Evaluation of the Organic-Pollution Based on the Determination of some Polycyclic Aromatic Hydrocarbons(PAHs) in Tigris River Water in 2012 at Baghdad City , Iraq

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Abstract

This study aims to predict the organic pollution produced from the presence of some polycyclic aromatic hydrocarbons (PAHs) and determination it's concentrations (µg/L , ppb) in Tigris river water by a collection twenty-seven water samples from a selected three stations with nine sampling sites and three depths of water (5 cm , 2 m and 4 m) each site for 4.6 km distance of a geographic studied area which is located between the (Al-Senak and AL-Sarrafiah bridges) at Baghdad city – Iraq on May, 2012. The geographic location was determined with a Global Positioning System (GPS) and Geographic Information System (GIS) software program. The concentrations of fourteen components (PAHs) were performed using the reverse phase of high performance liquid chromatography (RP-HPLC) technique. Samples were chemically treated using liquid-liquid extraction method , filtered , extracted , dried , evaporated and pre-concentrated in order to be ready for analysis . The determined concentrations of (PAHs) for the studied area did exceed the criteria values proposed by the International Environmental Organizations like American Environment Protection Agency (U.S-EPA) and British Health Agency (BHA) . The results were showed that the maximum values of the total concentrations (PAHs) were found to be 228 µg/L (5 cm depth , site F, Medicine city station , Al-Resafa bank) , 192.1 µg/L (2 m depth , site D , Medicine city station , Al-Karkh bank) and 80.1 µg/L (4 m depth , site D , Medicine city station , Al-Karkh bank) , while the minimum values were found to be be 51.2 µg/L (5 cm depth , site I, Al-Sarrafia bridge station , Al-Resafa bank) , 33.4 µg/L (2 m depth , site G , Al-Sarrafia bridge station , Al-Karkh bank) and 4.8 µg/L (4 m depth , site G , Al-Sarrafia bridge station , Al-Karkh bank) .

Key words: Baghdad-Tigris river water , 14 pollutants – PAH , RP-HPLC , 2012

Introduction

River water safety continues to be a major public health concern throughout the world [1] . While the impact of water borne infectious disease is more devastating in the third world nations , outbreaks still occur in developed countries . During the period (1971- 1998) , there were 691 waterborne disease outbreaks have reported in United states [2] . Pollution rivers growth and industry have caused serious environmental pollution which has become issues beyond a region or a country and is the introduction of the contaminates which are the synthetic chemicals, normal straight hydrocarbons (NSH) , chlorinated phenols , polycyclic aromatic hydrocarbons (PAHs) , volatile organic compounds (VOC) , oils and greases

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into environmental system [3-7] . (PAHs) already present at the low concentrations in surface and depths of river water .The contaminates at high concentrations are considered to effect wildlife, causing eggshell thinning , tumors and other deformities [8] . The hydrocarbons contamination takes the form of horizontal layers in the banks with variable thickness between 2 cm to 5 cm and which is easily detectable through it's dark color and pronounced oil smell . Results of this study should be of a value not only to the Iraqi Ministry of Environment, but also to the Iraqi Central System for Standardization and Specific Controlling, as it formulates new regulations. (PAHs) here (14-components) according to the increasing of the high carbon's atoms, defined as : 1. naphthalene (C_{10}) , 2. acenaphthylene (C_{12}) , 3. acenaphthene (C_{12}), 4. fluorine (C_{13}), 5. phenanthrene (C_{14}), 6. anthracene (C_{14}), 7. fluoranthene (C_{16}) , 8. pyrene (C_{16}) , 9. benzo(a)anthracene (C_{20}), 10. chrysene (C_{18}) , 11. benzo(b)fluoranthene (C_{20}) , 12. benzo(k)fluoranthene (C_{20}), 13. benzo(a)pyrene (C_{20}) and 14. Indeno ((1,2,3-cd)pyrene (C_{22}). In the (PAHs) components : acenaphthylene (C_{12}) with acenaphthene (C_{12}), phenanthrene (C_{14}) with anthracene (C_{14}), benzo (a)anthracene (C_{20}), benzo(k) fluoranthene (C_{20}) and benzo(a)pyrene (C_{20}), they have the same higher carbon atoms, but they have a different stereo-space each chemical molecular's structure with a different retention time accordingly. Fondekar and Gupta were determined the concentrations of dissolved hydrocarbons in some parts of the North Indian Ocean and found the values in the range of 0.6 – 26.5 µg/L [9] . The concentration of the total hydrocarbon content in lake water were determined as 1.6 µg/L [10] . River water samples were extracted twice with 50 ml CCl_4 by a UNESCO method for the years 1982-1984 [10] . The concentrations of hydrocarbons were reported as 0.4-126 µg/L in river sediment and 0.6-41 µg/L in river water [5,7] . The next paper will study the determination of the concentrations of normal saturated hydrocarbons (NSH) and chlorinated phenols in the same river , stations and sites in a near future . This paper describes the preliminary levels of (PAHs) , (C_{10} – C_{22}) at the different depths , sites and stations of the Tigris river in Baghdad . It have two famous banks in Baghdad city, the west and the east banks are called Al-Khark and Al-Resafa sides respectively. The Tigris river is one of the largest rivers of the Middle East stretching for over 1900 km of which 1415 km are within Iraq , with a catchment area of 235000 km^2 , sharing with Euphrates river as the main sources for life , especially for drinking water since they pass the major cities in the country [3] . It runs through the capital of Iraq (Baghdad) and has an enormous importance according to the industrial and shipping activities.

