Contamination of Polynuclear Aromatic Hydrocarbons-(PNAH) in Sediments: Identification And Distribution in the River of Shatt Al-Arab-(ROSA)

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Abstract

The sediments were analyzed for total organic carbon content-(TOCC), grain size-(GS), and PNAH levels and origins. The sediments were taken from 9 stations-(ST) on ROSA. Gas chromatography-(GC) analysis showed that the PNAH level in ROSA sediments was comparatively low to medium compared to other world locations. The PNAH total levels varied from 31.86 ng/g dry weight-(DW)-(ST 9) to 88.99 ng/g DW-(ST 6). The highest PNAH levels were close to oil pollution sources at ST 2, 4, 6, and 8. The TOCC ranged from 0.32 % to 1.64 %. The data suggested that the PNAH levels in the ROSA were linked to TOCC and GS. The PNAH compounds and ratios and analysis of principal components-(AOPC) indicated that the PNAH sources in the river were biogenic-(organisms), pyrogenic-(combustion), and petrogenic-(petroleum). Ecological risk evaluation showed that PNAH did not cause any deleterious impacts on the ROSA.

Keywords: *Water pollution, aromatic hydrocarbons, organic carbon, Shatt Al-Arab.*

Introduction

The PNAH are a widespread and stable group of pollutants in the aquatic environment. They have long transportation capacity and causes harmful environmental impacts[1]. There are many PNAH in nature but 16 compounds of them are usually studied, classified by the US-EPA as highly toxic. PNAH are generally hydrophobic and slightly soluble in water. PNAH of high-molecular-weight-(POHMW)-($\leq$ 4 rings) are slightly soluble in water, low evaporation and highly lipophilic than PNAH of low-molecular-weight-(POLMW)-($\geq$ 3 rings)[2].

Because of the hydrophobic nature of PNAH, tend to correlate with organic materials in the aquatic environment, so sediments are the ultimate PNAH stores in the water and are a good tools for monitoring PNAH[3]. The PNAH accumulation in sediments is due to the industrial and nature releases of them[4]. PNAH industrial emissions include petrogenic and pyrogenic sources. Pyrogenic sources include fossil fuel combustion, trees and weeds burning, and volcanic eruptions, etc. Whereas, PNAH petrogenic sources are linked to the spills of oils[4]. The PNAH from petrogenic or pyrogenic sources show different behaviors and distribution. Pyrogenic PNAH are more closely associated with sediments and resistant to biodegradation than petrogenic[2].

Exposure to hydrocarbons has many health-damaging effects such as reproductive disorders, mutations in DNA, and cancer. Several guidelines for estimating PNAH damage to aquatic organisms have been documented by authors and environmental concern international organizations[1].

The employ PNAH ratios having the same molecular mass enables us to explain the PNAH formation and sources. Various criteria have been established to

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demonstrate the PNAH origin in aquatic sediments such as phenanthrene/anthracene-(PH/AN), fluoranthene/pyrene-(FL/PY), anthracene/anthracene+phenanthrene-(AN/AN+PH), benzo[a]anthracene/benzo[a]anthracene+chrysene-(BA/BA+CH), and fluoranthene/fluoranthene+pyrene-(FL/FL+PY)[6].

Despite great global interest in the PNAH effects on the ecosystem. Little is known about their concentrations and sources in some world countries. Iraq has many industries, but it has not focused much on monitoring PNAH in its environment. There is also restricted knowledge about the range to which different combustion processes attribute to PNAH releases.

This paper aims to study the PNAH existence, distribution and sources in the ROSA sediments. The ROSA is an important and unique ecosystem due to the presence of many aquatic habitats and species that live in a completely different environment (Arabian Gulf). However, it is described as having considerable inputs of various pollutants that come from urban areas and industrial locations. This ecosystem, over the years, due to its proximity to many villages, towns and various human activities such as agricultural, industrial and municipal efficacies, possesses the PNAH accumulation and other pollutants in its sediments[7].

