Determination of Priority Poly Aromatic Hydrocarbons Using Solid Phase Extractionand HPLC in Diyala River

Hadi Hassan Jasim and Muntadhar Salih Sultan[1]
Department of Chemistry, University of Al-Mustansiryah, Baghdad-Iraq.
[1]E-mail: muntadharsss@yahoo.com.

Abstract

In this paper sixteen polycyclic Aromatic Hydrocarbons (PAHs) were estimated in eight sites along Diyala River where entering Baghdad province until flows into Tigris River, (PAHs) organic compound dscontain two or more fused rings. Some of these compounds are classified as carcinogenic and mutagenic pollutants. Solid Phase extraction was used in this work to concentrate PAHs in water samples using Sep-back C18 showed percentage recoveries between (82-97) percent. High Performance Liquid Chromatography (HPLC) with UV-Vis detector was used for determination of PAHs. The result of PAHs concentrations were found in the water samples range between (zero -186.86)ng/ml. According to our results sites number one, two, six, seven and eight have the least values of total PAHs concentration with 10.8, 12.0, 39.3, 30.7 and 14.9 ng/ml respectively, while, three, four and five sites have a largepolluted with 396.5, 660.9 and 189.5 ng/ml respectivelybecause these sites are near pollutants sources. Naphthalene, Anthracene and Fluoranthene with total concentrations415.8, 259.2 and 286.4 ng/ml respectively, compounds Benzo [a] pyrene and Dibenz [a, h] anthracene arenot detected in all sites.

Keywords: poly aromatic hydrocarbons (PAH), High performance liquid Chromatography (HPLC), Solid Phase Extraction (SPE), Diyala River.

Introduction

Polycyclic aromatic hydrocarbons, also known polynuclear aromatic hydrocarbons, contain more than one fused rings without heteroatoms or substituents [1]. American Environment Protection Agency (USEPA) and the European Community [2-5] classified sixteen PAHs as priority pollutants (Acenaphthene (Ace), Acenaphthylene (Acy), Anthracene (Anth), Benz [a] anthracene (B[a]anth), Benzo [a] pyrene (B[a]p), Benzo [b] fluoranthene, (B[b]flan), Benzo [ghi] perylene (B[ghi]pery), Benzo [k] fluoranthene (B[k]flan), Chrysene (chy), Dibenz (a,h) anthracene D[a,h] anth, Fluoranthene (Flan), Fluorene (Fln), Indeno (1,2,3-cd) pyrene (I[123-cd]py), Naphthalene (Naph), Phenanthrene (Phe) and Pyrene (py))[1-3]. PAHs classified as important environmental pollutants because they have high stability [5], and their accumulation action in food chain in fatty tissues [4]. High molecular weight of PAHs such as benzo [a] pyrene have carcinogenic and mutagenic action [3, 6], low molecular weight PAHs also have toxic equivalence factor [7]. PAHs introduced to the environment from natural and anthropogenic process essentially from incomplete combustion of fossil fuel (coal, petroleum) in power station process, vehicular emissionand domestic heating [3, 8]. Diyala River is important tributary of the Tigris River [9]. Diyala River Enters into the city of Baghdad from the east passing through areas where the sewage waterare thrown into river this enhanced the pollution, then enter Rustumiya area, where that is the largest heavy water treatment plant in Baghdad, the outlet of this big plant run into the river after treatment, then Diyala River run into the Tigris River. The information in literature regarding PAH levels in Iraqi environmentis very rare. The aim of this paper is to determine the concentrations of PAHs in diyalaand Tigris Riversin Baghdad at several locations.

Experimental Sample collection and preparation

Samples were collected from eight selected pointsalongdiyalaand Tigrisriverswater. The sampling sites were distributed in such a way that three of them before Al-rustamiya sewage treatment station and two sites after station, last three sites are selected before and after entry Diyala River in the Tigris River as shown in Fig.(1).

Fig.(1) Diyala and Tigris rivers confluence in Baghdad.