Material and methods

1. Instruments

A Shimadzu High Performance Liquid Chromatography (HPLC) model DGU 20 A_3 equipped with flame ionization detector (FID) type SPD-20AV and column (C_{18}) of tracer extrasil-ODS , 25 x 0.46 cm . The used concentrations for naphthalene and anthracene standards were 10 µg/L and 100 µg/L respectively as the blank solutions .The standard sample of (PAHs) is a product of Supelco company, cataloque Lot. No. LB24238 with concentration of 2000 µg/L in acetonitrile solvent. The blank experiments were performed prior to inject the standard and sample solutions into the (HPLC) under the same conditions. An LBP2900, i-

sensy, Canon Printer was used to record the detecter signal.

2. Field sampling and sample collection stations

About 27 liters of the water samples was collected on May 2012 in 27-cleaned polyethylene bottles from the Tigris river water at the stations : [Al-Nahar station ; sites (A , B and C) , Medicine city station ; sites (D , E and F) and Al-Sarrafia bridge station ; sites (G , H and I)] . The sites (A , D and G) were represented Al-Karkh bank , while the sites (C, F and I)) were represented Al-Resafa bank . Each site is within 5 cm , 2 m and 4 m depths of water . It means (3 stations x 3 sites each station x 3 depths each site) to get 27 water samples overall . The distance of the geographic studied area is about 4.6 km . The locations of the sampling stations and sites of the river are shown in **(Figure 1)** . Each sample was collected in 1.5 L capacity volume of polyethylene bottles . The collected samples apparatus is called a Vindor with strong pyrex cylinder of 1.25 L capacity volume, 5 cm thickness rubber stopper , strong wire of 20 m graduated length (0.5 m each) and circular cap tool of stainless steel material to close the stopper at a desired depth . When the bottle was filled with water, it was closed and drawn up carefully. Then, the samples were stored in a dark and a cool chamber .

3. Extraction , pre-concentration and analysis of the extract

The extraction were carried out within 24 hours after it's collection using a liquid-liquid extraction (LLE) method [7] . Each 40 ml sample was filtered with whatman filter paper (i.d 70 mm) to remove debris and suspended materials , then poured into 250 ml separator funnel . 30 ml of the mixture solvents (1:1 v/v; methanol: methylene chloride) were added. It was stirred vigorously for 4 hours and set aside for 30 minutes at room temperature. The water phase was drained from the separator funnel into 250 ml beaker . Following the second and third LLE , the water phase was poured back into the separator funnel to re-extract with 20 ml of the same solvent mixture . Dry the combined extract over 10 gm of anhydrous sodium sulfate . The extract was concentrated to 8 ml using rotatory evaporator and analyzed with (HPLC) . The concentrated solutions were injected into the (HPLC) instrument and different peaks belong to the (PAHs) components were obtained in the chromatogram . Each component was identified and quantified by comparing it's retention time and peak area with those of known concentration of standard solution which was also , injected into (HPLC) instrument under the same experimental conditions . The components concentrations of (PAHs) were calculated based on the following equation :

