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Determination of PAHs in Surface Water of Al-Dalmaj Marsh, Al-Diwaniya Province, Iraq

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Abstract
Polycyclic aromatic hydrocarbons (PAHs) occurs in an environment as organic pollutants, these pollutants are resulting from anthropogenic and natural pyrolysis of organic compounds during fossil fuel utilization, forest fires, and chemical manufacture. Sixteen of these compounds have been classified as human carcinogens. In this study five sampling sites have been selected randomly, all these sites locate in Al-Dalmaj marsh in Al-Diwaniya province. Thirteen compounds of PAHs compounds are measured using solid phase extraction method to extract the PAHs compounds from water samples. The analysis for water samples performed by GC technique. The results show variation from site to site in concentrations and in type of pollutants abundant. Site four shows highest pollution with nine compounds while site three shows the lowest pollution with four compounds. The maximum pollution among all measured compounds was 14.903 mg/L for Fluorene in site Four while the minimum one was 0.027 mg/L for Acenaphthylene in site three.
Keywords: Surface waters pollution, PAHs, Solid phase extraction, Al-Dalmaj marsh, Al-Diwaniya province.

Introduction

Polycyclic Aromatic Hydrocarbons (PAHs) or polynuclear aromatic hydrocarbons are an important class of environmental pollutants owingto their prevalence and potentially adverse health effects. PAHs are ubiquitous environmental pollutants found in aquatic environments, soil and air[1-3].PAHs emitted into the environment as a result of industrial processes enter the surface water of lakes, rivers and marshes together with atmospheric deposition.These compounds may also enter to rivers directly along with municipal and industrial effluents [4]. Their concentrations range from not more than 10 ng/L in slightly polluted water to more than1000 ng/L in heavily polluted water [5, 6].

PAHs are defined as these compounds that consist of two or more fused aromatic rings, containing only hydrogen and carbon atoms[7,8]. Human activities such as agriculture and industrial production, combined with population growth and heavy urbanization may negatively affect the aquatic environment, this effect including the decomposition of wetland habitats and a heightened risk for humans and aquatic organisms [9-11].

Most PAHs are suspected mutagens and carcinogens they are widespread in the water, soil and air [12,13].These compounds are formed mostly by the incomplete burning of organic materials [14,15]. PAHs compounds may appear in the atmosphere either in the gas or particulate phase [16].

Due to the mutagenicity and carcinogenicity for these compounds, they were listed in several priority pollutant agencies such as the Agency of Toxic Substances and Disease Register (ATSDR), the European Community (EC), the Environmental Protection Agency (EPA), Cancer (IARC) and the International Agency for Researchand in 1984 in the United States Environmental Protection Agency (USEPA) (US Environmental Protection Agency, 1984) [17].The main source for exposure of PAHs to humans is 88-98% connected with food [18]. Penetration of PAHs through humans food can follow two paths: the first is directly when eat smoking fish, for example and the second is indirectly from polluted air or polluted water. PAHs compounds tend to beinglypophylic in nature its accumulate in the fatty tissues of organisms; as such they formed from the fatty tissues of fish at higher temperatures during the grilling, barbecuing or smoking processes.The production of PAHs is well-known to appear through the pyrolysis of fat at temperatures of more than 200°C [19, 20], and it is highly stimulated at temperatures of more than 700°C during food preparation [21].Pyrolysis of other organic compounds such as carbohydrates and proteins might be released, but the highest concentrations of PAHs have been appeared to arise from fat pyrolysis[22].Figure 1, shows structures of 13 PAHs.

The main objective of this study was to evaluate the level of contaminated samples with 13PAHs from five selected sites in Al-Dalmaj marsh.

