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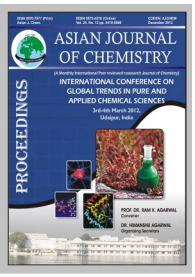

Determination of Polycyclic Aromatic Hydrocarbons in Surface Water of Shatt Al-Hilla River†

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Polycyclic aromatic hydrocarbons were analyzed in surface water of Shatt Al-Hilla river (middle of Iraq). Surface water samples originated from 14 sites with a differentiated human influence starting from Sadat Al-Hindya to southern border of Hilla governorate. Polycyclic aromatic hydrocarbons were extracted simultaneously by solid phase extraction using syback-18 with dichloromethane as solvent and then analyzed by HPLC. The polycyclic aromatic hydrocarbons concentrations were ranged between (1.08-1177.20) ng.mL^{-1}. The results showed the most pollutant sites was S7, which is represent the sewage pipe that came from Sooq Al-Hilla were contaminated with 12 compounds of polycyclic aromatic hydrocarbons. Fifteen polycyclic aromatic hydrocarbons were present in Shatt AL-Hilla among which 16 polycyclic aromatic hydrocarbons on the US-environmental protection agency priority pollutants list. The contamination with polycyclic aromatic hydrocarbons were variant from site to site in both (values of concentrations and existence of contaminants compounds) that may be return to the type pollutant sources, which it also was differ from site to site. Bulk deposition and domestic effluent are suggested as the main sources of polycyclic aromatic hydrocarbons pollutants in surface waters.

Key Words: Surface waters, Polycyclic aromatic hydrocarbons, HPLC, Shatt Al-Hilla.

INTRODUCTION

Polycyclic aromatic hydrocarbons are defined as a group of chemicals that are formed during the incomplete burning of coal, oil, gas, wood, garbage, or other organic substances, such as tobacco and charbroiled meat[1]. Most of these compounds have been classified by the world health organization (WHO, 1997), as carcinogenic, while others have been confirmed to be at least, mutagenic to mammals[2].

Most of the polycyclic aromatic hydrocarbons have low solubility in water and as a results they will be deposited in sediments. Moreover, compounds have very low photodegradation and biodegradation and to accumulate in high concentrations[3].

Many techniques have been used to extract polycyclic aromatic hydrocarbons from water samples, Chen[4], was used solid phase micro extraction method to extract polycyclic aromatic hydrocarbons compounds of water samples, Kafilzadeh *et al.*[5], has been used liquid-liquid extraction Jeffrey *et al.*[6], were used solid phase extraction disks, Ming-Chi *et al.*[7], were used microwave assisted headspace solid-phase micro extraction method.

Solid phase extraction is a simple treatment technique which passed a liquid sample through a sorbent. The analyte or interferences of samples are retaining on a sorbent by differences mechanism. The analytes were eluted in a small volume of solvent, concentrated and also cleaned up the sample[8].

Polycyclic aromatic hydrocarbons analysis in environmental samples is a challenging task because of the relatively low concentrations and the complexity of the mixtures in the sample analysis for polycyclic aromatic hydrocarbons compounds involves three major steps: 1) Sample preparation; 2) Sample cleanup, extraction and concentration; 3) Final detection and quantification.

E. Manoli *et al.*[9] and Kabzinski[10], were determined polycyclic aromatic hydrocarbons compounds in surface water using HPLC, Yeasmin *et al.*[11], have been used (GC-MS) to determination polycyclic aromatic hydrocarbons compounds.

Kanchanamayoon and Tatrahun[8], were determined 11 polycyclic aromatic hydrocarbons compounds in water samples using LC-18 solid phase to extract this compounds. This paper aimed to measure the concentrations of 16 polycyclic aromatic hydrocarbons compounds in surface water of Shatt AL-Hilla and identify the major contributing sources in different sites located on this river.

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EXPERIMENTAL

Description of study area and sampling: Shatt AL-Hilla consider as main source for drinking, agricultures use and hunting of fishes for the population they live around this river. Many pollution sources are present near these river such as draining sewage, agriculture pumps, layout pipes of purification stations of drinking water and treated waste water of textile factory in addition to the pollution by atmospheric deposition of polycyclic aromatic hydrocarbons compounds and others volatiles compounds. Shatt AL-Hilla starting from Saddat AL-Hindya and finished southern Al-Hilla city in Sadder Al-Dughara pass through a several villages and cities. The sites have been selected during a bout trip to exploring the contaminated sites with polycyclic aromatic hydrocarbons compounds which illustrate by following:

i) S1 which represents the site near Saddat AL-Hindiya to investigate the pollutant influent in Shatt AL-Hilla that located before interring the study area; ii) S2 which represents the site near purification station for drinking water (AL-Sadda Al-Muaffa) about 4 km from Saddat AL-Hindiya, this station has lay out pipe used to remove the slurry, sediments and impurities precipitate from crude water which purified to used as drinking water; iii) S3 which represents the site near AL-Jebal treatment station about 2 km from Saddat AL-Hindiya, This station was discharge the contaminated water through river; iv) S4 which represents the pollution which from the agriculture pumps in AL-Sada AL-Muafa region about 6 km from Saddat AL-Hindiya; v) S5 which represents the site near AL-Mahaweel city about 20 km northern of Al-Hilla city; vi) S6 which represents the site near of AL-Batta Bridge about 2 km northern AL-Hilla city (the drivers were used this region for washing their cars); vii) S7 which represents the site near walking bridge which supplied with pipe that carry out waste water came from big market of AL-Hilla (Sooq AL-Hilla) in the center of AL-Hilla city; viii) S8 which represents the pipe of treatment unit in AL-Farisy region 2 km from city center; ix) S9 which represents the Effar region about 5 km southern of city center, this region contaminated with a lot of agriculture pumps; x) S10 which represents AL-Hussain bridge about 7 km southern of Al-Hilla city. This region polluted with treatment unit of domestic water for AL-Dublla city; xi) S11 which represents AL-Bo Shnawa station of drinking water about 15 km from AL-Hilla city, this station supply with drain pipe to remove slurry and sediments from precipitating tanks; xii) S12 which represents the AL-Rewashed site about 20 km from AL-Hilla city; xiii) S13 which represents the AL-Hashimiya station of drinking water about 35 km southern of AL-Hilla city, this station supply with drain pipe to remove slurry and sediments from precipitating tanks; xiv) S14 which represents the end point of study area about 45 km southern of AL-Hilla city, this site has been selected to evaluate the effect of all pollutants sources at this point.

The sites of pollutants illustrated in following map of Shatt AL-Hilla River in Fig. 1.

Fourteen samples of surface water were collected in 2.5 L amber glass container fitted with a screw cap and lined with foil and labeled S1 to S14, to ensure that no degradation will happen for less molecular weight of polycyclic aromatic

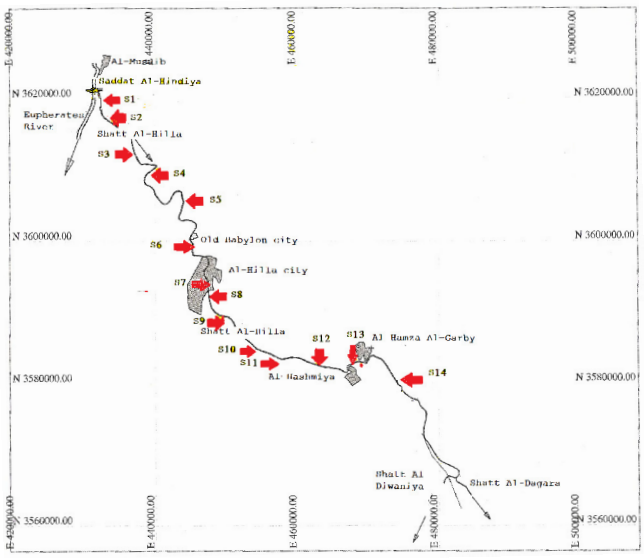

Fig. 1. Map of contaminated sites of Shutt AL-Hilla River.

hydrocarbons compounds when its exposed to the light and transferred directly to the laboratory as soon as and kept at 4 ºC.

All glassware's were pre cleaned with detergents, hot water, rinsed with distill water and then dried for 1 h at 180 ºC. According to EPA method 550 specific polycyclic aromatic hydrocarbons compounds have been extracted using solid phase extraction columns (Supelcoclean^{TM} ENV-18 solid phase extraction Tupe.bed wt. 500 mg volume 6 mL, pkg of 30 ea). The suspended of polycyclic aromatic hydrocarbons compounds were eluted from column cartridge by 10 mL of ethylene dichloride solvent, the solution then concentrated to 1 mL by rotary evaporator. After sample extraction, a portion of extract (50 µL) were injected onto reversed-phase HPLC Shimadzu LC-10 AVP. Polycyclic aromatic hydrocarbons compounds were eluted using water/acetonitrile gradient as shown bellow, polycyclic aromatic hydrocarbons were detected using UV absorbance at 254 nm with high sensitivity using background correction method the extraction procedure performed on precipitation and surface water samples is briefly described in Fig. 2.