The study area is located in the city of Basrah, between longitudes, 29°56’33.8’’ N and 30°48’10.6’’ N and latitudes, 47°45’03.8’’ E and 48°34’37.4’’ E in southern Iraq. The region consists of a number of urban, suburban, and rural settlements surrounding the ROSA. Many lands in the area are used to grow different crops and trees. Solid waste disposal and wastewater treatment sites are also part of land use. Moreover, the area is distinguished for containing some heavy and light industries, in addition to power stations and oil refineries scattered along the ROSA banks. The area also has sites for burning municipal, agricultural and household waste. The average annual temperature is 25 °C, ranging from 13 °C-(January) to 33 °C-(July). The average annual downpour is 141 mm, and its duration is from October-(1 mm) to December-(29 mm).

Materials and Methods

The used glassware has been completely cleaned out. All solvents were of an analytical degree and distilled before work. Anhydrous sodium sulfate-(Na_2SO_4) ashed in 450 °C. Silica and alumina were solvents washed and dried prior to use.

Forty-five samples of superficie sediment were taken at a depth of 10-30 cm from 9 ST located along the ROSA during 2019. The ST were Karmatt-Ali-(ST 1)-(30°48’10.6” N-47°45’03.8” E), Nahran-Amar-(ST 2)-(30°45’05.0” N-47°39’53.0” E), Al-Hurtha-(ST 3)-(30°39’48.0” N-47°44’41.0” E), Basrah-Center-(ST 4)-(30°33’00.0” N-47°47’10.0” E), Abu-Al-Khaseeib-(ST 5)-(30°27’44.5” N-48°00’06.0” E), Abadon-(ST 6)-(30°03’42.0” N-48°27’03.0” E), Al-Sibea-(ST 7)-(30°20’16.5” N-48°15’34.5” E), Al-Faw-(ST 8)-(29°58’28.6” N-48°29’09.5” E) and Ras-Al-Beshea-(ST 9)-(29°56’33.8” N-48°34’37.4” E).The samples were then transferred to the laboratory with plastic bag and stored at 3.5 °C. The sediments were exsiccated, homogenized, grinded with mortar and maul, and sifted with 400 µm sieve before analysis.

PNAH was extracted from sediment samples depending on the procedure of Jiao et al.[2]. About 30 g of sediment was placed in Soxhlet and extracted for 18 hours using hexane and methylene chloride (250 ml, 1:1). The extract was reduced to 2.5 ml by nitrogen gas. The extract was then cleaned up with a chromatographic column containing activated silica and alumina (10 g, 100-200 mesh) and Na_2SO_4 (1 g). PNAH was eluted with benzene (20 ml). Benzene was removed and the remaining sample was analyzed by GC.

To validate the sediment samples, they were spiked with a standard mixture (1 µl, 100 mg/l) of 16 PNAH to distilled water (500 ml) pre-extracted with solvent (30 ml) (blank). After that, the spiked sediments were extracted and analyzed. The PNAH standard were employed to calibrate the GC.

The PNAH were analyzed by using GC-(Agilent-USA) equipped with flame ionization detector-(FID) (Agilent-USA). The detector and injector running temperatures were 300 °C and 320 °C. The column temperature was set at 50 °C to 8 minute and then 8 °C/minute for 350°C. The rate of PNAH standards recoveries ranged of 87.6 % to 96.8 %. The limit of detection varied of 0.16 to 0.81 ng/g DW.

The sediment GS analysis was performed based on the traditional procedure of Folk[8]. The TOCC were estimated by titration technique of Walkey's and Black[9].

PNAH concentrations were statistically analyzed. The standard error-(SE) for replications was calculated. One-way analysis of variance-(ANOVA) was used to compare between samples multiple groups. Statistical significance was determined as P <0.05. The AOPC was employed to identify different PNAH sources. The data on the correlation matrix was analyzed by SPSS-(version16) of Windows-(I.B.M., Armonk, USA).

