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Determination of Polycyclic Aromatic Hydrocarbon (PAHs) As Organic Pollutants in Tigris River at Salah-Aldin Governate, Iraq

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Abstract

The present study was conducted on Tigris River at Salah –Aldin governate, Iraq , selected five site distributed along the river during November 2012 to June 2013. The first site located close to satiation for refinery drinking water at aldour city, while the last site was at Abo-Dalf area. The level of fourteen compounds of Polycyclic Aromatic Hydrocarbon (PAHs) used in this study listed below as organic pollutants; Naphthalene, Acenaphthalene, Fluorene, Phenanthren Anthracene, Pyrene, Benzo(a) anthracene, Chrycene , Benzo (b) Fluoranthene, Benzo(k) Fuoranthene , Benzo(a) pyrene, Dibenzo (a,h) anthracene , Benzo (ghi) Perylene and Indeno(1,2,3-cd) pyrene. The lowest level of PAHs in water was B(a)P(0.0005µg/L) in summer term at site No.(2) while the highest value of the same compound in the site No.(1) (1.510 µg/L) at autumn term also. The lowest level of PAHs in sediment was B(a)Fand Pyr(0.001 ng/g) at winter term in site No.(5) ,while the highest value of Acpy (98.981 ng/g) at autum term at site No.(3)

Keywords: Analysis, PAHs, water, pollutions

الخلاصة

تمت الدراسه على نهر دجله ضمن محافطه صلاح الدين وذلك باختيار (5) خمسه مواقع على طول النهر وللفتره من كانون الاول 2012 ولغايه مايس 2013 وكانت المواقع قرب مصادر سحب ماء الشرب. تتراوح كميات المركبات الهيدروكاربونيه المتعدده والتي تعتبر ملوثات عضويه بين 0.0005 مايكروغرام /لتر الى 1.5 مايكروغرام /لتر في الماء في فصل الربيع بينما كانت الكميات في التربه من 0 .001 نانوغرام /غرام الى 98.981 نانوغرام /غرام في فصل الربيع ايضا

Introduction

In view of environmental pollution, we studied organic pollution of Polycyclic Aromatic Hydrocarbons (PAHs), which are produced from incomplete combustion of oil and its derivatives, wood, charcoal and other organic materials. PAHs are among the most important and dangerous pollutants at the present time due to their toxic effect on the body, as they enter the body through drinking water and food, PAHs may also enter the body through skin-to-soil contact, as these compounds are absorbed by the tissues that contain fats and are stored mostly in the kidneys, liver, spleen, adrenal glands, and ovaries, which causes different diseases. Carcinogenicity possible at the chance of one person in 100,000 developing cancer is possible, even when the amount of these compounds is below the permissible limit (1&2) .

The compounds (Figure-1) contain carbon (C) and hydrogen (H) only, consisting of more than one aromatic ring combined with each other through two or more carbon (C) atom(3). The first of these compounds is naphthalene, which is considered the simplest compound in this group, as it consists of two benzene rings fused together and the proportion of carbon (C) and hydrogen

(H) in it (6%, 94 %) respectively$^{(4)}$, and by increasing the number of aromatic rings in large compounds, the percentage of carbon (C) increases and hydrogen (H) decreases, (Benzo(a)pyrene), which contains five rings, contains 95% carbon (C) and 5% hydrogen (H) respectively$^{(5)}$. These compounds have a great biochemical and toxicological importance in human and animal life because of their cancerous diseases and configuration. These compounds are widely distributed in the environment$^{(6)}$.

These type of compounds are exit in the environment either natural or as a result of human activity through his industrial. Because of the diversity of sources of these compounds, they are found in water, air and soil and in many natural sources such as crude oil and coal$^{(7)}$. They are resulted from the incomplete combustion of for power generation, as well as from engines, coal tar and coke ovens $^{(8)}$. PAHs enter in an ecosystem consist of two important sources Pyrogenic and petro-genic$^{(9)}$. The chemical and physical Properties of PAHs are white to pale yellow solids, and naphthalene is the lowest in this family with a melting point of 81c^{0} and boiling point of 200c^{0}. The PAHs are poorly soluble in water and have low vapor pressure$^{(10)}$. These make them in the form of suspended particles in air and water, and with increasing molecular weight, the solubility and vapor pressure of them do not exist. Low PAHs molecular weights in the environment, there are more than (one hundred) compounds from the group of PAHs that are sometimes called aromatic compounds due to their structure and toxicity with increasing molecular weight$^{(11)}$.

The metabolism of PAHs found in the environment (water, soil, air and food) and their carcinogenic action, interest in studying the metabolism of these compounds has increased in recent years by following different methods of analysis. It includes the introduction of an oxygen (O) atom in the composition of PAHs to form the epoxide (Epoxide) by the enzyme (Monooxygenase) with (Nicotinamide Adenine Dinucleotid) NADPH and then the decomposition accompanied by the formation of (Dihydrodiol Epoxide) as the final product$^{(12)}$. Through scientific laboratory experiments of benzo(a)pyrene, the muscular effect PAHs on living organisms was identified. Quantities of benzo(a)pyrene were administered to a group of pregnant rats$^{(14)}$. Toxicity of PAHs depend on the proportion of human exposure to them. Exposure may be through breathing and inhaling air contaminated with car exhaust smoke, fumes emitted from factories and electric generators, cigarette smoke, cooking and heating emissions, and others$^{(13)}$. Exposure may be as a result of ingestion of contaminated and carrier food and water for these compounds, it may be from skin contact with prolonged exposure to fumes and smoke . PAHs have the ability to soluble in fats, so they are stored in all parts of the body of the organism and accumulate in fatty tissues such as the lung, intestine, skin, liver, kidney, adrenal gland and ovaries$^{(14)}$. PAHs vary in the environment due to the diversity of its sources, and this family generally shares its resistance to the action of chemical agents under normal conditions due to its aromatic bonds$^{(15)}$.

