Determination of Some Aromatic Hydrocarbon in Water of Tigris River near Al-Dora refinery

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Abstract:

This study aims to assess the concentrations of some Poly Aromatic Hydrocarbons in water, in order to monitor effectively and provide possible recommendations to improve the water quality in the aquatic ecosystem of Tigris River near Al-Dora refinery. Distribution and concentration of the sixteen polycyclic aromatic hydrocarbons (PAHs) were studied in surface water. Solid-phase extraction was used for water samples, and then analyzed by HPLC. Results showed that the highest and the most dominant (PAH) was ancephthlnene (3-ring PAH), with concentration of (40.33 ng/l), while the lowest concentration was for Indeno (1, 2, 3-cd) pyrene (5-ring PAH), with (0.33 ng/l). The highest and the lowest mean concentrations of PAHs were observed in autumn and summer, respectively. Ratios of specific PAH compound including Phenantharene/Anthracene and Fluoranthene/Pyrene were calculated to evaluate the possible sources of PAHs contamination. These ratios reflect a petrogenic origin of PAHs for water samples in December 2012, February 2013, April 2013 and October 2013, while in June 2013 and August 2013 attributed to pyrolytic origins.

Keywords: Polycyclic Aromatic Hydrocarbons (PAHs), HPLC, Pyrolytic, Petrogenic, Tigris River.

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تحديد تركيز بعض الهايدروكابونات الحلقية في مياه نهر دجلة قرب مصفى الدورة

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الخلاصة :

تهدف هذه الدراسة إلى تقييم تركيزات بعض الهيدروكربونات العطرية في مياه نهر دجلة ، و ذلك من أجل المراقبة الفعالة و تقديم التوصيات الممكنة لتحسين نوعية المياه في النظم البيئية المائية في نهر دجلة بالقرب من مصفى الدورة . تمت دراسة توزيع و تركيز ستة عشر من الهيدروكربونات العطرية متعددة الحلقات في المياه السطحية . وقد استخدم استخراج الطور الصلب (Solid Phase extraction) لفصل واستخلاص عينات المياه، ومن ثم تحليلها بواسطة(HPLC). وأظهرت النتائج أن أعلى وأبرز مركب هو (ancephthlnene)(ثلاثي الحلقات)، مع تركيز (40.33 نانوغرام/لتر)، في حين كان أقل تركيز للـ(Indeno {1, 2, 3-cd} pyrene) (خماسي الحلقات) ، بتركيز (0.33 نانوغرام / لتر). وقد لوحظت أعلى وأدنى متوسط التركيزات الهيدروكربونات العطرية في الخريف و الصيف ، على التوالي . تم حساب نسب الهايدروكاربونيات العطرية متعددة الحلقات بما في ذلك (Phenantharene/Anthracene) و (Fluoranthene/Pyrene) لتقييم المصادر المحتملة لتلوث الهيدروكربونات العطرية متعددة الحلقات. هذه

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النسب تعكس أصل ناتج عن الاحتراق غير الكامل للنفط او عبر عمليات التكرير النفطي الحاصلة داخل
المصفى والي تؤثر بالنهر عن طريق عملية طرح المياة الصناعية الحاوية على الهيدروكربونات العطرية
متعددة الحلقات للمصفى الي النهر وذلك في الاشهر التالية (ديسمبر 2012، فبراير 2013، أبريل 2013
وأكتوبر 2013) بينما في (يونيو 2013 و أغسطس 2013) تعزى لأصول ناتجة عن التحلل الحراري.