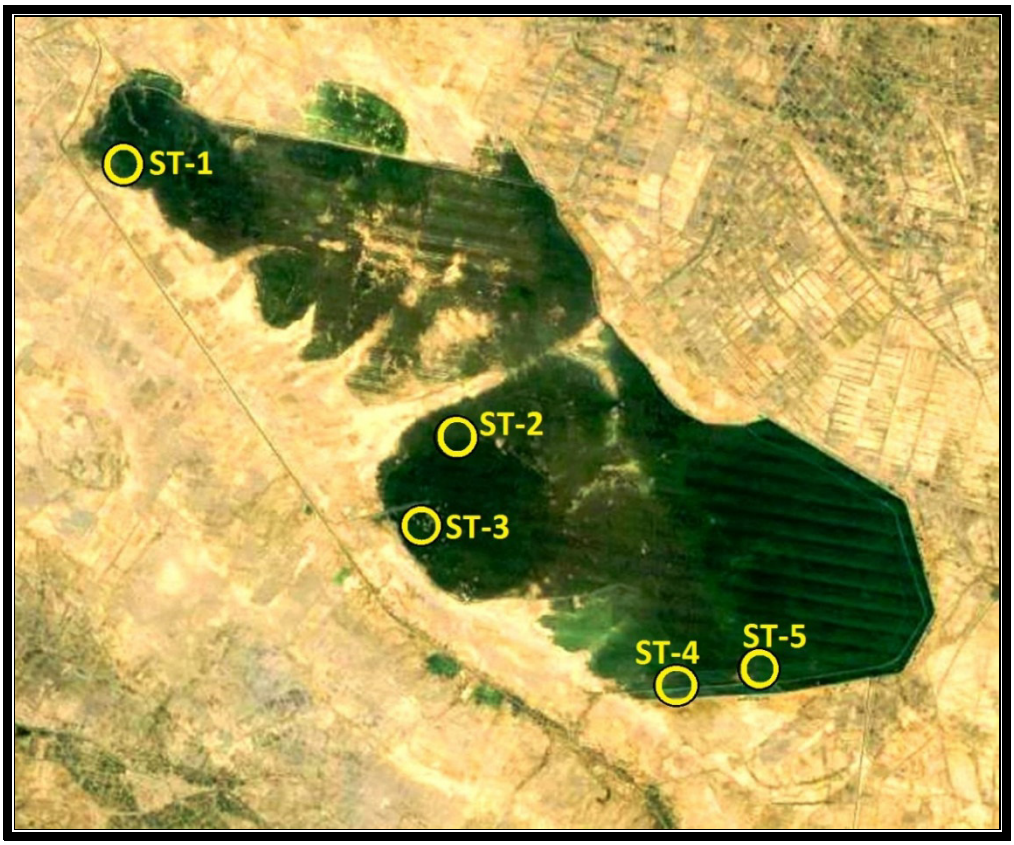

Figure 1. Map of the study area

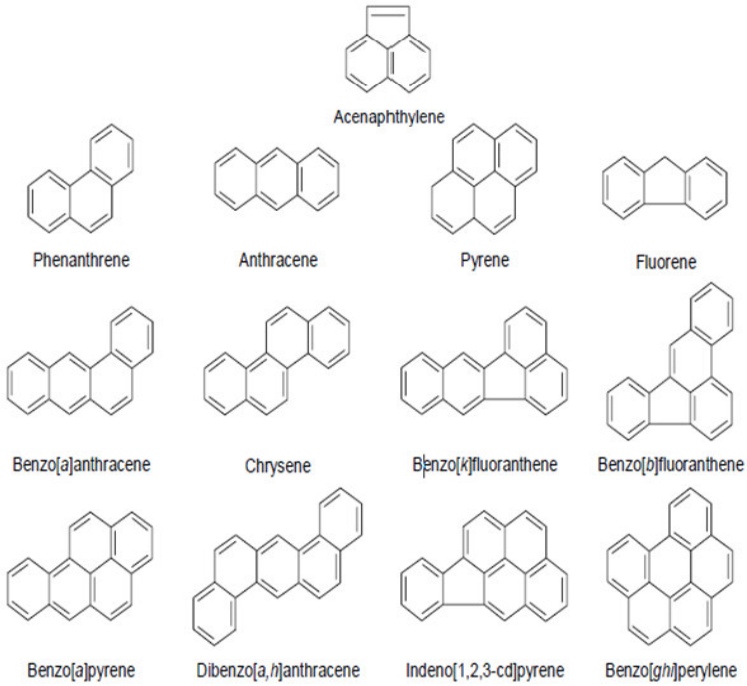

Figure 2. Structures of the 13 US-EPA PAHs

Experimental

Study area

Al-Dalmaj marsh is a large wetland locate between Al-Diwaniya province west and Wasit province east, this marsh is famous that have a several types of yearly migrate birds cams from Asia and Europ. Several types of fishes are frequent in this marsh, figure 1, shows the map of the study area[23].

Table (1) show coordinate of station in Aldelmj marsh

ST-1	ST-2	ST-3	ST-4	ST-5
N''43.22' 18˚32 E ''49.93' 15 ˚45	N''55.98' 15 ˚32 E''40.90' 15 ˚45	N''16.15' 11˚32 E''47.09' 21˚45	N 4.54' 9 ˚32 E''22.15 24˚45	N''52.65' 6˚32 E''23.62' 28˚45

Chemicals & reagents

The standard mixture solution of PAHs(13) compounds: Acenaphthylene, Fluorene, Phenanthrene, Anthracene,Pyrene, Chrysene, Benzo[a]anthracene, Benzo[b]Fluoranthene, Benzo[k]fluoranthene, Benzo[a]Pyrene, Di benzo[a,h]anthracene, Benzo[g,h,i]perylene, and Indeno[1,2,3-cd]pyrene was purchased from Sigma-Aldrich EPA 525 PAH Mixture A. This standard was stored at 4°C, protected from light.