Environmental Pollution

water represented by sea water, rivers, lakes, streams and wells have a great role in human life, as they are used for industrial and agricultural uses. Determination of these pollutants in the water is important for assessment of PAHs contamination in water . There are permissible limits for the concentrations of these compounds in water used for various purposes, the water is considered polluted when the concentrations of Benzo (a) Pyrene, Benzo (k) Fluoranthene, Inden(1,2,3-cd) Pyrene, Benzo (b) Fluranthene higher than permissible limit$^{(16)}$. Sediments are contaminated with PAHs in industrial and agricultural countries, as industry is the main source of pollution for surface water, and therefore pollutants is precipitated from water to sediments, because water is used in many industries as a basic material or an auxiliary material in production. As industrial processes produce various organic and inorganic pollutants, and most of the wastes resulting from the leakage of large quantities of these pollutant compounds into rivers, causing their pollution, and that has a significant negative impact(17).There are two important Involved in the formation of PAHs, pyrolysis and prosthesis exceeding (500C0) results in the breaking of the C-C and H-C bonds accompanied by the formation of many types of fragments that interact with each other as free radicals to build PAHs compounds (18) .

Separation Techniques for Samples .

In this study two samples were used to identify or quantitatively determine any organic compounds in samples either water or sediment by simple measurement no matter what its concentration or the complexity of the matrix. Most procedures fall short of this ideal because of interference with the required measurement by other constituents of the sample.

Many techniques for separating and concentrating the species of interest have been devised would be of no value to the analytical chemist, interference with the required measurement by other constituents of the sample., such techniques are aimed at exploiting differences in physico-chemical properties between the various components of a mixture volatility, solubility, charge, molecular size, shape and polarity are the most useful in this respect. , most depend on the selective transfer of materials between two immiscible phases. The most widely used techniques and the phase systems .The current study used either liquid—liquid extraction of water with organic phase or solid-liquid extraction of sediment and then determination both samples by HPLC technique. For quantitative analysis, the amount of sample taken is usually measured by mass or volume. Where a homogeneous sample already exists, it may be subdivided without further treatment, with many solids such as ores, however, crushing and mixing are prior requirements. The sample often needs additional preparation for analysis, such as drying, ignition and dissolution(20).

Aim of Study

The research objectives are summarized to ;

1 .Determining the water quality of the Tigris River .

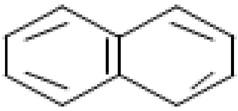
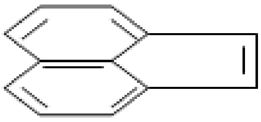
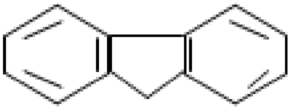
2 .Estimation of the percentages and concentrations of PAHs in the water and sediments of the Tigris- river.

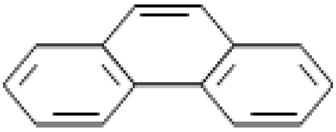
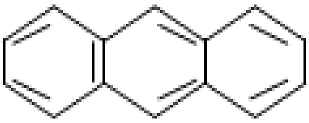
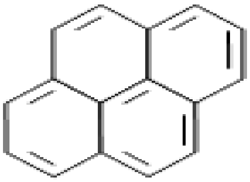
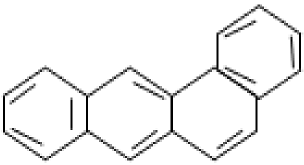
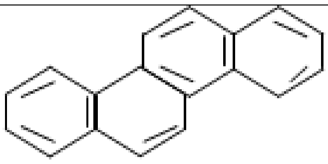
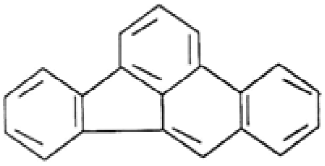
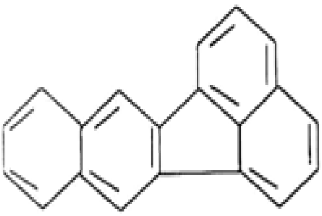
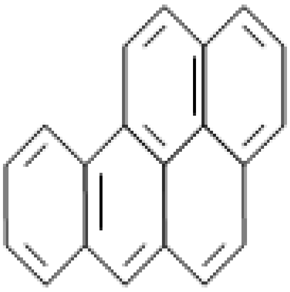
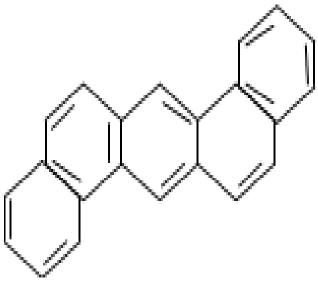
3. To detect the origin of PAHs in water and sediments.

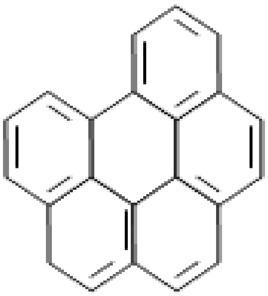
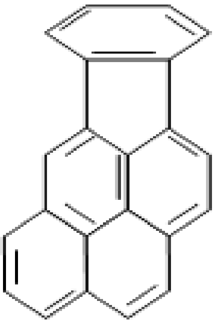
4. To asset the pollution of pAHs in water and sediment.