Conc. , µg/L (ppb) of (PAHs) each component =

$$\mathbf{A_s / A_{std} \times V_{injected\ std}\ (\mu L) / V_{injected\ s}\ (\mu L) \times Conc._{std}\ (mg/L) \times Z \times 1000 / Y}$$

Here (A_s , A_{std} , $V_{injected\ std}$ (µL) , $V_{injected\ s}$ (µL) , $Conc._{std}$ (mg/L) , Z , 1000 and Y) represent the peak area of a component sample solution , the peak area of a component standard solution , the injected volume of a sample solution (30 µL) , the injected volume of a standard solution (1 µL) , the concentration of a standard solution (5 mg/L) , concentrated volume (8 ml) , number transforms ppm into ppb units and the primary concentration (40 ml) respectively .

Results and Discussion

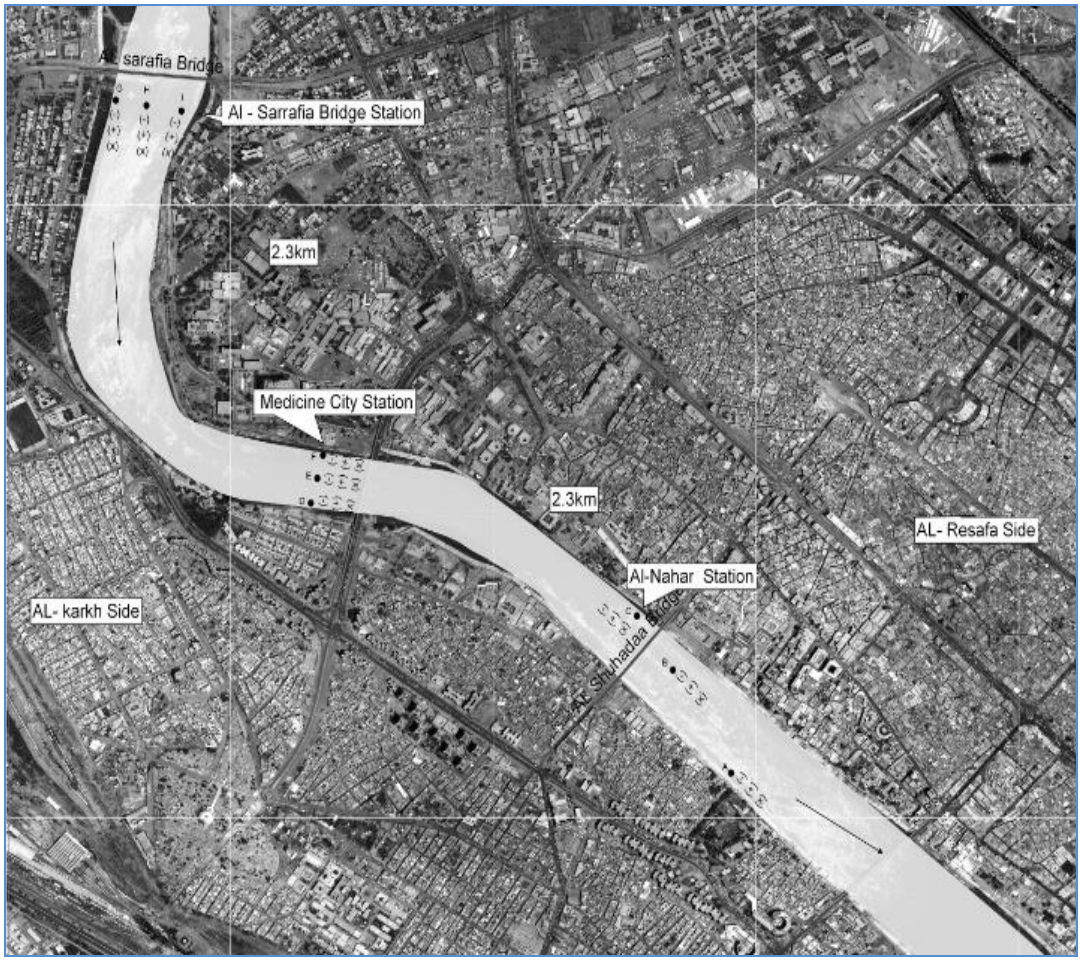

Fig. 1 . Map of the Tigris river at Baghdad city , Iraq showing the locations of sampling stations and collection sites 0f water samples : (+) , (-) and (x) represent 5 cm , 2 m and 4 m depths of water respectively and the flowing water is from the north into the south of Baghdad

Tabel 1. Concentration of individual PAH_S in 5 cm depth of water at various sites and station of Tigris river .