Introduction
   Environmental contamination of natural resources with persistent organic pollutants (POP) is of great world-wide concern. Polycyclic aromatic hydrocarbons (PAHs) are an example of such pollutants [1]. As an example, some of the PAHs have been determined to be carcinogenic by several regulatory agencies (US Environmental Protection Agency (EPA), US Department of Health and Human Services (DHHS) and the International Agency for Research on Cancer (IARC)[2].
   Petroleum-based products are the major source of energy for industry and daily life. Leaks and accidental spills occur regularly during the exploration, production, refining, transport and storage of petroleum and petroleum products [3].
   PAHs analysis in environmental samples is a challenging task because of the relatively low concentrations and the complexity of the mixtures in the samples. Usually, environmental sample analyses for PAH compounds involves three major steps: 1) Sample preparation, 2) sample cleanup, extraction and concentration, and 3) final detection and quantification. Most of the available standard procedures are time consuming, manual work oriented, and also are ineffective for detecting PAH compounds associated with suspended solids in water samples [4].
   An oil refinery or petroleum refinery is an industrial process where crude oil is processed and refined into more useful petroleum products, such as gasoline, diesel fuel, and asphalt base, heating oil, kerosene, and liquefied petroleum gas [5].
   Environmental Protection Agency (EPA) has fixed 16 PAH compounds as priority pollutants [2]. They can be classified according to the number of condensed aromatic rings as light (2–3 rings) or heavy (4–6 rings) PAHs, the latter being more stable and toxic than the light ones [6].
   PAHs are widely dispersed in nature and are formed by pyrolysis or incomplete combustion of organic material and high-temperature processing of crude oil, coal, or other industrial carbon-containing compounds [7].
   PAHs are nonpolar, hydrophobic compounds that do not ionize. Volatilization, photolysis, hydrolysis, microbial degradation, and adsorption and subsequent sedimentation determine the fate of PAHs in the environment [8].
   Poly aromatic hydrocarbons (PAHs) are known contaminants of oils and lipids. The toxicity of several of these compounds is well established and limit values have been established. Unfortunately, there is a large gap in our knowledge on the toxic properties of many of these compounds, particularly the PAHs. Therefore it is very difficult to determine the potential health hazards of mixtures of these compounds. For this reason we have developed biological detection methods that are based on the mode of action of these compounds that allow a more direct measurement of potential human health hazards when compared with chemical analysis. [9].
   If you are exposed to substances such as PAHs, many factors will determine whether harmful health effects will occur and what the type and severity of those health effects will be. These factors include the dose (how much), the duration (how long), the route or pathway by which you are exposed (breathing, eating, drinking, or skin contact), the other chemicals to which you are exposed, and your individual characteristics such as age, sex, nutritional status, family traits, lifestyle, and state of health. [10].
   Some polycyclic aromatic hydrocarbons (PAHs) are potent carcinogens and, in air, are typically attached to particles. The primary exposure to carcinogenic PAHs is found in air occurs via inhalation of particles. PAHs occur in indoor air as complex mixtures, the composition of which may vary from site to site. Experimental data on metabolism, gene expression and DNA adducts suggest that interactions between PAHs in mixtures may be complex and highly unpredictable for various PAH compositions (inhibitory, additive, synergistic). [11].

Materials and methods
   The study area located along Tigris River at Al-Dora especially near Al-Dora refinery figure 1. Three locations were randomly chosen in this study, the positions of stations were determined by the

Global Positioning System (GPS): The 1st sampling site (control), the second sampling site (discharge point) and the 3rd sampling (after discharge point). The water sample was taken bimonthly from December 2012 to October 2013.
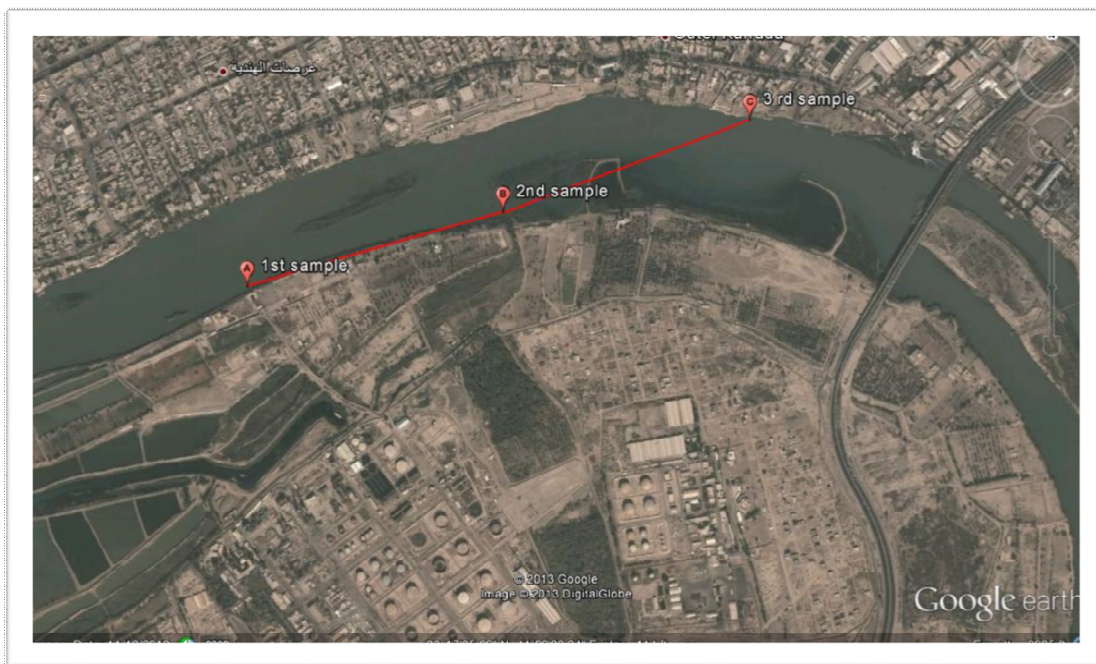