5. To investigate the availability of PAHs in both samples.

Figure-1- Chemical Structure of PAHs

 Naphthalene	 Acenaphthylene	 Fluorene

 Phenanthrene	 Anthracene	 Pyrene
 Benzo(a)anthracene	 Chrysene	 Benzo(b) Fluoranthene
 Benzo(K) Fluoranthene	 Benzo(a)pyren	 Dibenzo(a,h)anthracene

 Benzo(ghi)perylene	 Indeno(1,2,3-cd) Pyrene

Experimental Work and Results

Studying Area

The Tigris River is one of the two most important rivers in Iraq, as it originates in the highlands of southeastern Turkey, and its length from its source to its mouth is (1718 km), of which (1418 km) of the length of its course inside Iraqi territories. It joins between Turkey, Syria, Iraq and Iran, and the total area of the basin is 47000 km^3. The Tigris river feeds many of the tributaries that connect to it inside Iraq, some of which are large rivers such as the Great Zab that meets the Tigris River at Nimrud district (49 km) south of Mosul, and the Little Zab, which meets the

Tigris River south of Sharqat (36 km) . The Azab River, which originates from the Iraqi highlands in Sulaymaniyah and flows into the Tigris River south of Balad district (15 km) and the Diyala River, which connects to the Tigris River at Baghdad governate. The sites were selected based on several reasons, including the lack of studies and research of this kind that were conducted on the area and the lack of data that explain the environmental nature of the river water and the extent of environmental pollution

in it, as well as the nature of the area and the possibility of choosing the best sites that are suitable as study stations, taking into account the direct effects of the population centers in these stations, in addition to the existence of means of transportation between the two sides of the river using motor boats, in addition to the security conditions, five main stations were selected. Site—1-- site is located on the northern side of the river located at ((east454350.88) and (north 313416.63) characterized by the presence of rocks on the edge of the river and higher current speed than the rest of the stations, as it is a sloping area, as well as the lack of aquatic plants and the lack of animals in it . Site—2-- site is located near the area (the crossing) . It is located at (east 283426.60) and (north283426.60), the presence of slip plants, water weeds and the presence of small pebbles at the edge of the river. The area is characterized by a medium flow rate due to the increase in its width and the presence of aquatic plants. Site—3--this site is located near the (Al-Massarah) east464342.60) and (north 283426.60) . it is simplicity characterized by the presence of median islands of blink and . Site—4--this site is located near (the university village area (east 464341.84)and (north 243449.330).This is 3.17km away from the third station. And its depth (12m) is a sloping area and a high current speed, and it is characterized by the presence of rocks and the lack of plants and animals . Site—5--this site is located near (Abu Dalaf) station. It is located at (east 474317.71) and (north)(213498.57), the speed of the river's flow in this station is reduced to increase its width and the presence of aquatic plants in it . .

. Figure-2- Studying Sites Area

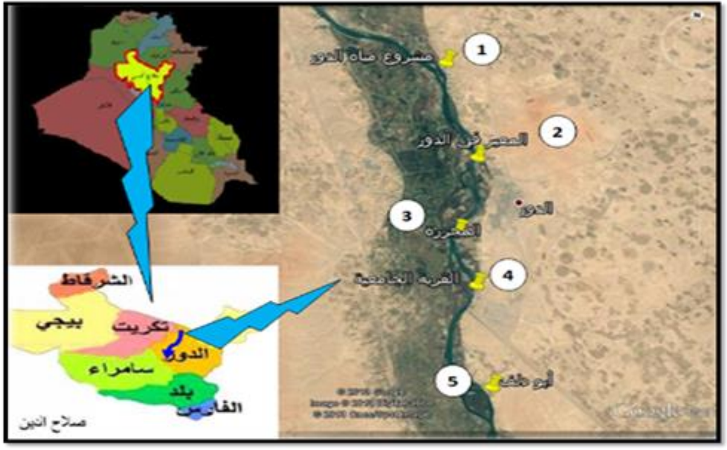


Figure-3-Studyin

Waters

Glass bottle is closed and stored at 4°C, i.e. in the refrigerator, then shaken for one hour, the sample is transferred to the separating funnel, where two layers are formed, the upper layer is water and the lower layer is the organic layer, where the lower layer is collected in a clean, sealed, glass bottle, the extracted sample is passed into a sample cleaning tube containing Anhydrous sodium sulphate, the sample is passed into the Rotary Evaporator (R.E) to dry it at a temperature of (50°C°) and the water passing through the water refrigerator Circulator at a temperature ($10C^0$), after the drying process is finished, (1ml) of Acetonitrile solvent is added and measured by HPLC.

Sediments

We take (10g) of the dried sample (the sample is dried with the addition of anhydrous sodium sulphate) and put it in a volumetric flask of 100ml capacity) and add (25ml) of absolute acetone and shake manually for 5 minutes, then put it in the refrigerator (temperature $4\ C^0$) for a full night inside An glass bottle is sealed. Mix the sample by placing it in the shaker vibrator for one hour, where two layers are formed. We separate the upper layer (the filtrate) from the lower layer (the sediment). For an hour, repeat the process of adding acetone and shaking with a vibrator, separating the two layers three times, so that it is collected from While we add 25ml of acetone to the lower layer (the residual precipitate) and shake with a vibrator for an hour, the process of adding acetone and shaking with the vibrator is repeated and separating the two layers three times so that it collects from the refined upper layer (75ml). As for the remaining precipitate, then we take the product (75 ml) and insert it into 2500. Centrifuge (1 cycle / minute for 5 minutes) . Two layers will be formed. The upper layer is transferred to the separating funnel and we add (50ml) of hexane and (100 ml of deionized water) the lower two layers will be neglected, while the upper layer is taken and added to it to (50ml of KOH potassium hydroxide with 20% base ethanol solution) then we pass the sample into the R.E rotary evaporator to concentrate the sample into (10ml) then we pass the sample into a silica gel (SiO_2) column, which is a glass column whose dimensions are 40cm x 1.5) prepared. To put a small amount of glass wool at the bottom of the column and place a quantity of deionized water, the two lower layers will be neglected, while the upper layer is taken and added to it (50 ml) of (20% KOH) basic ethanol solution). Then we pass the sample into the R.E rotary evaporator to concentrate the sample to 10 ml (then pass the sample into a silica gel column). Silica Gel (SiO_2), which is a glass column whose dimensions are 40 cm (x 1.5) are prepared by placing a small amount of glass wool at the bottom of the column and above it is placed a quantity of Silica Gel (the size of the silica gel 120-60) a distance of 25 cm and then a quantity of Alumina(Al_2O_3) Aluminum Oxide a distance (5cm), then we put an amount of Anhydrous Sodium sulphate a distance (5cm) and clean the column after each sample he first step, it must be passed through the column (30ml) of hexane to activate the column. After that, the sample is passed, then it passes 30ml of Benzene, passes the (30)ml of hexane, so that all the polar and polar hydrocarbon compounds are released, where the added hexane and benzene are combined after adding the sample after collection, it is passed through a rotary evaporator to dry the sample and then dissolved with a solvent (1ml) of Acetonitrile in a ratio of 90:10 acetonitrile to water.