No.	Compounent of PAHs	Concentraction of compounents PAHs (ppb)								
		Al-Nahar station			Medicine city station			Al-Sarrafia bridge station		
		A	B	C	D	E	F	G	H	I
1	Naphthalene	24.9	8.8	17.6	34	10	46	31	10	10
2	Acenaphthylene	0	0	13	0	0	33	6.6	0	7.5
3	Acenaphthene	0	15	0	23	0	42	5	3.3	0
4	Fluorene	12.4	0	0	8.4	22	21	0	0	0
5	Phenanthrene	0	7.9	25.8	0	21	8.2	0	0	0
6	Anthracene	0	8.3	10.1	0	2.8	5.0	0	0	4.3
7	Fluoranthene	0	6.5	10.7	0	0	0	0	9.7	0
8	Pyrene	3.1	0	7.9	0	11	0	4	1.4	7.4
9	Benzo(a)anthracene	0	12.7	0.6	6.0	19	12	5.1	2.5	4.4
10	Chrysene	0	0	0	0	0	3.6	0	0	0
11	Benzo(b)Fluoranthene	0	14.7	0	0	15	4.2	0	32	0
12	Benzo(k)Fluoranthene	0	6.5	18.1	28.3	0	13	0	7.2	14
13	Benzo(a)Pyrene	39.1	0.17	0	0	17	19	0	34	10.
14	Indeno(1,2,3-cd)Pyrene	26	1.5	18.5	0	0	21	0	28	2.6
	Total Conc.PAH	105.5	98.9	109.7	99.7	117.9	228	51.7	128.1	51.2

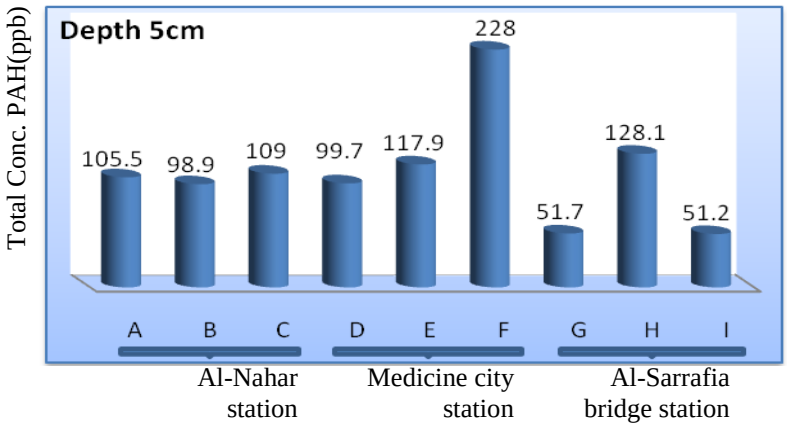

Fig. 2 . Comparision the total concentration of PAH_S in 5cm depth of water at various sites and stations of Tigris river.

Tabel 2. Concentration of individual PAH_S in 2 m depth of water at various sites and station of Tigris river .