Water sample were collected using polyethylene containers five liter volume, cleaned by diluted chromic acid, then washed with distilled water. In the site, containers shake well with river water twice then filled with water. Filling procedure was by immersing containers in river in the same current direction of water at 30 cm depth, then sealed lock immediately. The samples were collected stored in the refrigerator at (0-4 ^{o}C) in a dark place until the test.

Materials

PAH Standard Kit used in this study was supplied by SUPELCO Analytical and Sigma-Aldrich GmbH/ Germany. Themobile phase solvents used in the study (Acetonitrile, Methanol and Water) HPLC grade supplied from (sigma-Aldrich, HiMedia Laboratories England & J.TBaker Netherland) respectively.

Instruments and Materials

High performance liquid chromatography (HPLC): type Shimadzu (LC–20 AD) was

used for separating and detecting PAHs compounds with Column type (EC 160/4 NUCLEOSIL 100-S C18 PAH): Stainless steel, Length 150mm, I.D 4.6 mm, the column specially designed for PAHs analysis according to USEPA and specification are Stationary support Silica, polymeric coated, spherical Particle shape, 5µm Particle size, bonded phase with Special high-purity octadecyl-modified silica phase, Pore size 100^{o}A. UV-Vis detector used (Shimadzu SPD-20A Prominence).A special syringe made for HPLC type (M. SYRINGFE, 100F-LC) was used forinjection of sample of 20 µl into mobile phase to column.

Preconcentration by Solid Phase Extraction

Solid phase extraction techniques used column type (CHROMABOND C18 PAH supplied from MACHEREY-NAGEL Company) to give guaranteed results. Extraction column was conditioning by add 6 ml methanol, then 6 ml distilled water.1000ml of each water samplewere filtered by wattman filter paper, 10 ml methanol was added to each water sample, and passing through extraction column (flow rate 15 to 20 ml/min), and thenthe extraction column was dried by stream of nitrogen for 10minute. 10 ml of acetonitrile was eluted through the dried column and finally concentrated to less than 1 ml by rotary evaporator and complete volume to 1 ml.

Results and Discussion

HPLC Analysis

Analytical chromatography was performed with a flow rate of 1.0 ml/min at room temperature. The injection volume was 20 µL. The column was stabilized for at least 2 hoursuntil uniform zero baseline before chromatography. Many conditions are carried out and studied for best separation. Best separation condition found with isocratic mobile mixture phase prepared from acetonitrile, methanol and water (65, 15 and 20 %) respectively at 260 nm wavelength. The output signal from the UV-Vis detector was displayed continuously on the computer. Each PAH test alone to detect retention time then test mixture of sixteen PAHs together for each concentration. Calibration curve was constructed from the relation between the concentrations of each PAHs (1, 2, 3, 4 and 5 µg/ml) and its absorbance through the area of HPLC chromatogram using UV-Vis detector.

Each water sample were collected are carried out with HPLC at the best conditions to separate and detect concentrations of sixteen PAHs.

Samples were collected at the water surface and 30 cm below water level from the edges and the center of the river in order to be near to the actual samples for the river water pollution from the eight different sites. Solid phase extraction technique should be used for preconcentration of PAHs because their low solubility in water, this method is considered one of the best to reduce pollution according green chemistry compared with liquid-liquid extraction method. Cep-pak C18 PAH specialized made for PAHs was used for concentrate PAHs in water samples, this technique give recovery ratio between (82-97)%, by mean of 89.8% with percentage error ratio between (3-18)% and mean percentage of error ratio 10.19%, this ratio consider good recovery for PAHs. Chromatogram and retention time table for sixteen PAHs listed in the table below:

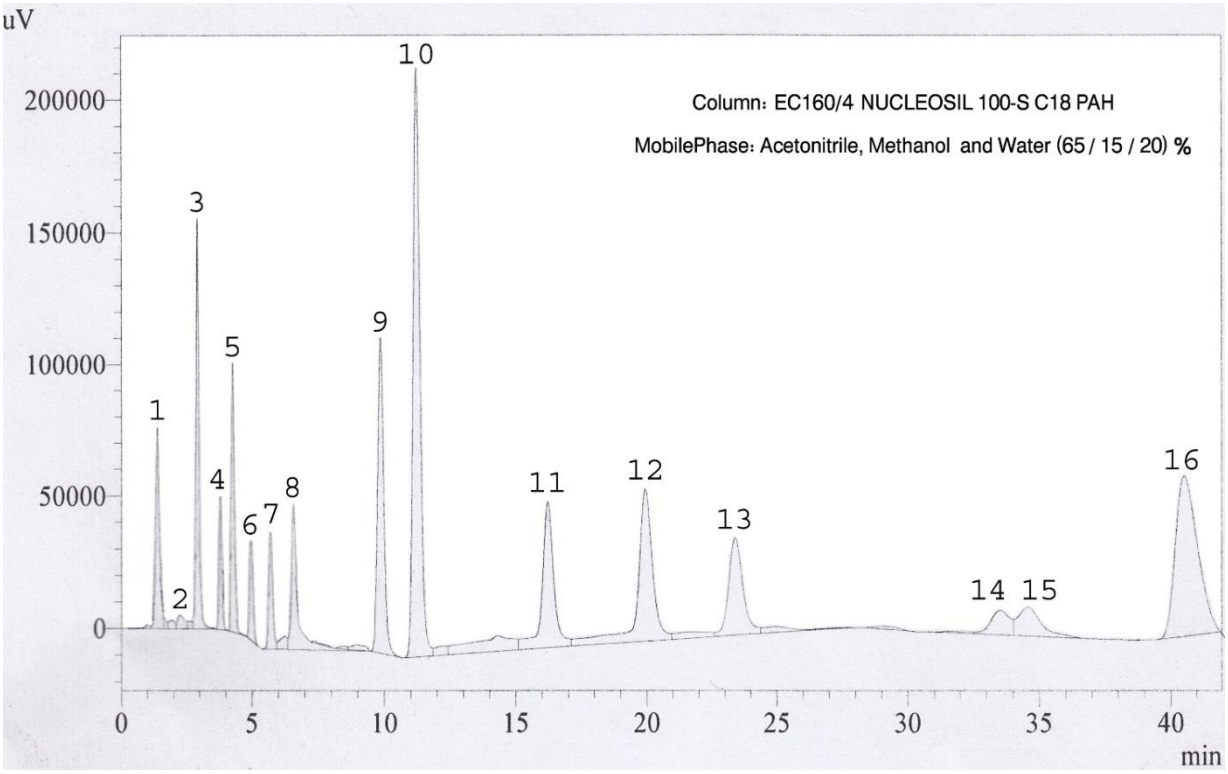

Fig. (2) HPLC Chromatogram for 16 PAHs(5mg/l) at 260nm, flow rate 1 ml/min, mobile phase (Acetonitrile 65%, Methanol 15% and Water 20%)1-Naph. 2- Ace. 3- Acy.4- Fln. 5-Phe. 6-Anth.7- Flan. 8- Py. 9- Ch. 10- B[a]anth. 11- B[b]flan. 12- B[k]flan. 13- B[a]p 14- B[ghi]pyr. 15- D[a,h]an. 16- I[123-cd]py.

Table (1)
Retention time table for 16 PAH.

No.	*Priority Pollutant*	*Retention Time min.*
1	Naphthalene	1.39
2	Acenaphthene	2.27
3	Acenaphthylene	2.92
4	Fluorene	3.79
5	Phenanthrene	4.28
6	Anthracene	4.97
7	Fluoranthene	5.71
8	Pyrene	6.58
9	Chrysene	9.87
10	Benzo (a) anthracene	11.23
11	Benzo (b) fluoranthene	16.22
12	Benzo (k) fluoranthene	19.95
13	Benzo(a) pyrene	23.40
14	Benzo (ghi) pyrelene	33.51
15	Dibenzo(a,h)anthracene	34.56
16	Indeno (1,2,3-cd) pyrene	40.52

Acynaphthene has a very small area at 260nm chromatogram because it has very poor absorbance at this wave length as shown in Fig.(2).