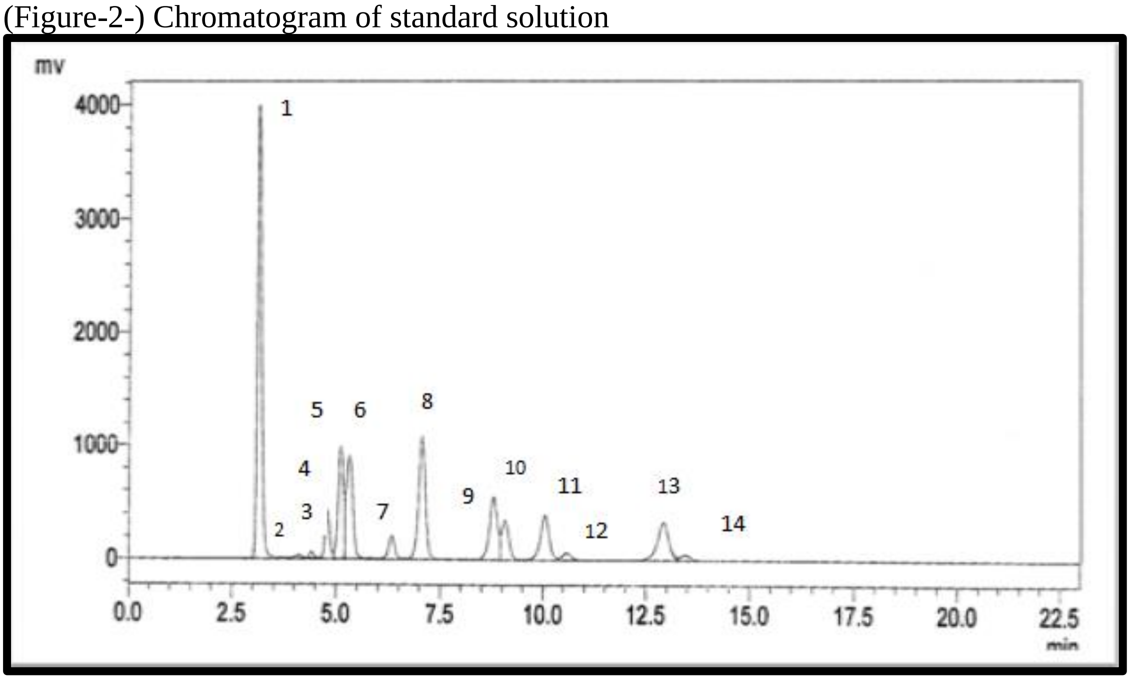
Determination of PAHs in Sample By HPLC

There are many techniques that have been used to separate and analyze PAHs in various environmental pollution fields, the most common of which is chromatography. Chromatography is a physical method of analysis and separation that includes the use of two phases, one of which is a stationary phase with a relatively large surface area, and the other is a mobile phase that travels through the stationary phase and usually contains the sample to be examined. Many workers have identified widely applicable global techniques for analyzing PAHs, the most accurate of which is HPLC (High Performance Liquid Chromatography) (HPLC) . Reverse phase technology is used, but in recent years more than (80%) of HPLC separation processes use reverse phase technology. In this technology, the stationary phase consists of non-polar micro particulate particles and the mobile phase is polar (water - a polar organic solution such as methanol, isopropanol, or acetonitrile). Samples were measured by HPLC at the College of Pharmacy , Tikrit University. According to the analytical variables of the HPLC device as in Table (1) and compared with the concentration of the standard solution(Figure-2) and the retention time of each compound are listed in Table(2)

Table-1- Analytical parameters for HPLC used in this research

value	parameters
10µl	**Volume of injection**
C_{18}	Type of column
Room Temperature	Temperature
ml/mint1	Flow Rate
UV	Detector
SiO_2	Mobile phase
Acetonitrile(ml) + Water(90: 10)	Stationary phase
nm254	Wave length
Reversed Phase (R. P.)	of HPLC

(Figure-2-) Chromatogram of standard solution



Table—2- Retention times of PAHs

Items	compound	Retention times(minutes)	Items	compound	Retention times (minutes)
1	Nap	3.100	8	Chry	7.07
2	Acpy	3.701	9	B(b)F	8.795
3	Flu	4.004 The	10	B(k)F	9.09
4	Phen	4.415	11	B(a)p	10.05
5	Ant	4.796	12	DbA	10.584
6	Py	5.110	13	B(ghi)P	12.927
7	B(a)A	5.812	14	IND	13.453

Result and Discussion

Determination of PAHs in Water Samples by HPLC

Naphthalene is the only hydrocarbon compound consisting of only two ((2-ring) within the group of PAHs on which the current study is being conducted. The results were illustrated in Table (3) and indicate that the highest value of naphthalene (0.764 µg/l) in Autumn at the first and fifth stations, while the lowest value was ND(not detected) in the summer at the first and fourth stations, and in the spring at the second station, while the percentages in each station were listed (9.429% , 3.938% , 3.466 %,13.472% and8.360%) representing the sites (Al-Dour water purification project, the crossing, the massacre, the university village, Abu Dalaf) respectively. The results of our work were less than the results recorded in the study conducted on the Mai, B.X. et al(18) and Magi, E., et al(19) .This indicates that the water pollution in the Tigris River in this study area is higher than the Klip River, the Jiulong river estuary in China and the Gao-Ping river, Taiwan, as well as showing the percentage of the compound Naphthalene is higher than the total PAHs during the study period is (13.472%) , this results indicates high due to temperature, exposure to light and input of sewage to the river. The results of the current study (Table 4) of the tricyclic hydrocarbon compounds showed fluctuations in their values according to seasons and stations and shows that the highest values were recorded in the winter season and the lowest values were recorded in the spring season, also, the values decreased in the autumn season due to the high values in the winter season due to emissions resulting from burning coal, trees and automobile exhaust, whose concentrations increase by increasing rain, which leads to the descent of volatile compounds with rainwater into the river water . PAHs are containing three or less benzene rings are considered to be low-molecular-weight PAHs -LMW compounds that have a higher vapor pressure, and can usually be found in the gas phase, meaning that they are semi-volatile, partially in the atmosphere as in vapors, which are subject to atmospheric cracking processes, hence, they make them frequently move around the environment by deposition and re-volatilization between the bodies of air, soil and water. The compounds have It has the ability to dissolve in fats more than water, and this explains its presence in high concentrations in water, the decrease in values may be due to the processes of photo oxidation, chemical oxidation and biodegradation by aquatic microorganisms.