Result and Discussion

PNAH are introduced to the aquatic environment through natural and industrial operations[4]. The PNAH estimation in the ROSA sediments reflected their emission sources (pyrogenic or petrogenic). The total PNAH (naphthalene-(NA), acenaphthylene-(AC), acenaphthene-(AE), fluorene-(FU), phenanthrene-(PH), anthracene-(AN), fluoranthene-(FL), pyrene-(PY), benzo[a]anthracene-(BA), chrysene-(CH), benzo[b]fluoranthene-(BF), benzo[k]fluoranthene-(BK), perylene-(PE), benzo[a]pyrene-(BP=), indeno[1,2,3-cd]pyrene-(IP) and benzo[g,h,i]perylene-(BG)) concentrations ranged from 31.86 ng/g DW-(ST 9) to 88.99 ng/g DW-(ST 6) with high concentrations in the ROSA sediments close to the locations of high pollution sources (ST 2, 4, 6 and 7) (Fig. 1). The ROSA is habitat of numerous industries and human events, which may illustrate the marked variation in PNAH concentrations in the different ST sediments. The ROSA is exposed to PNAH pollution from various sources, including sewage waste, the waste of industrial, agricultural and household and the oil disposal from petroleum refineries and tankers, as well as the oil natural leakage from the ROSA oil production sites[7]. By comparing of the PNAH levels in the ROSA sediments with other world sites, the PNAH levels are high compared to studies of Wang et al.[10] and Zrafi et al.[6], and lower than those reported by Shilla and Routh[1] and Adeniji et al.[11].

The PNAH determination origin depends on the aromatics identification of particular sources. The FL and PY existence refers the pyrolysis importance because these components consist of condensing POLMW at elevated temperatures[6]. The CH is an ideal aromatic that indicates to petroleum origin because of its resistance to biodegradation and non-biological factors[12]. Therefore, the high CH concentration in the ROSA sediments (ST 2, 4, 6 and 7) suggest a petrogenic origin. The PE origin remains dialectical. Lin et al.[3] reported the PE origin in the marine environment sediments from terrestrial organisms. While, Wang et al.[11] showed that the PE origin is more from the aquatic environment. Shilla and Routh (2018) indicated that the PE source in the marine sediment is organic detritus. Likewise, small PE concentrations may come from industrial activities (Zrafi *et al*., 2013). In current sediments, PE is present in all ST (5.57 - 8.78 ng/g) with high concentrations at ST 1, 3, 5, 8 and 9, a large part of which is reckoned to the terrestrial origin.

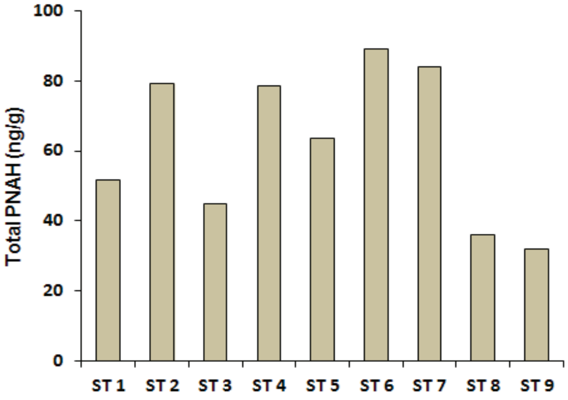

Fig. 1: PNAH spatial profiles in the ROSA sediments.

POLMW and POHMW identification is a valuable tool in determining oil pollution sources. Petroleum sources have comparatively high levels of POLMW-(2 and 3-rings), while POHMW-(≤ 4-rings) is an ideal feature of pyrolysis sources[1]. In the ROSA sediments, POHMW-(4 to 6-rings) predominated over POLMW (Fig. 2). This may be due to the high POHMW adsorption by sediments and POLMW constantly subjected to the biodegradation[10]. POHMW has been found to be environmentally stable caused carcinogenicity and genotoxicity, and these effects increase as their molecular weight increases[11].