Figure. 1-The map of three sampling stations in Tigris River

Water samples were collected during the morning between 9:00 am, to 11:00 am. Surface water samples were collected in the study stations from the upper 30 cm and 2-4 m from the riverbank. One liter black bottles were used, each was pre-washed by river water, soap solution, distilled water and, 1% nitric acid as recommended [12].

Determination of PAHs by HPLC In water samples :
The determination of polycyclic aromatic hydrocarbons (PAHs) using high-performance liquid chromatography (HPLC) with UV and fluorescence detection has been well established. Although most of the PAHs can be detected by these methods, some environmentally important polyaromatic compounds, such as acenaphthylene, do not show fluorescence and can only be determined by UV detection at higher concentrations. [13].

Sample preparation and preservation:
Samples taken for PAHs analysis should be stored in glass containers, protected from light and refrigerated until extracted. Polycyclic aromatic hydrocarbons are typical extracted by using dichloromethane and then exchanged into acetonitrile prior to analysis, aqueous samples were extracted using solid phase cartilage mini column sepack-18. After sample extraction a portion of the extract (10 µl) is injected onto a reversed-phase HPLC column and the PAHs eluted using a water / acetonitrile gradient as shown below. The PAH are detected using UV absorbance at 254 nm with high sensitivity using background corrected methods. [12].This method was to determine the 16 PAHs using UV detection and is consistent with US EPA methods 550.1 , 810.1 and 8310.3 as well as other regulatory methods worldwide. According to EPA 550 specifies starting with 1 L of sample, will pass on mini Colum (Speacl – C – 18) this will retain the PAHs then Elute them from the Colum by 5 ml pure methanol that mean pre-concentration to a volume of 5 ml before performing the HPLC analysis. In this case, divide the Numbers resulting from HPLC analysis by 200 to determine the real concentration. we took in our mind Temperature control is recommended to ensure stable retention time. [14].The Statistical Analysis System- SAS (2010) was used to effect of different factors in study

parameters. Least significant difference –LSD test was used to significant compare between means in this study. [15]

Results and discussions

The concentrations of the 16 detected polycyclic aromatic hydrocarbons (PAHs) in water surface of Tigris River near Al-Dora refinery are shown in (Tables 1-1A and 1-1 B). In terms of individual PAH composition in water most compounds analyzed were detected at all location sites.

Poly aromatic hydrocarbon presence can be described better if we discuss them as a group and compare them with their presence so the relation between the concentration of each one of them or as a groups according to their number of rings can be a good way to discuss their presence and sources so in this study the highest and the most dominant PAHs is Ancephthlnene with concentration (40.33 ng/l) in the 2nd station on august 2013 , while the lowest concentration was for Indeno(1,2,3-cd)pyrene with (0.33 ng/l) in the 1st station in both April and June . This study can show a good view for these 16 PAHs presence in the water so we can know the dangerous of their concentration and how these centration should be considered as highly effected on human or not as we now all the 16 PAHs is considered (from highly carcinogenic to moderated carcinogenic) and it can be a good indicator for the petroleum or other industrial pollution .Anthropogenic PAHs stem mainly from combustion of fossil fuels and spillage of petroleum. [16] .The sources of PAHs, whether from fuel combustion (pyrolytic) or from crude oil (petrogenic) contamination, may be identified by ratios of individual PAH compounds based on peculiarities in PAH composition and distribution pattern as a function of the emission source. [17]. Ratios of phenanthrene to anthracene (Ph/An) and fluoranthene to pyrene (Fl/Py) have been widely used to distinguish petrogenic and pyrogenic (pyrolytic) sources of PAHs. [18]. PAHs of petrogenic origin are generally characterized by Ph/An values >10, whereas combustion processes often result in low Ph/An ratios (<10). For the Fl/Py ratios, values greater than 1 have been used to indicate pyrolytic origins and values less than 1 are attributed to petrogenic source [19]. In the present study, Ph/An ratios for water samples were (0.72 in December 2012), (1.31 in February 2013), (1.27 in April 2013), (1.4   in June 2013), (0.46 in August 2013), (0.77 in October 2013). While for Fl/Py ratio values were (0.95 in December 2012), (0.86 in February 2013), (0.78 in April 2013), (1.01   in June 2013), (1.03 in August 2013), (0.43 in October 2013). This can be shown in (December 2012, February 2013, April 2013 and October 2013) attributed to petrogenic source, While in (June 2013 and August 2013) attributed to pyrolytic origins .Figure 2 shown the Bimonthly variation of PAH in Tigris River during 2012/2013.