Mobile Phase :A: Deionized water/B: Acetonitrile. Gradient:

Time (min)	B (%)
0	60
1	60
15	100
17	100

Flow rate: 1.5 mL/min, Inj. Volume: 50 µL, UV Detection : 254 nm

RESULTS AND DISCUSSION

The concentrations of the 15 detected polycyclic aromatic hydrocarbons from surface water of 14 sites located in Shatt Al-Hilla are shown in Table-1, which illustrate the differences between all sites in number of polycyclic aromatic hydrocarbons compounds were detected and in the concentrations of these compounds, may comeback to the effect of the source that exist in this site. The variable in the kind of pollutant sources were produced polycyclic aromatic hydrocarbons compounds contributed to variation in results another reason

TABLE-1
CONCENTRATIONS OF 16 POLYCYCLIC AROMATIC HYDROCARBONS COMPOUNDS OF SURFACE WATER SAMPLES IN FOURTEEN SELECTED SITES

Compound	S1 conc./ng .mL^{-1}	S2 conc./ng .mL^{-1}	S3 conc./ng .mL^{-1}	S4 conc./ng .mL^{-1}	S5 conc./ng .mL^{-1}	S6 conc./ng .mL^{-1}	S7 conc./ng .mL^{-1}	S8 conc./ng .mL^{-1}	S9 conc./ng .mL^{-1}	S10 conc./ng .mL^{-1}	S11 conc./ng .mL^{-1}	S12 conc./ng .mL^{-1}	13 conc./ng .mL^{-1}	S14 conc./ng .mL^{-1}
Naphthalene														
Acenaphthylene											173.4		51.6	122.8
Acenaphthene				9			96.8	19.1	1.08					
Fluorene	11.5	10.68		6.2			255.6	11.58		14.72			162.4	241.6
Phenanthrene	12			9.6	2.26	28.6	202.4		17.24	54.7			282.8	1177.2
Anthracene	10.4		248.2			8.24	91.2				67.56		156.8	
Fluoranthene	8	4.6	8	9	10.76		82.88			36		250	166.8	364.28
Pyrene			143.6		8		101.6					140.36	67.56	148.8
Benzo(a)anthracene	8.6	7.9			82.28	34.72			22.88	36				
Chrysene		8.16	425.6				86	16						
Benzo(b)fluoranthene	10.3			15.2			119.2						68.8	
Benzo(k)fluoranthene	12.6	35.8			29.56	20.36	86.8						676	101.36
Benzo(a)pyrene		64.2	183.56	2.9			202		19.32					
Dibenzo(a,h)anthracene	228.8	7.9	54.4				472			17				
Benzo(g,h,i)perylene	194.4			10.7										
Indeno(1,2,3-cd)perylene	93.2	7.7	421.6	8.8			292							

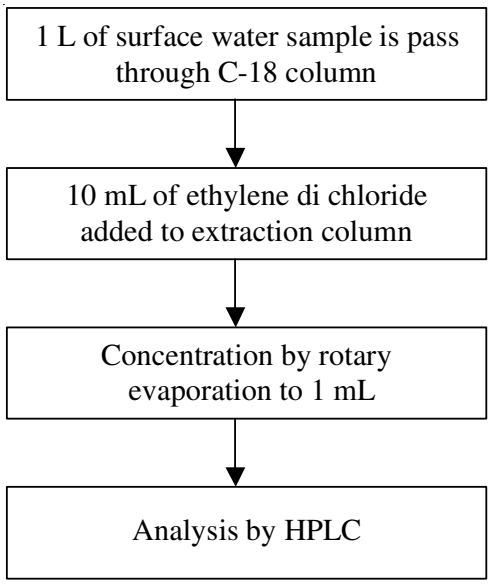

Fig. 2. Scheme of extraction procedure

for different may be return to the degradation factors, which presented in this sites (bacterial, sun light intensity, temperature degree and flouting body, which act some of them as a good absorbent to the polycyclic aromatic hydrocarbons compounds such as flouting died plants or flouting residue plants[12]. Another reason had been contributed that effect of crowded traffic, which increased the percent of polycyclic aromatic hydrocarbons compounds if we take in consideration the sites are distributed in urban and rural places. Table-1 illustrate that no Naphthalene in all sites has been detected and that because of law stability of this compound which consist of two fused aromatic rings and that made of this compound a less stability than others. Minimum concentration of polycyclic aromatic hydrocarbons compounds was (1.08) ppb of Acenaphthelene from site No. 9 while the maximum concentration was (1177.2) ppb of Phenenthrene from site no.14

Site No.7 was the most contaminated site than others (12 compounds of 16), while both sites 11 and 12 were contaminated with only tow compounds.

Site No. 7 was the most pollutant place than others because of the effecting the sewage layout from the Al-Hilla Big market, this pollutant came from the discharge of used oil derivatives and the crowding traffic near this region were a lot of un completed burning process are exist in this site.

Conclusion

Fifteen polycyclic aromatic hydrocarbons compounds of sixteen had been determined in all fourteen selected sites in surface water of Shatt al-Hilla River by HPLC. The results illustrate that all sites were contaminated in different percent of polycyclic aromatic hydrocarbons compounds according to human activity which present in these sites, also site No.7 was the most contaminated site than others.

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