packed container and kept in the laboratory in deep freeze.

In the laboratory, sediment samples were extracted according to Goutx and Saliot (1980) method, whereas the water samples were extracted according to UNEP (1998).

RESULTS AND DISCUSSION

PAHs in water samples

Total concentration of polycyclic aromatic hydrocarbons at five stations in water samples ranged from 42.859 ng/L at Al-Burka to 331.87 ng/L at Al-Multaka and shown predominance of light

molecules which were Acenaphthylene, Phenanthrene, Fluorene, Anthracene and Acenaphthene whereas a Naphthalene was undetectable in all stations during the study except at Al-Multaka where recorded 3.165 ng/L. However, the heavy molecules were appeared dominance of Pyrene, Benzo[b] fluoranthene, Benzo[k] fluoranthene, Chrysene and Fluoranthene respectively. Benzo [a] pyrene, Dibenzo [a,h] anthracene, Benzo [g,h,i] perylene and Indeno [1,2,3-c,d]pyrene were undetectable in all water samples during the study (Table 1).

PAHs in sediments

Table 2 shown total concentration of polycyclic aromatic hydrocarbons in sediment at five stations ranged from 342.87 ng/g in Al-Burka to 417.18 ng/g at Lusan Harer and predominate the low molecular weights which have (2-3) fused rings were Fluorene, Phenanthrene Acenaphthylene. Whereas Acenaphthylene no detection in Al-Burka,

Table 1. Polycyclic Aromatic Hydrocarbons in Water

Compounds name	Lusan Harer water, ng/L	Al-Musahab water, ng/L	Al-Multaka water, ng/L	Al-Nkara water, ng/L	Al-Burka water, ng/L	R.S.D.
Naphthalene	0	0	3.165	0	0	±1.42
Acenaphthylene	16.158	73.483	78.307	28.739	30.503	±28.40
Acenaphthene	3.857	0	10.903	3.135	4.861	±3.99
Fluorene	20.643	15.493	29.803	10.467	0.104	±11.10
Phenanthrene	11.454	8.291	6.756	0.405	0.341	±4.93
Anthracene	90.488	0	33.006	1.474	5.506	±38.42
Fluoranthene	0	0	0	0	0.274	±0.12
Pyrene	6.811	100.973	51.571	0.189	0.042	±44.18
Benzo[a]anthracene	21.937	0	0	0	0.338	±9.77
Chrysene	0	1.809	1.639	0.109	0.05	±0.92
Benzo[b]fluoranthene	1.754	1.705	1.001	0.151	0.081	±0.81
Benzo[k]fluoranthene	85.386	33.753	115.725	0	0.759	±51.77
Benzo[a]pyrene	0	0	0	0	0	0.00
Dibenzo[a,h]anthracene	0	0	0	0	0	0.00
Benzo[g,h,i]perylene	0	0	0	0	0	0.00
Indeno[1,2,3-c,d]pyrene	0	0	0	0	0	0.00
Sum. of the PAHs	258.487	235.507	331.876	44.669	42.859	±17.85
Sum. of low M. W. of PAHs	142.6	97.267	161.94	44.22	41.315	
Percentage of low M. W. of PAHs	55.17%	41.30%	48.79%	98.99%	96.39%	
Sum. of high M. W. of PAHs	115.888	138.24	169.936	0.449	1.544	
Percentage of high M. W. of PAHs	44.83%	58.69%	51.20%	1.01%	3.60%	
low/high	1.230	0.704	0.953	98.486	26.758	
Phenanthrene/ Anthracene	0.127	0.000	0.205	0.275	0.062	
Fluoranthene/Pyrene	0	0	0	0	6.524	
Anthracene/(Anthracene/ Phenanthrene)	0.888	0.000	0.830	0.784	0.942	
Benzo[a]anthracene/ (Benzo[a]anthracene+Chrysene)	1	0	0	0	0.871	

Acenaphthene and Anthracene are no detection in Al-Musahab, whereas Naphthalene is no detection in all stations except at Al-Multaka where was 25.317ng/g. However, the domination of high molecular weights (which have more than four fused rings) was Pyrene, Benzo[b] fluoranthene, chrysene except Lusan Harer no detection, Benzo[k] fluoranthene except Al-Nkara no detection, while Benzo [a] anthracene was recorded at Lusan Harer and Al-Burka and the Fluoranthene was detected only at Al-Burka.