The highest concentrations were obtained in autumn and spring, while the lowest concentration recorded in summer. This may be related with the climatic condition of Iraq and the effect of photo oxidation, volatilization and high degradation during the hot season [20].

As comparing with other studies, several studies performed in the United States reported values of carcinogenic PAHs for drinking-water in the range 0.1–61.6 ng/l ,Similarly, the examination of a number of drinking-water supplies for six PAHs (fluoranthene, benzo[b]fluoranthene, benzo[k]fluoranthene, Benzo(a)pyrene, benzo[g,h,i]perylene and indeno[1,2,3-c,d]pyrene) indicated that the collective concentrations generally did not exceed 100 ng/l. The concentrations of these six PAHs were between 1 and 10 ng/l in 90% of the samples and higher than 110 ng/l in 1% [10] .

Regarding the concentrations of the 16 PAHs, these span the range of 106.5– 150.3 ng/l in several European and Canadian cities, while lower values of 85.2–94.6 ng/l have been reported in Taiwan, China. Studies which were performed in Europe have reported levels of Benzo(a)pyrene in the range of < 1 ng/l in Germany to 10 ng/l in Poland [10] .

Values of Benzo(a)pyrene in the same range (1.4–2.5 ng/l) have also been reported in Taiwan, China. Assuming an average drinking-water consumption of 2 l/day, the potential dose of carcinogenic PAHs via drinking-water ranged from 0.2 to 123 ng/day, 170–300 ng/day for the 16 PAHs and < 2–20 ng/day for Benzo(a)pyrene [17].
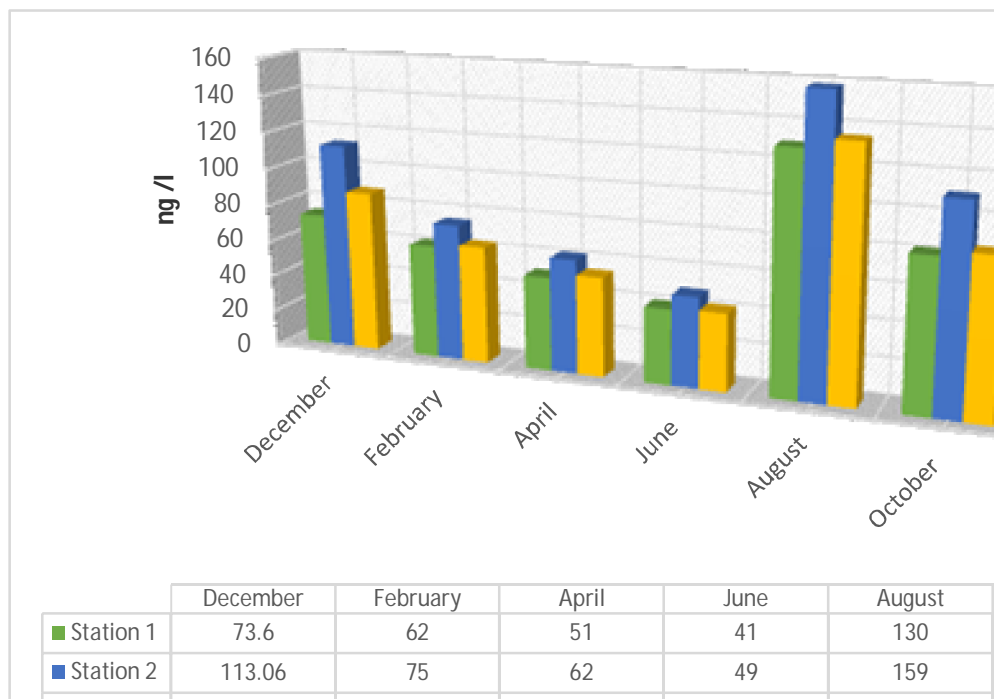
	December	February	April	June	August
■ Station 1	73.6	62	51	41	130
■ Station 2	113.06	75	62	49	159