With the geochemistry advancement, some ratios were developed to distinguish between PNAH sources. PH/AN <3 denotes pyrogenic source and >3 indicates petrogenic source[3]. FL/PY ratio of less than 1 indicates a petroleum source, while a ratio greater than 1 refers pyrolysis[6]. AN/AN+PH ratio of less than 0.1 indicates petroleum and diagenesis origin, while more than 0.1

are properties of combustion operations[4]. FL/FL+PY less than 0.4 denotes crude oil, diesel and gasoline combustion, and between 0.4 to 0.5 refers crude oil burning and more than 0.5 indicates to pyrogenic sources[1]. BA/BA+CH <0.20 is the petroleum characteristic, from 0.20 to 0.35 indicates crude oil burning, and more than 0.35 means combustion processes[11]. The current ratios indicated that the sediments PNAH in the ST 2, 4, 6 and 7 are from petrogenic and combustion sources. While the PNAH source in the ST 1, 3, 5, 8, and 9 may be from the pyrolysis origin (Table 1), however, the last ST cannot be excluded from the petroleum inputs due to the presence of many oil effectiveness in the ROSA attributed to PNAH.

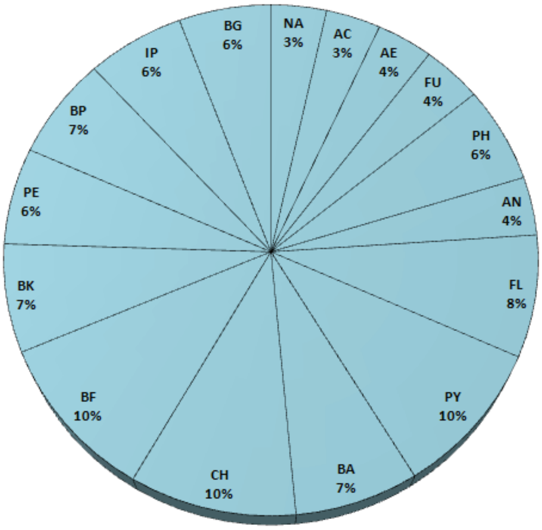

Fig. 2: PNAH distribution in the ROSA sediments.

PNAH contamination sources were identified in the ROSA sediments using AOPC. The major components in AOPC results formed 41.3%, 18.9% and 12.1% of the total variance (Table 2). PC-1 was highly loaded on POLMW, and identified as petrogenic. PC-2 was strongly loaded on parent-PNAH, and could be identified as a pyrogenic. PC-3 was heavily loaded on none of the PNAH, which was determined as an unknown source. The AOPC data showed that there are various PNAH sources in the sediments.

Several factors affecting PNAH levels have been found in sediments. Among them, TOCC and GS are examined in this study. TOCC % and GS for the sediments are shown in Table (3). TOCC % ranged from 0.33 % (ST 9) to 1.63% (ST 6). The difference in TOCC between ST sediments may be due to the variation in environments and organic matter sources. A direct relationship has been found between PNAH and TOCC % (r= 0.99). The organic matters significance for sediments in the PNAH partitioning demonstrated by[4].

Guidelines of sediment quality-(GOSQ) are a good instrument for assessing the harmful effects of pollution in aquatic sediments[11]. The range of low impacts-(ROLI), range of medium impacts-(ROMI), level of threshold impacts-(LOTI), and level of probable impacts-(LOPI) are employed to estimate the PNAH environmental toxicity in sediments (Fig, 3). In the following chemical concentrations ranges, the harmful bio-influences anticipated scarcely (<ROLI/LOTI), occasionally (≥ROLI/LOTI and <ROMI/LOPI) and repeatedly (≥ROMI/LOPI) (Olayinka *et al*., 2019). The estimations exhibited that PNAH concentrations were lower than the values of ROLI and LOPI at all investigating ST by comparing pollutant levels with GOSQ. It can be concluded that PNAH does not cause any harmful bio-effects in the ROSA sediment.

Conclusions

Sediment analysis provides worthy data on the PNAH levels and origins in the environment. This investigate demonstrated the dominance of POHMW over POLMW. Comparing with other world sediments, PNAH contamination was moderate. The most polluted ST with PNAH are close to heavy oil pollution sources (ST 2, 4, 6 and 7). The PNAH distribution in sediments shows a direct relationship with TOCC and GS. PNAH environmental risk assessment indicated that PNAH levels do not produce any instant bio-effects on the ROSA. Depending on PNAH profiles, markers and ratios and AOPC can be deduced that the PNAH origin in the ROSA was biogenic-(biosynthesis and biodegradation), pyrogenic-(combustion of fossil fuel, coal, wood, etc.), and petrogenic-(oils). Further investigates should be done on PNAH to detect their impacts and control their elevated levels harmful to mans, animals and plants in the ROSA.