No.	Compounent of PAHs	Concentraction of compounents PAHs (ppb)								
		Al-Nahar station			Medicine city station			Al-Sarrafia bridge		
		A	B	C	D	E	F	G	H	I
1	Naphthalene	14.9	14.5	19.4	34.5	2.3	8.9	19.5	11	4.2
2	Acenaphthylene	12	15	9.1	48.5	20.6	5.8	0	25	17
3	Acenaphthene	7.1	6.5	0	13.4	6.9	0	13.9	4.5	18
4	Fluorene	3.1	0	0	33	0	0	0	0	0
5	Phenanthrene	5.5	11.5	30.4	26	0	8.1	0	5.7	0
6	Anthracene	0	0	13.2	0	12.9	0	0	23	0
7	Fluoranthene	10.1	2.1	9.7	14.4	0	0	0	0	0
8	Pyrene	6.2	5.4	10.9	0	10.3	0.8	0	12	4.9
9	Benzo(a)anthracene	1.3	0	12.2	0	3.9	16.4	0	17	0
10	Chrysene	2.3	0	5.9	8	0	0	0	0	0
11	Benzo(b)Fluoranthene	0	14.7	0.05	6.8	5.1	22.3	0	0	0
12	Benzo(k)Fluoranthene	7.1	7.5	4.9	1.3	2.9	3.3	0	8.2	4.7
13	Benzo(a)Pyrene	0	0	5.8	6.2	5	2.3	0	18	10
14	Indeno(1,2,3-cd)Pyrene	10.1	1.1	2.1	0	10.9	2.4	0	11	0
	Total Conc.PAH	79.7	77.8	123.6	192.1	80.5	70.3	33.4	135.4	58.8

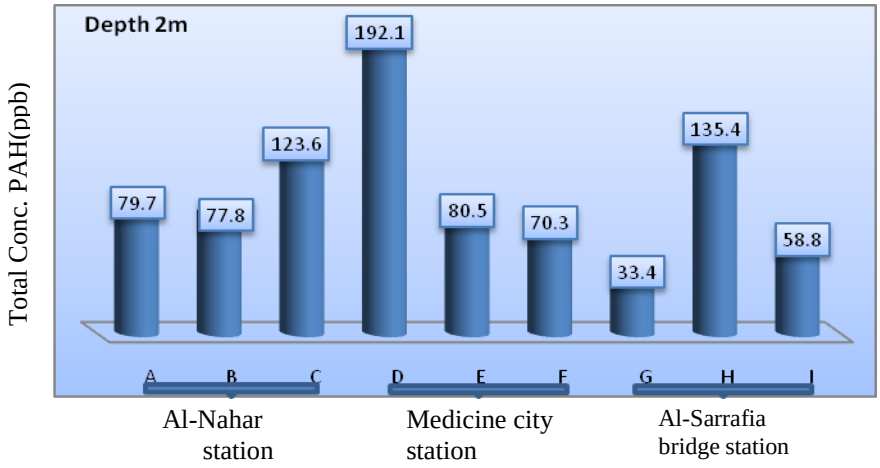

Fig. 3 . Comparision the total concentration of PAH_S in 2m depth of water at various sites and stations of Tigris river.

Tabel 3. Concentration of individual PAH_S in 4 m depth of water at various sites and station of Tigris river .

No.	Compounent of PAHs	Concentraction of compounents PAHs (ppb)								
		Al-Nahar station			Medicine city station			Al-Sarrafia bridge station		
		A	B	C	D	E	F	G	H	I
1	Naphthalene	4	3.6	4.8	8.6	5.8	2.4	4.8	2.7	2.5
2	Acenaphthylene	3	3.7	2.3	12.1	5.1	1.5	0	6.2	7.8
3	Acenaphthene	1.7	1.6	0	3.3	1.7	0	0	11	0
4	Fluorene	0.7	0	0	8.3	0	0	0	0	0
5	Phenanthrene	1.4	2.8	7.6	6.5	0	2	0	1.4	5.2
6	Anthracene	0	0	3.3	0	3.2	0	0	5.8	0
7	Fluoranthene	2.5	5.4	2.4	3.6	0	0	0	0	1.9
8	Pyrene	1.6	1.3	2.7	0	2.5	0.2	0	3.1	3
9	Benzo(a)anthracene	0.3	0	3	0	9.7	4.1	0	4.1	0
10	Chrysene	0.5	0	1.5	2	0	0	0	0	0
11	Benzo(b)Fluoranthene	0	2.1	0	17	1.3	5.5	0	0	0
12	Benzo(k)Fluoranthene	1.7	1.8	1.2	3.2	0.7	0.8	0	2	0
13	Benzo(a)Pyrene	0	0	1.5	15.5	1.3	0.6	0	4.5	1
14	Indeno(1,2,3-cd)Pyrene	2.5	2.7	0.5	0	2.7	0.6	0	2.7	2.6
	Total Conc.PAH	19.2	27.1	65.8	80.1	34	24.9	4.8	43.5	24.1