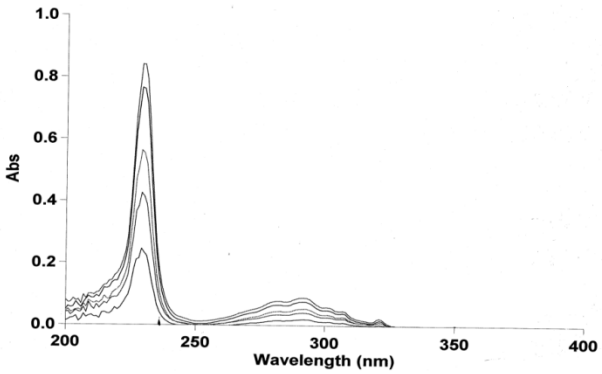

Fig. (3) UV-Vis scanning spectrum for Acenaphthene (1, 2,3, 4, 5) mg/l, acetonitrile solvent.

Higher absorbance of acenaphthene was obtain of wave length 228 nm. So the HPLC detector set at 228nm as shown in Fig (3).

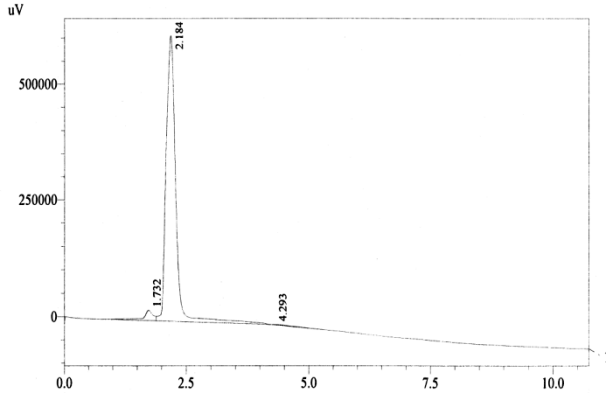

Fig. (4) HPLC Chromatogram for acenaphthene at 228nm.

There is no literature data on Diyala and Tigris rivers for PAH concentrations for comparison with this study.

The concentrations of the 16 detected polycyclic aromatic hydrocarbons (PAHs) in water samples of Diyala and Tigris Rivers are listed on Tables No.(2).

The naphthalene and phenanthrene were the most dominant PAH compounds with the average distribution of 30.7 and 21.1% of the total PAHs in the river water, respectively. As can be seen in water samples, the highest concentration was related to naphthalene (2-ring PAH) which the highest value in eight sites was 186.86 ng/L. At the same time, concentration not detected of two PAHs components in water samples related to benzo [a] pyrene and dibenz [a,h] anthracene.

Table (2)
Concentration (ng/l) of individual PAHs at 8 locations.

Site	*No.1*	*No.2*	*No.3*	*No.4*	*No.5*	*No.6*	*No.7*	*No.8*
Naph.	**7.24**	**ND**	**88.352**	**186.86**	**57.94**	**31.7**	**28.97**	**14.76**
Ace.	**ND**	**1.67**	**5.95**	**15.32**	**2.21**	**0.67**	**ND**	**ND**
Acy.	**1.542**	**3.808**	**38.862**	**48.597**	**17.292**	**0.693**	**0.403**	**0.062**
Flo.	**ND**	**4.494**	**12.84**	**16.91**	**28.61**	**3.78**	**0.97**	**ND**
Phenan.	**ND**	**ND**	**34.421**	**37.826**	**15.946**	**0.411**	**ND**	**ND**
Anth.	**ND**	**ND**	**115.799**	**134.935**	**8.454**	**ND**	**ND**	**ND**
Fluoran.	**ND**	**1.561**	**90.424**	**137.125**	**56.354**	**0.971**	**ND**	**ND**
Pyr.	**2.003**	**0.47**	**3.456**	**52.774**	**1.607**	**0.202**	**ND**	**0.075**
Chry.	**ND**	**ND**	**2.483**	**10.417**	**0.821**	**0.779**	**0.207**	**ND**
B[a]anth.	**ND**	**ND**	**1.412**	**15.62**	**0.228**	**ND**	**ND**	**ND**
B[b]fluoran	**ND**	**ND**	**0.051**	**0.795**	**ND**	**ND**	**ND**	**ND**
B[k]fluoran	**ND**	**ND**	**2.399**	**ND**	**ND**	**ND**	**ND**	**ND**
B[a]pyr.	**ND**	**ND**	**ND**	**ND**	**ND**	**ND**	**ND**	**ND**
B[ghi]pyr.	**ND**	**ND**	**0.039**	**0.451**	**ND**	**0.118**	**0.102**	**ND**
DiB[ah]anth.	**ND**	**ND**	**ND**	**ND**	**ND**	**ND**	**ND**	**ND**
In[123cd]pyr	**ND**	**ND**	**ND**	**3.339**	**ND**	**ND**	**ND**	**ND**
Total PAHs	**10.79**	**12.00**	**396.49**	**660.97**	**189.46**	**39.32**	**30.65**	**14.90**