Our current study showed that the highest value of Acnephthalene was(1.037 µg/L) in the summer at the first station, while the lowest calculated value of ND was in the winter at the third station, and the percentages for each station were as follows (16.513%),(14.60 %) ,(13.168%) ,(4.792%)and (14.765%) . The four rings of PAHs are highest value was recorded in the first site region in this study ,because of the fast current of the river, which leads to an increase in the surface area exposed to light. Table(4) shows the concentrations of hydrocarbons (4-ring), where the compound Pyrene recorded the highest calculated value of(0.638 µg /L) in the winter at the fourth station and the lowest imperceptible ND was in the autumn at the third and fourth sites and in the winter at the fifth station. The percentage of stations was as , (6.588%),(6.221%),(97.940%) ,(16.574%) and (5.125%) . The results of our current study are less than what was recorded in a study conducted on the Euphrates river (1.22 µg/L) as the highest value recorded for pyrene in the waters of the river , which indicates that the pollution of the PAHs in the Tigris River is less than the pollution in the Euphrates. Fluorene recorded the highest value (0.917 µg/L) in the spring at the fourth sites, while the lowest value of ND was recorded in the spring also at the first and fifth stations, and in the summer at the fourth station, and the percentages for each station were as follows as in the Table (4) (%) (15.766%),(19.178%),(17.887%),(12.242%)and (23.119%). The results of our study were lower than the results of the study conducted on Giantang river, Hongzhou canal and inland river in China 1.55 µg/L, 1.64 µg/l, 5.64 µg /L)) respectively.(20) Dibenzo(a,h)anthracene had the highest value of this compound(0.378µg/L) in the spring season at the third station, and the lowest value was ND in the fall season at all stations and in the spring season at all stations except for the third station which recorded the highest value of the compound and in the summer At the second station. Table (-4-) shows the percentage of each station (0.845%) ,(0.173%) ,(8.784%) ,(1.638%) and(0.246%). The results indicate that it is higher than what was reached by other workers(21), in his study on the surface waters of the Nigerian coasts in Eleme in particular, the results ranged from (1.04-1.03 µg/mL), while it was less than the results of the study carried out by Al-Azawey (22) on the Hilla River ,Iraq . Benzo(ghi)Perylene is one of six- ring PAHs recorded the highest value (0.23 µg/L) in the winter at the fourth station, while the lowest ND value was in the fall at the first, second, third and fourth stations, winter and spring at the first and second station, and in the summer at the third station. The percentage of stations according to was (0.067%),(0.178%) ,(0.569%) ,(5.305%) and (2.953%). The results showed an decrease in the concentrations of PAHs (6-ring) in the winter and a increase in the other season , also, the percentage was (20%) in the fourth station of the total PAHs according to the relationship (4-ring < 2-ring < 3 -ring < 6-ring <5-ring).

Table(3) Concentration and Percentage of PAHs in water at different sites of Studying Area

5	4	3	2	1	Sites PAHs		
1.189	**2.311**	**0.62**	**0.773**	**1.829**	**Nap**	**Mean**	
8.360	**13.472**	**3.466**	**3.938**	**9.429**	**Nap%**	**percentage**	

2.1	0.822	2.355	2.881	3.203	Acpy	Mean	
14.765	4.792	13.168	14.679	16.513	Acpy %	percentage	
3.288	2.1	3.199	3.764	3.058	Flu	Mean	
23.119	12.242	17.887	19.178	15.766	Flu%	Percentage	
2.401	2.84	1.66	4.288	2.457	Phen	Mean	
16.882	16.556	9.282	21.848	12.667	Phen%	percentage	
2.64	1.063	2.453	0.150	0.083	Ant	Mean	
18.562	6.197	13.716	0.764	0.427	Ant%	percentage	
0.729	2.843	1.42	1.221	1.278	Py	mean	
5.125	16.574	7.940	6.221	6.588	Py%	percentage	
2.836	0.645	2.578	3.776	0.894	B(a)A	Mean	
19.940	3.760	14.415	19.239	4.609	B(a)A %	percentage	
0.105	0.393	0.093	0.223	1.022	Chry	Mean	
0.738	2.291	0.520	1.136	5.269	Chry %	percentage	
0.156	0.501	1.822	1.29	1.026	B(b)F	mean	
1.096	2.920	7.906	6.572	5.289	B(b)F %	percentage	
0.211	0.355	0.139	0.628	0.897	B(k)F	Mean	
1.483	2.069	0.777	3.199	4.624	B(k)F %	percentage	
0.572	ND	0.045	0.243	1.692	B(a)p	mean	

4.021	**ND**	**0.251**	**1.238**	**8.723**	**B(a)p%**	**percentage**	
0.035	**0.281**	**1.571**	**0.034**	**0.164**	**DbA**	**Mean**	
0.246	**1.638**	**8.784**	**0.173**	**0.845**	**DbA%**	**percentage**	
0.42	**0.91**	**0.118**	**0.035**	**0.013**	**B(ghi)P**	**mean**	
2.953	**5.305**	**0.659**	**0.178**	**0.067**	**B(ghi)P%**	**percentage**	
0.62	**1.989**	**0.530**	**0.435**	**1.71**	**IND**	**Mean**	
4.359	**11.595**	**2.963**	**2.216**	**8.816**	**IND%**	**percentage**	
14.222	**17.153**	**17.884**	**19.626**	**19.396**	**Total PAHs**		