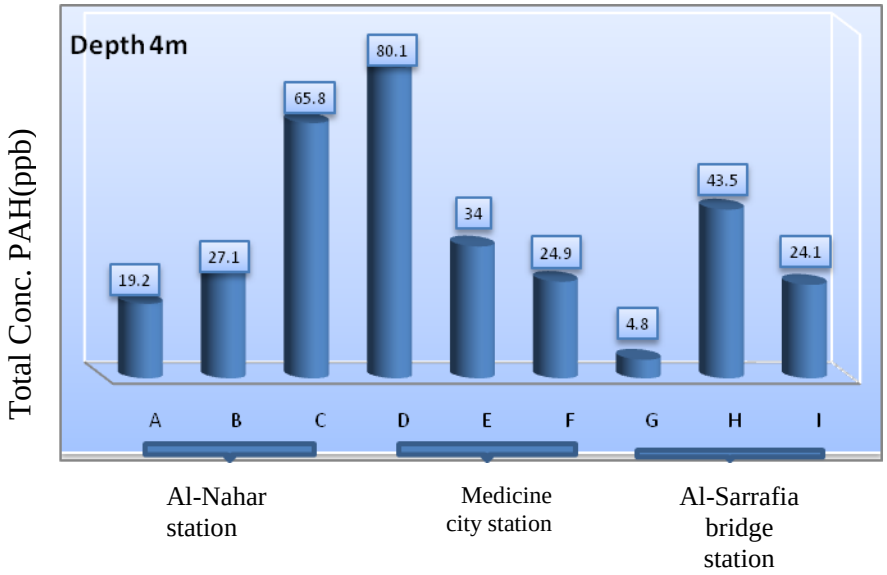

Fig. 4 . Comparison the total concentration of PAH_S in 4m depth of water at various sites and stations of Tigris river .

The main goal of this study to evaluate some organic pollutants which were produced from the presence of the fourteen components of the high carbon atoms ($C_{10} - C_{22}$) of Polycyclic Aromatic Hydrocarbons (PAHs) and to determine it's concentrations for the distance located between the senak bridge station (south of Baghdad) and the Al-Sarafia bridge station (north of Baghdad) in the Tigris river water at Baghdad city , Iraq on May 2012 . The locations of the three stations and the nine sites were predicted on a map with a Global Positioning System (GPS) and each site was then , located on the mapping medium using the (ARC-GIS) software program **(Figure 1)** . All the focused concentrations were determined using the Reverse Phase of High Performance Liquid Chromatograph (RP-HPLC) technique

. The (PAHs) components were detected in Tigris river water which were represented in (**Tables 1, 2 and 3**) . Some of the (PAHs) components were not observed in the water samples .That is probably due to the very low concentrations which can not be detected by HPLC-FID . The (PAHs) components can be classified into the following classifications : [Naphthalene (C_{10}) is (2 rings PAHs)] , [Acenaphthylene and Acenaphthene (C_{12}) , Fluorene (C_{13}) , Phenanthrene and Anthracene (C_{14}) are (3 rings PAHs)] , [Fluoranthene and Pyrene (C_{16}) , Benzo(a)anthracene (C_{20}) , Chrysene (C_{18}) are (4 rings PAHs)] , [Benzo(b) fluoranthene, Benzo(k) fluoranthene and Benzo(a)pyrene (C_{20}) are (5 rings PAHs)] and [Indeno(1,2,3-cd)pyrene (C_{22}) is (6 rings PAHs)] . In the Al-Nahar station , the concentrations of (PAHs) obtained from the water samples within 5 cm , 2 m and 4 m depths of water at western side (site A , Al-Karkh bank) , middle (site B) and eastern side (site C , Al-Resafa bank) are shown in **(Figure 1**) . The concentration's criteria of (PAHs) for river water is 1 µg/L each component to get 14 µg/L (PAHs) overall . Irrespective of the depths and locations , the water samples contained the maximum number of (PAHs) at 5 cm depth compared to that of 2 m and 4 m respectively . It can also , be observed the organic-pollution at Al-Resafa bank [109.7 µg/L , total concentration (PAHs)] is more than the correspondence of the Al-Karkh bank [105.5 µg/L , total concentration (PAHs)] .In the Medicine city station , the maximum concentration was found to be 228 µg/L (site F , Al-Resafa bank) , (**Figure 2)**. In the Al-Sarrafia bridge station , the maximum concentration was found to be 128.1 µg/L (site H , middle of river) owing to the diffusion process when the thickness's layer of each bank becomes (5 cm-50 cm) of (PAHs) , [7] . using the same route , we were observed the total concentrations of (PAHs) at 2 m and 4 m depths of water (**Figure 3)** and (**Figure 4**) respectively. The dominance of [1-6 rings (PAHs)] mainly attributed to Oil spillages , municipal and waste discharges , and atmospheric transport and the activity of some organisms , such as bacteria , algae and fungi [5-7] . The samples were taken from the higher contamination area, so this is not argument that the river was contaminated all .The organic pollution's order for the studied geographic location with a middle grade based on the criteria of the International Environmental Organizations such as (U.S-EPA and BHA) as follows :