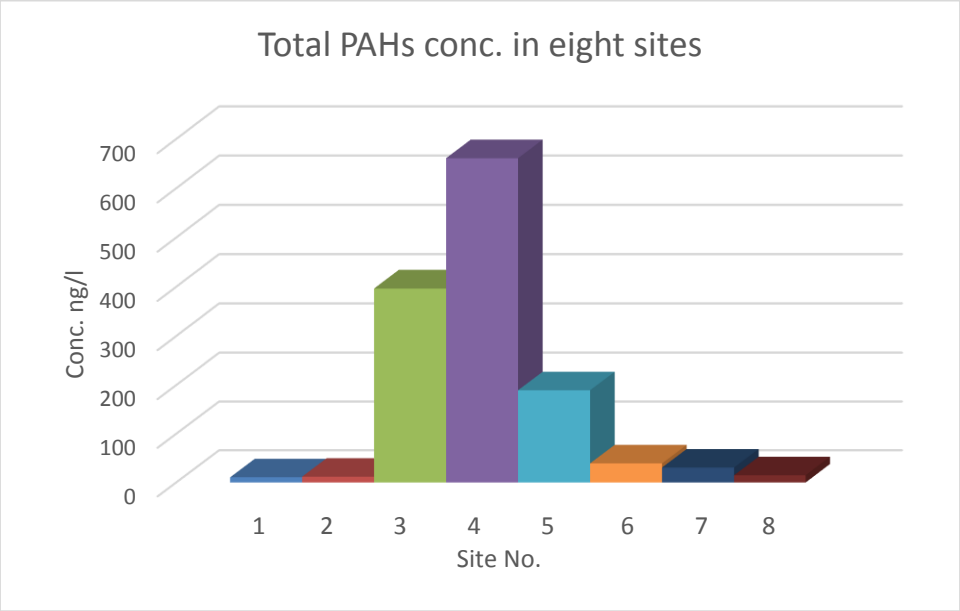

Fig. (5) Total PAHs concentrations ng/l in eight sites studied.

According to results obtained total concentrations of PAHs in the site No. 1 is 10.79 ng/ml this level is relatively low, in other words, Diyala River enters into Baghdad with low level of PAHs pollution, in site No. 2 slightly increase of PAHs pollution with total concentrations to 12.0 ng/ml, then PAHs pollution increase significantly at the site No. 3 to reach total concentrations to 396.49 nm/ml due to throw sewage water as well as thrown of outlet of northern part of Al-Rustumiya sewage treatment plant. Maximum of total PAHs concentrations reach to 660.97 ng/ml after thrown the outlet of southern part from Al-Rustumiya sewage treatment plant in site No. 4, then after about 10 km in Site No. 5 total concentrations of PAHs decrease to 189.46 ng/ml, a distance of about 5 km from the confluence of Diyala and Tigris, in site No. 6 the level of total PAHs concentrations will be 39.23 ng/ml this decrease due to large difference in the flow rate of two rivers, about 10 km after the confluence of two rivers in site No.7 total PAHs concentrations of 30.65 ng/ml, total concentrations in the Tigris river before its confluence with Diyala River Site No. 8 is 14.90ng/ml.