According to Table 3 there are three PAHs indices can be applied to assess sources and origins of PAHs in water samples. First of them LMW/HMW in this indices was shown petrogenic effected at Lusan Harer, Al-Nkara and Al-Burka while it was pyrogenic in Al-Musahab and Al-Multaka. However, the indices Phenanthrene/Anthracene unfolded predomination pyrogenic sources in all stations excepted Al-Musahab was undetectable for this indices. similarly, the ratio of Anthracene/

(Anthracene + phenanthrene) was discovered prevailing of the pyrogenic effected in all stations excepted Al-Musahab there is no detection. On the contrary, the pyrogenic source was recorded according Benzo[a] anthracene/(Benzo[a] anthracene + chrysene) in Lusan Harer and Al-Musahab while no detection in rest stations. According to Table 1 above these is one pollution indices that appeared at Al-Burka which was the ratio between Fluoranthene/pyrene where it was pyrogenic effected.

There are three indices can be applied to identify the origin sources of PAHs. The first of them LMW-PAHs/HMW-PAHs the Table above shown that the source of PAHs was petrogenic in all stations. However, pyrogenic in all stations according to Phe/Ant except at Al-Musahab was not detected similarly the source of PAHs was pyrogenic according Ant/(Ant + Phe) indices except again Al-Musahab there is on detection. In addition, there are two indices of PAHs Benzo[a]ant/Benzo[a]ant +

Table 2. PAHs in sediment samples in all stations

Compounds name	Lusan Harer sediment, ng/g	Al-Musahab sediment, ng/g	Al-Multaka sediment, ng/g	Al-Nkara sediment, ng/g	Al-Burka sediment, ng/g	R.S.D.
Naphthalene	0	0	25.317	0	0	±11.32
Acenaphthylene	12.927	58.786	62.646	229.91	0	±92.02
Acenaphthene	30.853	0	87.223	25.082	244.02	±98.43
Fluorene	100	123.943	23.842	83.739	38.892	±41.87
Phenanthrene	75.631	66.325	54.05	3.239	0.828	±35.52
Anthracene	43.39	0	26.405	11.794	2.726	±18.06
Fluoranthene	0	0	0	0	44.049	±19.70
Pyrene	54.49	80.778	41.257	1.517	2.19	±34.30
Benzo[a]anthracene	17.549	0	0	0	0.339	±7.81
Chrysene	0	14.479	13.109	0.869	2.707	±6.99
Benzo[b]fluoranthene	14.031	13.641	8.008	1.207	0.402	±6.53
Benzo[k]fluoranthene	68.309	27.002	92.579	0	0.647	±41.40
Benzo[a]pyrene	0	0	0	0	6.069	±2.71
Dibenzo[a,h]anthracene	0	0	0	0	0	0.00
Benzo[g,h,i]perylene	0	0	0	0	0	0.00
Indeno[1,2,3-c,d]pyrene	0	0	0	0	0	0.00
Sum. of the PAHs	417.18	384.955	434.438	357.358	342.87	±30.78
Sum. of low M. W. of PAHs	262.801	249.054	279.483	353.764	286.466	
Percentage Of low M. W. of PAHs	62.99%	64.69%	64.33%	98.99%	83.55%	
Sum. of high M. W. of PAHs	154.379	135.9	154.953	3.593	56.403	
Percentage of high M. W. of PAHs	37.01%	35.30%	35.67%	1.01%	16.45%	
low/high	1.702	1.833	1.804	98.459	5.079	
Phenanthrene/ Anthracene	1.743	0.000	2.047	0.275	0.304	
Fluoranthene/Pyrene	0	0	0	0	20.114	
Anthracene/(Anthracene/ Phenanthrene)	0.365	0.000	0.328	0.785	0.767	
Benzo[a]anthracene/ (Benzo[a]anthracene+Chrysene)	1	0	0	0	0.111	

chry). Which was pyrogenic at Lusan Harer and Al-Burka while it was undetectable at other stations as well as Flu/py indices appeared only at Al-Burka where was pyrogenic (Table 4).

In Fig. 2 and 3 illustrated the percentage of PAHs in water and sediment and emphasizes the truth which it the sources of PAHs are one by clear semi symmetry, where same PAHs compounds appeared in two Figures with different ratios. The study revealed that the sources of polycyclic aromatic hydrocarbons were petrogenic and pyrogenic with prevailing of Fluorene and Phenanthrene in high concentration referring to a petrogenic source, while occurrence Anthracene in most stations are indicating a pyrogenic origin and this agree with Al-Khion (2012) and Rinawati and Takada (2017) studies.