Table 1: PNAH ratio in the ROSA sediments.

Ratio	**ST 1**	**ST 2**	**ST 3**	**ST 4**	**ST 5**	**ST 6**	**ST 7**	**ST 8**	**ST 9**
PH/AN	0.660	9.085	0.841	7.719	1.093	7.918	8.730	0.527	0.480
FL/PY	3.708	0.311	2.801	0.707	3.459	0.521	0.292	3.155	3.069
AN/AN+PH	0.468	0.080	0.374	0.208	0.355	0.130	0.087	0.514	0.624
BA/BA+CH	0.294	0.242	0.768	0.396	0.282	0.295	0.461	0.531	0.659
FL/FL+PY	0.637	0.291	0.555	0.367	0.602	0.286	0.291	0.610	0.574

Table 2. PNAH principal components-(PC) factor loading in the ROSA sediments.

PNAH	**PC-1**	**PC-2**	**PC-3**
NA	0.94	0.24	0.27
AC	0.92	0.43	0.17
AE	0.85	0.32	0.52
FU	0.93	0.18	0.19
PH	0.87	0.29	0.55
AN	0.74	0.26	0.21
FL	0.37	0.78	0.27
PY	0.14	0.96	0.31
BA	0.35	0.85	0.55
CH	0.37	0.94	0.06
BF	0.33	0.84	0.35
BK	0.25	0.78	0.36
PE	0.43	0.88	0.15
BP	0.24	0.83	0.24
IP	0.18	0.77	0.14
BG	0.33	0.84	0.08
Variance (%)	18.9	41.3	12.1

Table 3. Sedimentary properties of the ROSA.

ST	Sediment kind	TOCC (%)
1	Puddly-Sand	0.68
2	Sandy-Slime	0.96
3	Slime	0.61
4	Sandy-Slime	0.82
5	Sandy-Slime	0.73
6	Sandy-Slime	1.63
7	Sandy-Slime	1.01
8	Sandy-Cay	0.56
9	Sandy-Slime	0.33