Medicine city station > Al-Nahar station > Al-Sarrafia bridge station

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تقويم التلوث العضوي المعتمد على تعيين المركبات الاروماتية المتعددة الحلقات (PAHs) في مياه نهر دجلة من عام 2012 م في مدينة بغداد ـ العراق

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الخلاصة :
تهدف الدراسة الى تحديد التلوّث العضوي الناتج من وجود بعض المركبات الاروماتية المتعددة الحلقات (PAHs) وتعيين تراكيزها بوحدة (جزء من البليون ، مايكرغرام/لتر) في مياه نهر دجلة . قد تمّ جمع (27) نموذج من ثلاث محطات مختارة ، كل محطة تتكون من ثلاث نقاط ، الاولى على ضفة الكرخ ، والثانية في منتصف النهر ، والثالثة على ضفة الرصافة بشكل خط مستقيم على عرض النهر . يتألف كل موقع من ثلاثة أعماق هي (5 سم ، 2 م ، 4 م) على طول مسافة الموقع الجغرافي للدراسة البالغة (6و4 كم) ، الواقعة بين جسر السنك ، وجسر الصرّافية في مدينة بغداد – العراق في تاريخ مايس – 2012 م . لقد تم رسم خارطة الموقع الجغرافي للدراسة بوساطة نظام التحديد العالمي للمواقع (GPS) ، ونظام المعلومات الجغرافي (GIS) . لقد تمّ تعيين تركيز (14) مركب من مكونات (PAHs) بوساطة تقنية (الطور العكوس – الكروموتوكرافيا السائلة ذات الأداء العالي)، (RP-HPLC) . لقد تمّ التعامل الكيميائي مع النماذج المائية بوساطة طريقة (إستخلاص سائل – سائل) ، ثم تتبعها عمليات : الترشيح ، التبخير ، التجفيف ، التركيز ليصبح المحلول جاهزا" للتحليل . بيّنت قيّم تراكيز (PAHs)، تجاوز قيّمها عن القيّم المعتمدة لدى المنظمات البيئية العالمية مثل وكالة حماية البيئة الامريكية (U.S-EPA) ، وكالة الصحة البريطانية (BHA) . أظهرت أن أقصى قيمة لتركيز (PAHs) هي (228 مايكروغرام/لتر) وجدت في (عمق 5 سم ، النقطة F ، محطة مدينة الطب ، ضّفة الرصافة) ، (1و192 مايكروغرام/لتر) وجدت في (عمق 2 م، النقطة D، محطة مدينة الطب، ضّفة الكرخ)، مايكروغرام/لتر) وجدت في (عمق 4 م، النقطة D، محطة مدينة الطب، ضّفة الكرخ). بينما ظهر أن أدنى قيمة لتركيز (PAHs) هي (2و51 مايكروغرام/لتر) وجدت في (عمق 5 سم، الموقع I ، محطة جسر الصرّافية ، ضّفة الرصافة) ، (4و33 مايكروغرام/لتر) وجدت في (عمق 2 م ، الموقع G ، محطة جسر الصرافية ، ضّفة الكرخ) ، (8و4 مايكروغرام/لتر) وجدت في (عمق 4 م ، الموقع G ، محطة جسر الصرافية ، ضّفة الكرخ) .