According to our results, the concentration of low molecular weight (2-3 ring) polycyclic aromatic hydrocarbons (LPAHs) in water samples of Diyala and Tigris rivers is higher than high molecular weight (four, five and six rings) PAHs (HPAHs) (Fig.(4)). The mean values of total concentration (ng/l) of LPAHs and HPAHs in eight sampling sites were 117.15 and 26.83 respectively.

Table (3)
Minimum, Maximum and Mean Concentrations (ng/l) of 16 PAHs in eight studied sites.

	Comp.	*Min.*	*Max.*	*Mean*
1	Naph.	ND	186.86	51.98
2	Ace.	ND	15.32	3.23
3	Acy.	0.062	48.597	13.91
4	Flo.	ND	28.61	8.45
5	Penan.	ND	37.826	11.08
6	Anth.	ND	134.935	32.40
7	Flan.	ND	137.125	35.80
8	Pyr.	ND	52.774	7.57
9	Chry.	ND	10.417	1.84
10	B[a]anth.	ND	15.62	2.16
11	B[b]flan	ND	0.795	0.11
12	B[k]flan	ND	2.399	0.30
13	B[a]pyr.	ND	ND	ND
14	B[ghi]pyr.	ND	0.415	0.09
15	DiB[ah]anth.	ND	ND	ND
16	In[123cd]pyr	ND	3.339	0.42