Table (4) Concentration of PAHs in water during period of study

PAHs µg/l))														season
6-ring		5-ring				4-ring			3-ring				2-ring	
IND	B(ghi)P	DbA	B(a)p	B(k)F	B(b)F	Chry	B(a)A	Pyr	Ant	Phen	Flu	Acpy	Nap	
0.011	ND	ND	1.510	0.880	0.084	0.092	ND	0.015	0.016	ND	0.343	0.057	0.764	Autumn
0.566	ND	0.009	0.059	ND	0.048	ND	ND	0.221	0.022	0.641	0.871	0.091	0.353	winter
ND	ND	ND	0.001	ND	0.015	ND	0.005	0.002	ND	0.266	ND	0.433	0.002	Spring
ND	0.006	0.068	ND	0.008	ND	0.047	0.28	0.287	ND	ND	0.051	1.037	ND	Summer
0.288 0.392±	0.001 0.002±	0.038 0.417±	0.523 0.854±	0.444 0.616±	0.049 0.472 ±	0.069 0.622±	0.142 0.194±	0.131 0.144±	0.190 0.004±	0.453 0.265±	0.421 0.415±	0.404 0.454±	0.373 0.381±	Mean
ND	ND	ND	0.133	0.104	0.096	0.141	ND	0.137	ND	0.130	0.146	0.126	0.449	Autumn
ND	ND	0.011	0.036	0.147	0.380	0.006	0.519	0.253	0.05	0.823	0.546	0.39	0.069	Winter

Spring	ND	0.300	0.628	0.285	ND	0.055	0.681	0.015	ND	0.041	ND	ND	ND	0.198
Summer	0.058	0.492	0.361	0.559	ND	0.107	0.428	0.031	0.026	ND	0.0005	ND	0.017	0.019
Mean	0.192 0.222±	0.327 0.155±	0.511 0.136±	0.449 0.305±	0.012 0.024±	0.138 0.083±	0.542 0.128±	0.048 0.062±	0.167 0.187±	0.097 0.533±	0.056 0.068±	0.002 0.004±	0.004 0.008±	0.108 0.126±
autumn	0.034	0.018	0.296	0.924	0.091	ND	0.559	ND	0.031	ND	ND	ND	ND	ND
Winter	0.050	ND	0.373	ND	0.497	0.324	0.326	0.031	0.099	0.023	0.005	0.023	0.028	0.023
Spring	0.003	0.173	0.821	0.359	0.008	0.035	0.504	ND	ND	ND	0.027	0.378	0.016	0.265
Summer	0.214	0.995	0.071	0.008	0.427	0.556	0.018	ND	0.534	0.035	0.001	0.372	ND	ND
mean	0.075 0.094±	0.395 0.525±	0.421 0.377±	0.430 0.462±	0.255 0.242±	0.305 0.261±	0.351 0.243±	0.031 0.062±	0.221 0.272±	0.029 0.008±	0.011 0.014±	0.257 0.203±	0.022 0.008±	0.144 0.171±
Autumn	0.016	0.200	0.202	ND	0.026	ND	ND	0.109	0.016	0.046	ND	ND	ND	0.035
Winter	0.754	0.061	0.075	0.199	0.302	0.638	0.210	0.092	0.072	0.090	ND	0.089	0.23	0.367
Spring	0.016	0.012	0.917	0.55	0.065	0.207	ND	0.003	0.006	0.019	ND	ND	0.02	0.426
Summer	ND	0.25	ND	0.570	ND	0.251	0.006	ND	ND	ND	ND	0.006	0.09	ND
Mean	0.262 0.426±	0.130 0.112±	0.398 0.453±	0.439 0.208±	0.131 0.149±	0.365 0.237±	0.108 0.144±	0.068 0.056±	0.031 0.0355±	0.051 0.0358±	ND ND	0.047 0.058±	0.113 0.106±	0.276 0.210±
Autumn	0.764	0.018	0.182	ND	0.052	0.015	0.037	ND	ND	ND	0.008	ND	0.013	ND
Winter	0.011	0.078	0.485	0.71	0.625	ND	0.376	0.033	0.017	0.036	ND	ND	0.079	ND
Spring	0.041	0.015	ND	0.135	ND	0.057	0.834	0.002	0.049	0.020	0.003	ND	0.008	0.31

ND	0.076	0.017	0.034	0.031	ND	ND	ND	0.3	0.356	ND	0.518	0.636	0.136	Summer
0.077 0.155±	0.044 0.038±	0.004 0.008±	0.015 0.016±	0.029 0.008±	0.033 0.022±	0.017 0.021±	0.415 0.399±	0.124 0.153±	0.344 0.286±	0.422 0.406±	0.395 0.185±	0.186 0.300±	0.238 0.354±	mean