Sampling and pretreatment:

Five samples of surface water from Al-Dalmaj marsh have collected trice. The depth of surface water samples were collected are ranged between 0.5 to 0.25 m using pre-cleaned amber glass bottle. The capacity for these bottles is 1 L supply with screw cap and lined with foil to prevent matching the PAHs compounds with plastic cap. Samples kept in cooler box with 4°C, transported to the laboratory immediately, to ensure that no degradation will happen for less molecular weight of polycyclic aromatic hydrocarbons when it is expose to the light or high temperatures degree through transfer samples to the lab. Water samples filtered through 0.5 µm filter paper.

Extraction procedure:

All glassware's that used in this work were pre cleaned with washing acids, solvents, detergents, hot water, rinsed with distill water and then dried for 60 min. at 180 ºC. Water samples extracted by Supelclean™ ENVI-18 SPE Tube bed wt. 500 mg, volume 6 ml, pkg of 30 ea from SupelcoCompany. These tubes conditioned with 5 ml of ethyl acetate and then conditioned with 5 ml of methanol followed by 2 x 5 ml of deionized water [24]. One liter of water sample after filtration was passed through the extraction column with flow rate 2mL/min. Suspended PAHs eluted of extraction column usingdichloro methane solvent. The passed solution reduced to 1 ml using rotary evaporator. The concentrated sample collected in small dark isolated glassy container and kept in4°C.

GC conditions

After sample extraction a portion of extract (2µl) injected by micro syringe in GC.The detailsof experimental parameters for GC Shimadzu 2104,that the injector mode is splitless at temperature 250°C sample injection 2 µL in column type Hp5 (30m * 0.25mm * 0.25µm) equipped with a flame ionization detector, HP-5 column, carrier gas was nitrogen. The GC oven temperature was programmed to increasefrom50 °C (2 min) to 200 °C (2 min) at a speed of 20 °C/min, to 240 °C (2 min) at 5 °C/min, and to 250 °C at 3 °C/min and then held for 15 min. The injector and detector temperatures were 275 °C and 300 °C, respectively. GC:, and the detector type flame ionization detector.

Results and Discussion

Due to the industrialization and urbanization, several kinds of pollutants find their way into all parts of our environment.PAHs are may be produced and released to the environment as a result of incomplete burning or as a result of pyrolysis of fuel and organic matter, during industrial processes and other human activities [25].Water contamination with PAHs is associated with the anthropogenic activities that represent the major source of PAHs compounds in addition to natural source.PAHs compounds are have special interest due to their potential hazard to human and natural life. Therefore, the determination of PAHs in the aquatic environment is quite essential and provides very important information on the anthropogenic input into the study area. Levels of the PAHs in previous study were reported petrogenicand anthropogenic origin and closely related, due to their molecular weights.

Table2. Concentrations of PAHs in selected sites

Compound mg/L	Site 1	Site 2	Site 3	Site 4	Site 5	Mean
Acenaphthylene	**0.80**	**0.16**	**0.27**	**0.55**	**1.85**	**0.72**
Anthracene	**1.31**	**1.25**	**-**	**6.11**	**-**	**1.73**
Benz[a]anthracene	**-**	**-**	**-**	**10.44**	**1.67**	**2.42**
Benz[b]fluoranthene	**-**	**-**	**-**	**1.63**	**-**	**0.32**
Benz[k]fluoranthene	**-**	**-**	**-**	**-**	**8.56**	**1.71**
Benz[ghi]perylene	**5.73**	**1.39**	**-**	**-**	**-**	**1.42**
Benz[a]pyrene	**-**	**-**	**-**	**3.41**	**-**	**0.68**
Chrysene	**3.01**	**3.11**	**2.10**	**10.49**	**-**	**3.74**
Dibenz[a,h]anthracene	**-**	**-**	**-**	**-**	**-**	**-**
Fluorene	**-**	**-**	**-**	**14.90**	**12.29**	**5.43**
Inden[1,2,3-cd]pyrene	**2.30**	**4.53**	**1.76**	**-**	**6.29**	**2.97**
Phenenthrene	**-**	**-**	**-**	**7.29**	**-**	**1.45**
Pyrene	**1.07**	**4.49**	**3.65**	**13.82**	**1.45**	**4.89**
Mean of summation						**2.11**