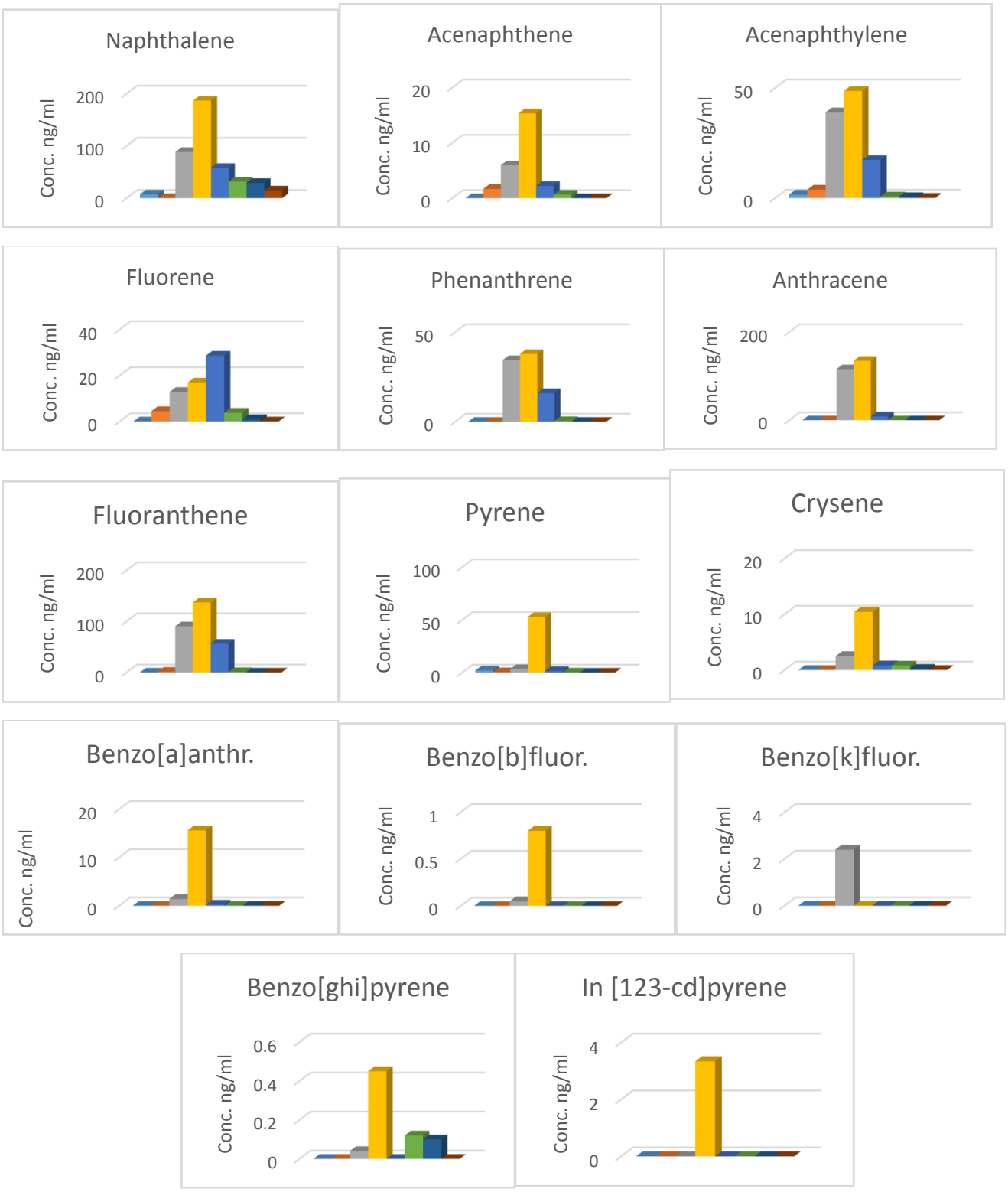

Fig. (6) PAHs concentrations Level in eight sites

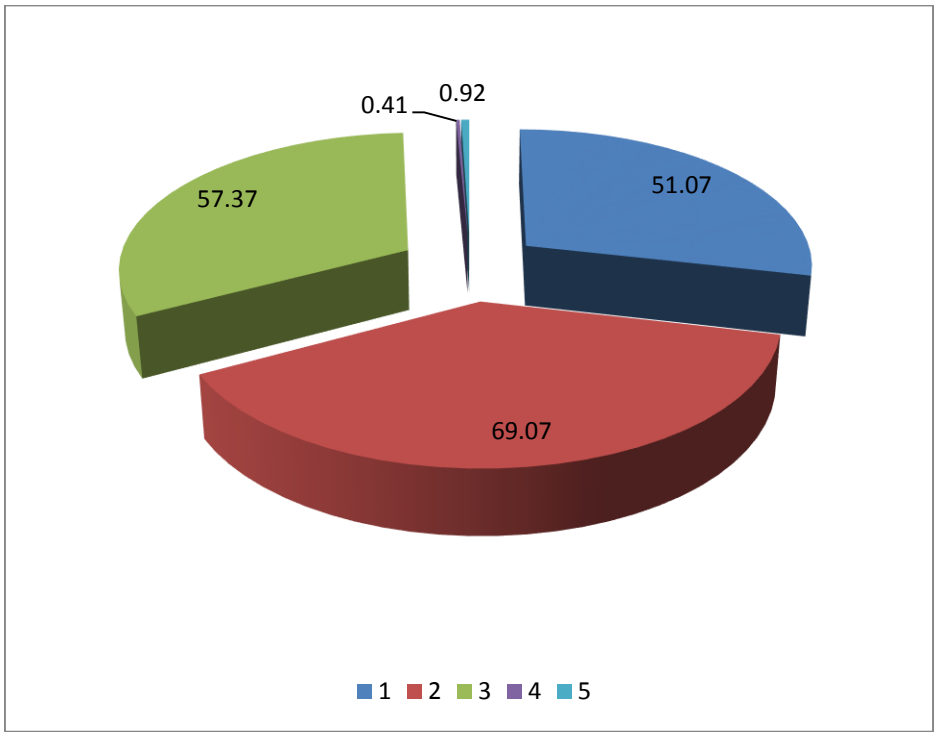

Fig.(7) The mean concentration (ng/l) of PAHs in water samples 1- two rings 2- three rings 3- four rings 4- five rings 5- six rings.

Conclusions

The results of this paper indicate that Diyala River show a PAHs pollution, total PAHs concentrations found high level before and after Al-rustamiya sewage treatment plant in about 15 km, then concentration decreased at Diyala entry in Tigris River.

Naphthalene Anthracene and Fluoranthene are the dominant PAHs while, Benzo [a] pyrene and Dibenz [a,h] anthracene are not detected in all sites.

Reference

[1] FetzerJ. C. "The Chemistry and Analysis of the Large Polycyclic Aromatic Hydrocarbons". Polycyclic Aromatic Compounds (NewYork: Wiley) 27 (2): p 143. 2000.