Determination of PAHs in Sediments Samples by HPLC

The results of this study(Table 5) showed an increase in the value of 2-ring PAHs) at the first site vary from other site in the autumn season, the increment concentrations of the compounds are due to the dependent on the solubility of PAHs in water on the extent of their transmission and diffusion. These compounds are less affected by light and biological oxidation, so they accumulate in high concentrations, as well as pollutants can be adsorbed on the surface of small particles suspended in water, and therefore they are subject to for sedimentation. The highest value of naphthalene (4.782 ng/g) in the all season at the first site was the lowest imperceptible value of ND was in the all season also at the second station, and the percentage of stations, (1.312%) ,(0.355%) , (0.116%) ,(0.210%) and (0.984%) were noticed. The concentration of this compound in the sediments was higher than its concentration in the water. This increase is due to the presence of the compound particles suspended in the atmosphere, which transport with raindrops into the river water and then accumulate in the river sediments . The results of our study were less than the results of the study It was carried out by Jianwang et al (23). on the Aojiang River in Wenzhou, China, Wenzhou and China, and less than the results of the study carried out by on the coast of the Adriatic Sea(24). The results of 2-ring (Naphthalene) PAHs showed lower than the other compounds in all sites due to being anhydrous and having a low molecular weight in addition to being the highest water soluble . The results of the current study(Table-6-) of these tricyclic hydrocarbon compounds showed fluctuations in their values according to seasons and stations, shows that the highest values were recorded in the winter season and the lowest values were recorded in the spring season, Also, the values decreased in the autumn season due to the high values in the winter season due to Emissions resulting from burning coal, trees and automobile exhaust, whose concentrations increase with increasing rain, which leads to the descent of volatile compounds with rainwater. The results showed the variation of the upper and lower values of PAHs ((4-ring) according to different seasons and stations .The highest value of PAHs ((4-ring) was in the winter season at the fourth station and the lowest value was in the spring at the first station. The higher concentrations in the winter season is that the high molecular weight compounds PAHs are less volatile in the environment and have adsorption to the particles formed during incomplete combustion and break down in the environment . The highest value of pyrene was 0.562 ng/g in the spring season at the fifth station, while its lowest value was imperceptible ND in the fall at the first and second stations. As for the percentage of stations a (0.198%) ,(0.406%) ,(0.111%) ,(0.080%) and (0.396%), the results of our study differed with the results of a study on the Adriatic Sea in the Chioggiaa area(25). The values ranged (3.3 -73.7 ng/g) , where the values of the results of the current study were lower than the values of the results of the other study. The results of (5-ring PAHs) showed a variation in the values for different stations and seasons , because these compounds with high molecular weight (HMW) are resistant to bacterial decomposition in an environment with low oxygen content even in the conditions where they resort to bioaccumulation. The results show the highest percentage (5-ring) at the first station (35.530%) and according to the relationship (5-ring < 3-ring < 2-ring < 4-ring < 6-ring). The reason may be due to the organic matter represented by organic carbon. In the first station, organic carbon is high, as there is a direct relationship with PAHs and organic carbon.

Benzo(a)Pyrene This compound recorded the highest value (11.309 ng/gm) in the summer at the third station, while the lowest imperceptible ND value in the summer at the first station and was imperceptible in all seasons at the second station and in the autumn at the third station And the fifth and in the winter at the fourth station. And the percentage of stations (1.674%) ,[(4.564%) ,(9.252%) , (4.719%) and (ND) . The results of the current study is less than the results of the study carried out by Mohammed(26) on the Euphrates River, where the results were While the compound Dibenzo(a,h)anthracene recorded the highest value of 24.825 (ng/g) in the summer at the first station, while the lowest imperceptible value was in the fall at the second, third and fourth stations and in the winter at the first, third, fourth and fifth stations and in the spring at the second, third and fifth stations(26). As it is clear from the results in the highest values for the 6-ring compounds come in the fall season at the first station due to the sediment pollution that occurred from Physical pollution , the current result show the highest percentage of 6-ring vehicles at the first station (11.603%) according to the relationship (5-ring < 3-ring < 2-ring < 4-ring < 6-ring) . The highest value of Benzo(ghi)Perylene was recorded (9.830 ng/g) in the fall season at the first station. The lowest value was ND in the winter season at the first, second, third and fifth stations, and in the spring and summer seasons at all stations. The percentage for each station, it was (0.823%) (0.906%),0.203%) ,(4.675%) and (1.674%). The results in Table(6) were less than the results of a study on the Al-Kur River in Iran, which ranged (37.5-19.6 ng/g) , which indicates that the Tigris River is less polluted than the Al-Kur River(27) . Indeno(1,2,3-cd)pyrene, this compound recorded the highest value of (6.196ng/g)) in the autumn season at the first station, and the lowest imperceptible ND value in the winter season at the first and fifth stations, and in the autumn and spring seasons at the fifth station. Table (6) shows the percentage of stations; (2.633%) , 1.600%) ,(0.110%) ,(0.217%) and (ND)

Table(5) The percentage of PAHs in Sediments of Studying Sites

5	4	3	2	1	Sites PAHs		
3.696	0.602	0.724	1.418	4.898	Nap	ˡmean	1
0.984	0.210	0.116	0.355	1.312	Nap%	pecentage	
171.871	251.193	313.542	90.384	58.618	Acpy	mean	2

45.780	87.970	50.492	22.676	15.703	Acpy%	percentage	
4.602	60.627	78.665	103.119	41.631	Flu	mean	3
1.225	21.232	12.668	25.871	11.153	Flu%	percentage	
11.689	38.732	13.524	34.27	37.509	Phen	mean	4
3.113	13.564	2.177	8.598	10.048	Phen%	percentage	
1.926	0.531	1.179	3.991	2.664	Ant	mean	5
0.513	0.185	0.189	1.001	0.713	Ant%	percentage	
1.49	0.229	0.692	1.621	0.741	Py	mean	6
0.396	0.080	0.111	0.406	0.198	Py%	percentage	
154.098	67.159	288.446	124.604	182.341	B(a)A	mean	7
41.046	23.519	46.451	31.262	48.850	B(a)A%	percentage	
4.001	0.756	0.031	ND	5.213	Chry	mean	8
1.065	0.264	0.004	ND	1.396	Chry%	Percentage	
0.176	21.41	0.284	36.058	1.343	B(b)F	mean	9
0.046	7.497	0.045	9.046	0.359	B(b)F%	percentage	
7.223	0.589	2.068	0.132	9.313	B(k)F	mean	10
1.923	0.206	0.333	0.033	2.495	B(k)F%	percentage	
17.135	26.421	29.305	ND	6.251	B(a)p	mean	11
4.564	9.252	4.719	ND	1.674	B(a)p%	percentage	
17.261	1.017	3.734	11.871	6.575	DbA	mean	12
4.597	0.356	0.601	2.978	1.761	DbA%	percentage	
6.287	13.35	1.265	3.615	3.072	B(ghi)P	mean	13
1.674	4.675	0.203	0.906	0.823	B(ghi)P%	percentage	
ND	0.621	0.686	6.381	9.830	IND	mean	