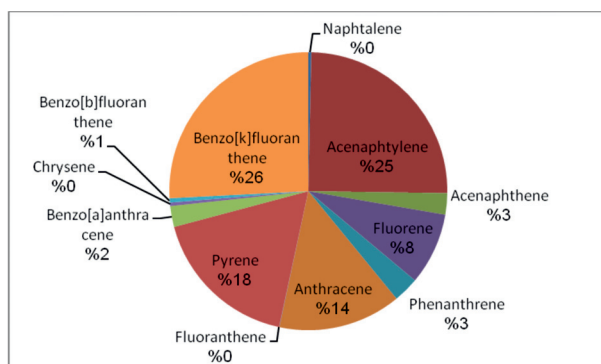


Fig. 2. Percentage of PAHs in Water Samples in area of study

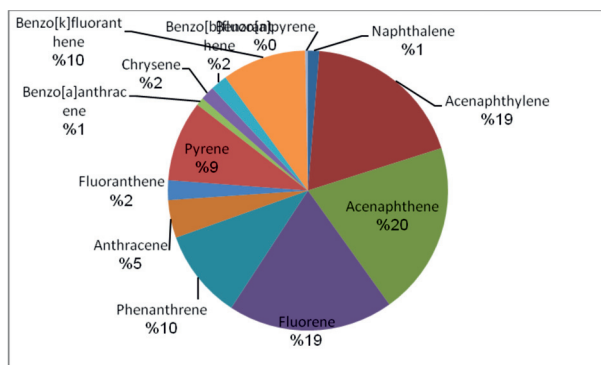


Fig. 3. Percentage of PAHs in Sediment Samples in area of study

In Fig. 4 demonstrated the pattern of total concentrations polycyclic aromatic hydrocarbon between water and sediments through the area of study which were (258.487 ng/L-527.322 ng/g) at Lusan Harer, (235.507 ng/L-384.955 ng/g) at Al-Musahb, (331.876 ng/L-434.438 ng/g) at Al-Multakam, (44.669ng/L-357.358ng/g) at Al-Nkara

and (42.859ng/L-342.87ng/g) at last station Al-Burka, where the study unfolded the increasing of PAHs in sediments in all stations with their comparison in water samples this result attributed to lipophilic of PAHs with low soluble in water and they tended to associated with particulate matters and finally precipitated in sediments (Kim *et al.*, 1999; Kafilzaadeh *et al.*, 2001). In addition, at Al-Multaka station, these is clear elevation in total concentrations of PAHs in water and sediments because this station located at confluence of two branches of rivers, Al-Musahab branch and Al-Silalbranch, these area sited in populous region and agriculture area, so it received the west discharge directly from two banks of Al-Garma River forward the north.

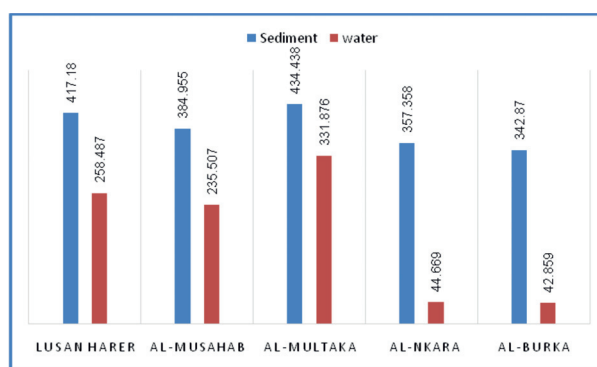


Fig. 4. Percentage of PAHs in Sediment Samples in area of study

Table 1 and 2 showed elevation of total PAH compounds, when comparison with previous studies as in Table 5 and 6 may be attributed to many reasons first of them the time of collection the samples in Winter at this time in Iraq, the temperature become low, so the degradation by various of microorganisms will reduce as well as the low rate in evaporation processes during the Winter. Moreover, at this time increasing the request of fuel and wood burning for heating that due to introduce PAHs directly into environment and this is confirmed by (Al-Saad, 1995; Al-Timari *et al.*, 2003; Al-Atbee, 2018). Besides, Al-Hammar marshes represent one of livelihood for local people so many activities can occur there such as fishing, hunting of birds and transportation by boots as well as this area regarded agriculture area all these activities can provide the marshes with oil and its derivation (Al-Khatib, 2008; Rushdi *et al.*, 2018).