Figure 2-Bimonthly variation of PAH in Tigris River during 2012/2013

Table 1-1 A and B -Show The PAHS Concentration Along the Study (From DEC 2012 –October 2013)

TABLE A	December			February			April		
PAHS	1st	2nd	3rd	1st	2nd	3rd	1st	2nd	3rd
NAPHTHALENE	10.2	12.4	13.3	9.9	11.2	10.3	6.8	9.9	7.1
ACENAPHTHYLENE	7	14.3	10.1	6.7	9.81	7.2	8.1	7.88	7.4
ACENAPHTHENE	21.4	33.3	26.6	17.7	20.19	17.4	16.6	17.1	15.9
FLURENE	2.3	5.5	3.1	3.4	4.12	5.11	2.7	3.01	2.6
PHENANTHRENE	8.8	11.3	9.7	6.8	8.11	6.5	4.9	7	5.3
ANTHRACENE	7.9	15.5	6.7	3.9	6.16	4.2	4.8	5.5	6.1
FLUORANTHENE	2	2.3	2.3	1.22	1.42	1.23	0.66	1.1	0.74
PYRENE	2.1	2.4	3.2	1.12	1.66	1.22	0.86	1.4	0.96
BENZO(A)ANTHRACENE	2.6	3.1	2.9	1.94	2.4	2.1	1.1	1.6	1.6
CHRYSENE	1.9	2.7	2.1	1.89	2.42	1.79	1.3	1.9	2
BENZO(B)FLUORANTHENE	1.5	2.1	1.7	2.1	1.5	2.3	0.55	1.1	0.76
BENZO(K)FLUORANTHENE	0.99	1.44	1.2	1.2	1.36	1.3	0.62	1.3	0.62

BENZO(A)PYRENE	1.45	2.21	1.6	0.77	1.22	0.87	0.76	1.3	0.93
DIBENZO(A,H)ANTHRACENE	0.98	1.31	1.1	1.3	1.1	1.2	0.49	0.7	0.64
BENZO(G,H,I)PERYLENE	1.78	2.6	1.9	1.68	2.15	1.76	1.21	1.4	1.3
INDENO(1,2,3-CD)PYRENE	0.7	0.6	0.6	0.44	0.51	0.41	0.33	0.4	0.34
TOTAL PAH	73.6	113.06	88.1	62.06	75.33	64.89	51.78	62.59	54.29
TABLE B	December			February			April		
PAHS	1st	2nd	3rd	1st	2nd	3rd	1st	2nd	3rd
NAPHTHALENE	6.54	7.01	7.1	9.39	10.44	9.99	11.4	13.1	12
ACENAPHTHYLENE	5.9	5.5	6	15.1	20.1	16.8	11.3	15.7	10.8
ACENAPHTHENE	12.3	14.1	11.1	33.2	40.33	36	22.1	27.6	20.9
FLURENE	1.8	2.7	1.9	8.67	9.72	8.9	3.3	6.7	4.1
PHENANTHRENE	4.4	6.11	4.7	13.2	15.5	12.8	7.91	10.9	8.44
ANTHRACENE	2.9	4.3	3.1	25.7	32.39	23.7	10.4	13.5	9.99
FLUORANTHENE	0.42	0.87	0.51	4.1	3.9	4.2	1.7	1.8	2
PYRENE	0.44	0.81	0.56	3.1	3.6	3.3	2.6	4.1	3.3
BENZO(A)ANTHRACENE	0.55	0.69	0.7	2.8	3.5	2.8	2.6	3.6	2.55
CHRYSENE	2	1.6	2.1	3.8	4.4	4.1	1.8	3.1	2.4
BENZO(B)FLUORANTHENE	0.45	0.92	0.44	3.5	3.8	4.1	1.95	2.5	2.1
BENZO(K)FLUORANTHENE	0.87	1.29	0.92	1.77	2.1	1.67	1.43	1.66	1.8
BENZO(A)PYRENE	1.32	1.55	1.43	2.1	3.9	1.9	1.5	2.76	1.8
DIBENZO(A,H)ANTHRACENE	0.5	0.5	0.6	1.88	1.98	2.1	0.77	1.39	1.1
BENZO(G,H,I)PERYLENE	0.66	1.1	0.76	1.65	2.76	2.5	1.6	2.55	1.9
INDENO(1,2,3-CD)PYRENE	0.33	0.41	0.4	0.55	0.99	0.76	0.44	0.59	0.64
TOTAL PAH	41.38	49.46	42.32	130.51	159.41	135.62	82.8	111.55	85.82

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