ND	0.217	0.110	1.600	2.633	IND%	percentage	14
375.427	**285.543**	**620.967**	**398.5774**	**373.263**	**Total PAHs**		**15**

Table(6) concentration of PAHs in Sediments during period of study

PAHs ng /g))															
6-ring		**5-ring**				**4-ring**			**3-ring**				**2-ring**	**Season**	
IND	**B(ghi)P**	**DbA**	**B(a)p**	**B(k)F**	**B(b)F**	**Chry**	**B(a)A**	**Pyr**	**Ant**	**Phen**	**Flu**	**Acpy**	**Nah**		
6.196	**9.830**	**22.601**	**0.076**	**ND**	**1.320**	**5.185**	**ND**	**ND**	**2.013**	**20.364**	**ND**	**ND**	**4.782**	**Autumn**	**1**
ND	**ND**	**ND**	**1.727**	**3.104**	**ND**	**ND**	**0.351**	**0.042**	**0.057**	**4.604**	**13.803**	**16.991**	**0.008**	**Winter**	
0.027	**ND**	**21.406**	**0.496**	**ND**	**0.011**	**0.014**	**0.676**	**0.066**	**0.126**	**0.881**	**ND**	**22.4**	**0.023**	**Spring**	
0.162	**ND**	**24.829**	**ND**	**4.291**	**ND**	**2.585**	**0.467**	**0.240**	**0.113**	**13.784**	**0.011**	**6.422**	**0.021**	**Summer**	
2.128 3.523±	**2.457 4.915±**	**22.945 0.211±**	**0.766 0.858±**	**3.697 0.839±**	**0.665 0.925±**	**2.594 2.585±**	**0.498 8.004±**	**0.116 0.108±**	**0.577 0.957±**	**9.908 9.308±**	**6.907 9.752±**	**15.271 8.126±**	**1.208 2.382±**	**±Mean**	
2.825	**ND**	**ND**	**ND**	**0.132**	**ND**	**ND**	**20.110**	**ND**	**1.0164**	**13.448**	**49.684**	**ND**	**ND**	**Atumn**	**2**
1.559	**ND**	**2.031**	**ND**	**ND**	**11.970**	**ND**	**11.357**	**0.400**	**0.757**	**5.024**	**17.759**	**7.931**	**0.025**	**Winter**	
0.420	**ND**	**ND**	**ND**	**ND**	**0.073**	**ND**	**26.994**	**0.190**	**0.351**	**4.002**	**0.079**	**31.531**	**0.623**	**Spring**	
0.079	**ND**	**0.446**	**ND**	**ND**	**0.031**	**ND**	**8.217**	**0.019**	**ND**	**0.371**	**ND**	**1.763**	**0.02**	**Summer**	
1.220 1.242±	**ND ND**	**1.238 1.120±**	**ND ND**	**0.033 0.066±**	**4.024 6.880±**	**ND ND**	**16.669 8.526±**	**0.203 0.190±**	**0.708 0.335±**	**5.711 5.530±**	**22.507 25.141±**	**13.741 15.711±**	**0.222 0.346±**	**±Mean**	

3	Autumn	0.234	98.981	41.579	6.468	ND	0.256	96.538	0.007	0.113	2.019	ND	ND	0.686	0.253
	Winter	0.047	31.041	12.306	1.108	0.184	0.049	28.650	0.008	0.016	0.016	3.377	ND	ND	0.179
	Spring	0.026	28.099	0.083	1.167	1.177	0.063	26.229	ND	0.042	ND	8.576	ND	ND	0.865
	Summer	0.147	32.619	4.586	0.699	0.135	0.081	26.748	ND	0.019	ND	11.309	0.632	ND	0.607
	±Mean	0.113 0.961±	47.685 34.248±	14.638 18.656±	2.368 2.746±	0.498 0.587±	0.112 0.967±	44.541 34.680±	0.0075 0.0071±	0.047 0.045±	1.017 1.416±	7.754 4.029±	0.158 0.316±	0.171 0.343±	0.476 0.319±
4	Atumn	0.077	91.706	19.982	1.208	ND	0.139	50.646	ND	0.054	0.059	11.293	ND	ND	0.041
	winter	0.004	37.54	5.814	0.237	0.038	0.011	4.149	0.235	7.118	0.176	ND	ND	3.387	0.217
	Spring	0.053	9.167	8.339	1.033	0.197	0.009	2.032	0.025	ND	ND	4.656	0.310	ND	0.119
	Summer	0.053	14.266	3.261	0.718	0.010	0.018	ND	8.605	ND	ND	2.908	1.593	ND	0.043
	±Mean	0.046 0.030±	38.169 37.767±	9.349 7.385±	0.799 5.089±	0.081 0.100±	0.044 0.063±	18.942 27.476±	2.955 4.894±	3.586 4.995±	0.117 0.082±	6.285 4.423±	0.951 0.907±	0.846 1.693±	0.105 0.083±
5	Autumn	3.150	87.198	ND	1.031	0.213	0.298	55.791	ND	0.097	0.132	ND	15.821	ND	ND
	Winter	0.004	18.495	1.534	ND	ND	0.001	32.769	0.025	0.001	1.727	2.463	ND	ND	ND
	Spring	0.216	3.525	ND	3.893	0.582	0.562	ND	1.963	ND	0.955	1.265	ND	ND	0.72
	Summer	0.05	11.068	ND	1.435	0.205	0.032	ND	ND	3.073	6.901	3.607	3.143	ND	ND
	±Mean	0.855 1.532±	30.071 38.571±	0.383 0.767±	2.119 1.548±	0.333 0.215±	0.223 0.262±	44.280 16.279±	0.994 1.370±	1.057 1.746±	2.428 3.051±	2.445 1.171±	9.482 8.964±	ND ND	0.18 0.36±

Conclusions

1. The concentrations of PAHs in water samples were lower than sediment.
2 .The detection of low molecular weight compounds (LMW-PAHs) is difficult
3 .The quality of the water of Euphrate River higher than the water of Tigris River
4. The highest percentage of naphthalene in the fifth sites and lower than other PAHs

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