Finally, Fig. 5 referred to liner relationship between the concentration of PAH compound in sediment and water where ($r^2=0.9164$). Therefore,

Table 3. The origin of polycyclic aromatic hydrocarbons in Water Samples

Station	LMW/HMW	Phe/Ant	Flu/py	Ant/Ant+Phe	Benzo[a]anthracene/ Benzo[a]anthrax +chrysene
LusanHarer	Petrogenic	Pyrogenic	N.D	Pyrogenic	Pyrogenic
Al-Musahab	Pyrogenic	N.D	N.D	N.D	N.D
Al-Multaka	Pyrogenic	Pyrogenic	N.D	Pyrogenic	N.D
Al-Nkara	Petrogenic	Pyrogenic	N.D	Pyrogenic	N.D
Al-Burka	Petrogenic	Pyrogenic	Pyrogenic	Pyrogenic	Pyrogenic

Table 4. The origin of polycyclic aromatic hydrocarbons in sediment

Station	LMW/HMW	Phe/Ant	Flu/py	Ant/Ant+Phe	Benzo[a]anthracene/ Benzo[a]anthrax + chrysene
Lusan Harer	Petrogenic	Pyrogenic	N.D	Pyrogenic	Pyrogenic
Al-Musahab	Petrogenic	N.D	N.D	N.D	N.D
Al-Multaka	Petrogenic	Pyrogenic	N.D	Pyrogenic	N.D
Al-Nkara	Petrogenic	Pyrogenic	N.D	Pyrogenic	N.D
Al-Burka	Petrogenic	Pyrogenic	Pyrogenic	Pyrogenic	Pyrogenic

Table 5. Comparison between the concentrations of total PAHs in water with previous studies.

References	Concentration ng/L	Location
Al-Hejuje, 2015	5.81-47.96	Shatt Al-Arab River/Basrah-Iraq
Jazza, 2018	18148.43-155416.327	Al-Musrah River/Misan -Iraq
Al-Atbee, 2018	2.44-37.78	Al-Chibayish marshes
Al-Agroudy <i>et al.</i> , 2017	11.71-499.59	Suez Canal/Egypt
Doong and Lin, 2003	10-4900	Gao-ping River/Taiwan
Emara <i>et al.</i> , 2008	0.002-3616.6	Mediterranean Sea/Egypt
Present stury	42.859-331.875	The southern part of Al-Hammar Marsh/Basrah-Iraq

Table 6. Comparison between the concentration of total PAHs in sediment with others studies in Iraq and World.

References	Concentration ng/g	Location
Al-Saad,1998	0.2-76.25	Shatt Al-Arab and Arabian Gulf
Al-Khatib,2008	0.1-145.8	Hor Al-Hawaiza
Al-Taee,2010	26.668-900.042	Shatt Al-Hilla
Jazza,2018	1066.47-44417.53	Al-Musrah River/Misan -Iraq
Zhou <i>et al.</i> , 2000	247-480	Xiamen Harbor/China
Kafilzadehet <i>al.</i> ,2011	167.4-530.3	The Kor River/Iran
Al-Agroudy <i>et al.</i> ,2017	103.41-238.76	Suez Canal/Egypt
Present study	342.870-434.438	The southern part of Al-Hammar Marsh/Basrah-Iraq

we can use the equation of straight line to predict of summation polycyclic aromatic hydrocarbons in water and sediment.

CONCLUSION

The study revealed the following things:-

- There are two main sources of polycyclic aromatic hydrocarbons, petrogenic and

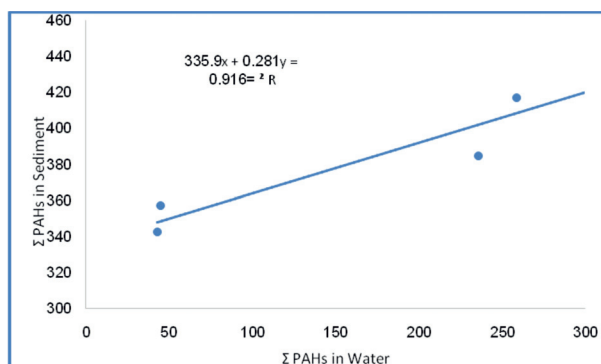


Fig. 5. Percentage of PAHs in Sediment Samples in area of study

pyrogenic with dominate the pertogenic because prevailing of low molecular weight of polycyclic aromatic hydrocarbons and this agree with Al-Khion (2012) as well as Rinawati and Takada (2017).

- According to Baumard *et al.* (1998) classification, that sediment pollution of areas study is moderate pollution.
- There is a direct variation between the total concentration of PAHs in sediment and water.

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Conflict of interests

The researcher asserts that there is no clash of interest.

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