[2] Bam forth S.M., SingletonI, "Bioremediation of polycyclic aromatic hydrocarbons: current knowledge and future directions", J. Chem. Technol. Biotechnol. 80, pp723–736 2005.

[3] SrogiK., "Monitoring of environmental exposure to polycyclic aromatic hydrocarbons" a review, Environ. Chem. Lett. 5 pp169–195, 2007.

[4] Fernández-Luqueño F., Valenzuela-Encinas C., Marsch R., Martínez-Suárez C., Vázquez-Núñez E., Dendooven L., "Microbial communities to mitigate contamination of PAHs in soil- possibilities and challenges: a review", Environ. Sci. Pollut. Res. 18, pp12–30, 2011.

[5] Malawska M., Wiłkomirski B., "An analysis of soil and plant (Taraxacumofficinale) contamination with heavy metals and polycyclic aromatic hydrocarbons (PAHs) in the area of the railway junction IławaGłówna, Poland", Water Air Soil Pollut.127, pp 339–349, 2001.

[6] Rajput N., Lakhani A., "Measurements of polycyclic aromatic hydrocarbons at an industrial site in India", Environ. Monit. Assess. 150, pp 273–284, 2009.

[7] ChoiS. D., BaekS. Y., Chang Y.S, "Influence of a large steel complex on the spatial distribution of volatile polycyclic aromatic hydrocarbons (PAHs) determined by passive air sampling using membrane-enclosed copolymer (MECOP)", Atmos. Environ. 41, pp6255–6264, 2007.

[8] B. Aichner, B. Glaser, W. Zech, Polycyclic aromatic hydrocarbons and polychlorinated biphenyls in urban soils from Kathmandu, Nepal, Org. Geochem. 38 p700–715 (2007).
[9] United Nations Economic and Social Commission for Western Asia (ESCWA) and the German Federal Institute for Geosciences and Natural Resources (BGR). Chapter 4 "Shared Tributaries of the Tigris River" p 15, 2012.

الخلاصة

في هذا البحث تم تقدير ستة عشر من المركبات الاروماتية متعددة الحلقات في ثمان مواقع على طول نهر ديالى عند دخوله مدينة بغداد حتى يصب في نهر دجلة، المركبات الاروماتية متعددة الحلقات هي مركبات عضوية تحتوي على اثنين او اكثر من الحلقات الروماتية. يصنف بعضها كمسببة للسرطان والتشوهات الخلقية. تم استعمال تقنية الاستخلاص بالطور الصلب لتركيز النماذج وكانت نسبة الاسترجاع بين (٨٢–٩٧) بالمئة. كروموتوغرافيا السائل ذات الاداء العالي استعملت مع كاشف الاشعة فوق البنفسجية–المرئية لتقدير نسب المركبات. التراكيز التي تم الحصول عليها في النماذج كانت بين عدم الكشف الى ١٨٦,٨٦ نانوغرام/ مل، المواقع بالارقام ١ و ٢ و ٦ و ٧ و ٨ كانت الاقل لمجموع التراكيز وهي على التوالي ١٠,٨ و ١٢,٠ و٣٩,٣ و٣٠,٧ و١٤,٩ نانوغرام/ مل، بينما كان مجموع التراكيز للمواقع الثالثة والرابعة والخامسة هي الاعلى تلوثا بالتراكيز ٣٩٦,٥ و ٦٦٠,٩ و ١٨٩,٥ نانوغرام/ مل على التوالي لان هذه المواقع اقرب الى مصادر التلوث.مجموع التراكيز للنفثالين والانثراسين والفلورانثين مع (٤١٥,٨ و ٢٥٩,٢ و ٢٨٦,٤) نانوغرام/ مل على التوالي في حين لم يتم الكشف عن المركبين بنزو (أ) بايرين و داي بنز (ا،ج) انثراسين في كل المواقع. المركبات ذات الاثنين والثلاث والاربع حلقات كانت هي الاعلى في معدل التركيز مع (٥١,١ و ٦٩,١ و ٤٧,٤ نانوغرام/ مل) على التوالي في المواقع الثمانية.