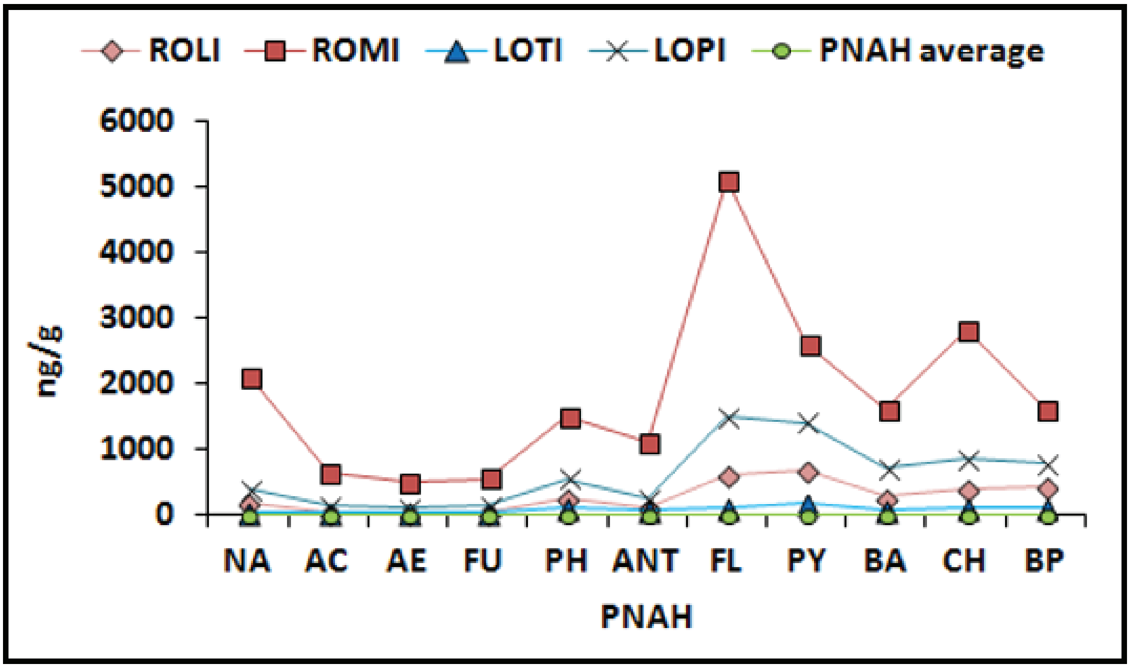

Fig. 3: PNAH average in the ROSA sediments relative to ROLI, ROMI, LOTI, and LOPI.

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Conflict of Interest- Nil

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Ethical Clearance- College

References

1. Shilla DJ, Routh J. Distribution, behavior, and sources of polycyclic aromatic hydrocarbon in the water column, sediments and biota of the Rufiji Estuary, Tanzania. Frontiers of *Earth Science*, 2018; 6: 70.
2. Jiao W, Wang T, Luo W, Hu W, Lu Y. PAHs in surface sediments from coastal and estuarine areas of the northern Bohai and Yellow Seas, China. *Environmental* Geochemistry and *Health*, 2012; 34(4): 445-56.
3. Li Q, Wu J, Zhao Z. Spatial and temporal distribution of Polycyclic Aromatic Hydrocarbons (PAHs) in sediments from Poyang Lake, China. PLoS ONE, 2018; 13(10): e0205484.
4. Chen Y, Jia R, Yang S. Distribution and source of polycyclic aromatic hydrocarbons (PAHs) in water dissolved phase, suspended particulate matter and sediment from Weihe River in northwest China. International Journal of Environmental Research and Public Health, 2015; 12(11): 14148-14163.
5. Lin T, Hu L, Guo Z, Qin Y, Yang Z, Zhang G, Zheng M. Sources of polycyclic aromatic hydrocarbons to sediments of the Bohai and Yellow Seas in East Asia, Journal of *Geophysical* Research Atmospheres, 2011; 116(D23): 23305.
6. Zrafi I, Hizem L, Chalghmi H, Ghrabi A, Rouabhia M, Saidane-Mosbahi D. Aliphatic and aromatic biomarkers for petroleum hydrocarbon investigation in marine sediment. Journal of Petroleum Science Research, 2013; 2(4): 146-155.
7. Farid WA. Assessment of Aliphatic Hydrocarbons in Sediments of Shatt Al-Arab River, Southern Iraq, North East Arabian Gulf. American Journal of Environmental Sciences, 2017; 13(6): 398-411.
8. Folk RL. Petrology of sedimentary Rocks. Hemphill publishing Co.Austin ,Texas, USA, 2017; 182 pp.
9. Walkey A., Black IA. An examination of the Degtjareff method for determining soil organic matter, and a proposed modification of the chromic acid titration method. Soil Science, 1934; 34: 29-38.
10. Wang C, Wang W, He S, Due J, Sun Z. Sources and distribution of aliphatic and polycyclic aromatic hydrocarbons in Yellow River Delta Nature Reserve, China Applied Geochemistry, 2011; 26: 1330-1336.
11. Adeniji AO, Okoh OO, Okoh AI. Levels of polycyclic aromatic hydrocarbons in the water and sediment of Bufalo River Estuary, south Africa and their health risk assessment. Archives of Environmental Contamination and Toxicology, 2019; 76: 657-669.
12. Tansel B, Fuentes C, Sanchez M, Predoi K, Acevedo M. Persistence profile of polyaromatic hydrocarbons in shallow and deep Gulf waters and sediments: Effect of water temperature and sediment-water partitioning characteristics. Marine pollution bulletin, 2011; 62(12): 2659-2665.