Five samples of surface water were collected from five selected sites of Al-Dalmaj marsh. The results exhibit high variety between the concentrations of PAHs from site to site as shown in table 1. The concentrations of acenaphthylenewhich consist of three fused aromatic rings is ranged from 0.16 to 1.85 mg/L, this compound occur in all samples, the highest value is 1.85 mg/L in site 5 while the lowest value is 0.16mg/L in site 2. Anthracenewhich consist of three fused aromatic rings appears in sites (1, 2 and 4), the highest value is 6.11mg/L in site 4 while the lowest value is 1.25mg/L in site 2. Benz[a]anthrecenewhich consist of four fused aromatic rings appears in sites 4 and 5 with concentrations 10.44mg/L and 1.67 mg/L respectively. The concentration of Benz[b]fluoranthene which consist of five fused aromatic rings is 1.63mg/L in site 4. Benz[k]fluoranthenewhich consist of five fused aromatic rings appears in site 5 only with concentration 8.56 mg/L. Benz[ghi]perylenewhich consist of three six fused aromatic rings is occur in sites 1 and 2 with concentrations 5.73 and 1.39 mg/L respectively. The concentration of Benz[a]pyrenewhich consists of five fused aromatic rings is 3.41mg/L in site 4. Chrysenewhich consist of four fused aromatic rings appears in sites 1,2,3 and 4, the highest concentration is 10.49 mg/L while the lowest concentration is 2.10 mg/L. Dibenz[a,h]anthracenewhich consist of five fused aromatic rings didn't appear in all sites. Fluorenewhich consist of three fused aromatic rings is appearing in sites 4 and 5 14.90 mg/L and 12.29 respectively.Indeno[1,2,3-cd]pyrenewhich consist of six fused aromatic rings occurs in all sites unless site 4. The highest concentration is 6.29 mg/L while the lowest concentration is 1.76 mg/L. Phenanthrenewhich consist of three fused aromatic rings appears in site 4 only with concentration 7.29 mg/L. Pyrenewhich consist of four fused aromatic rings occurs in all sites, the highest concentration is 13.82 mg/L while the lowest concentration is 1.07 mg/L.

Table 2, illustrate the summation of mean concentrations for 13 PAHs classified according to the number of fused rings that consist of its. Percentage abundance for all classes of PAHs (three fused rings, four fused rings, five fused rings and six fused rings) are listed in table 2.

Table3. Mean concentration of PAHs classified according to number of rings and representative percentage

	No. of rings			
	Three fused rings	**Four fused rings**	**Five fused rings**	**Six fused rings**
Σ of mean concentration mg/L	**9.33%**	**40.28%**	**9.87%**	**2.97%**
Percentage abundance	**43.01%**	**40.28%**	**9.87%**	**16.00%**

Figure 2, illustrate the distribution of four classes of 13 PAHs according to the percentage abundance.

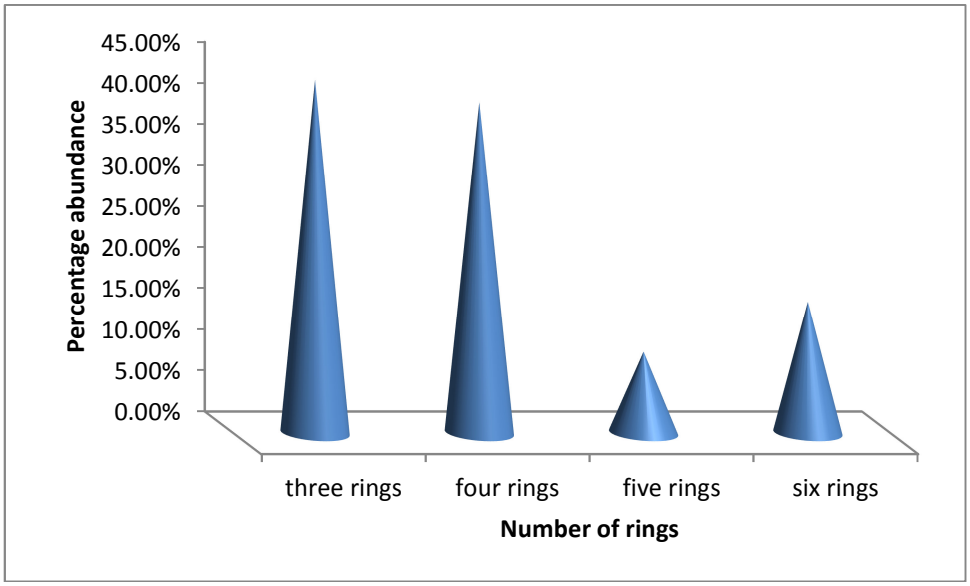

Figure3. Distribution of three, four, five, and six rings of PAHs in the surface water of Al-Dalamaj marsh

Conclusions

Five samples of Al-Dalmaj marsh were collected in 2014 for the period from January to May were extracted using solid phase extraction method and analyzed by gas chromatography technique. In general the results show high variation in pollution from site to site. Theresults are show high pollution within site 4. This site occurs pollution of nine compounds with high levels relatively. The highest concentration is 14.90 mg/L for Fluorene in site 4, while the lowest pollution appear in site 3.

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