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

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Polycyclic aromatic hydrocarbons occur in an environment as organic mixtures resulting from anthropogenic and natural pyrolysis of organic compounds during fossil fuel utilization, forest fires and chemical manufacture. Several of them have been classify as human carcinogens. According to effects of these compounds on human health, this study is necessary in Iraq. In this study, sixteen polycyclic aromatic hydrocarbons 2-6 fused aromatic rings determined and compared. Water samples from fourteen sites taken monthly. The variations for the concentrations of sixteen polycyclic aromatic hydrocarbons in surface water monitored for one year. Study starts from November 2011 to October 2012. The analysis performed by HPLC technique with UV-visible detector. Selected samples taken from fourteen sites on the both banks of the Shatt Al-Hilla river. Extraction method in this survey was done by solid phase extraction. The results showed high variations in concentrations of polycyclic aromatic hydrocarbons compound from site to site and from month to month depending on human activities per site and month. Benzo[a]pyrene was the highest concentration reaching (601.81) ppb in site six in November 2011. The summation of all polycyclic aromatic hydrocarbons samples for fourteen sites during twelve months were 13115.52 ppb. Among all these compounds, Fluorene recorded the maximum cumulative value of 1690.608 ppb, where as the minimum value amongst all polycyclic aromatic hydrocarbons compounds on cumulative term was for acenaphthene, which was 300.102 ppb.

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

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) refer to hydrocarbons containing two or more fused aromatic rings. All PAHs compounds are neutral and non-polar and they have high stability. All of them having high melting points and low vapor pressures and water solubility. Generally, the solubility and volatility of PAHs compounds are decrease and hydrophobicity increase with an increase in the number of fused aromatic rings[1]. Fires and agriculture fires, fossil fuels burning, metal-processing facilities, coke oven and internal burning engines in motor vehicles[2] can produce these compounds. The delocalization of π electron made these compounds exhibit high stability and low water solubility, leading to their accumulation in food chains[3]. US Environmental Protection Agency (EPA), US Food and Drug Administration (FDA), National Oceanic Atmospheric Administration (NOAA) and the European Union Priority pollutants are listed PAHs as pollutant because of their mutagenic and carcinogenic properties[4-6]. The procedures of enrichment and clean up are usually required prior determination of PAHs. There are several reports mention the application of solid phase extraction on the pre concentration of PAHs from water samples[7-11]. Solid phase extraction offers a faster, more cost effective sample preparation method with dramatic time savings compare with many traditional liquid-liquid extraction techniques[12]. Other advantages of solid phase extraction such as reduction in volume of solvents used, possibility of automation (by online coupling with HPLC or GC) and simplicity of operation[13]. Atmospheric deposition considered an important input of polycyclic aromatic hydrocarbons in surface waters[14]. Low molecular weight of PAHs (two and three rings) occurs in the atmosphere in the vapor phase whereas five rings of PAHs are bound to particles. Intermediate molecular weight (four rings) of PAHs are partitioning between the vapor and particulate phases, depending on the temperature of atmosphere[15]. Due to their trace level concentration in complex water, it is required efficient preconcentration and high sensitive and selective method for separation and analysis techniques[16]. Several researchers were applied different techniques to detect PAHs. High performance liquid chromatography/fluorescence detection[17,18], ultraviolet diode/array detection[19,20], gas chromatography-mass spectrometry[21-27]. Gas chromatography (GC)[28,29] and high performance liquid chromatography coupled to electro spray ionization mass spectrometry

(HPLC-ESI-MS)[30]. Health effects resulting from exposure to PAHs have discussed recently in the literature[31-33]. These include growth retardation, small head circumterence, low birth weight, low IQ, damaged DNA in urban children, *etc.*[34]. Seven PAH compounds have been classified by the USEPA as compounds of problem human carcinogens[35]. These are benzo[a]pyrene, benzo[a]anthracene, chrysene, benzo[k]fluoranthene, benzo[b]fluoranthene, dibenzo[a,h]anthracene and indeno-[1,2,3-cd]pyrene. Polycyclic aromatic hydrocarbons known for their carcinogenic, mutagenic and teratogenic properties are benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, benzo[g,h,i]perylene, coronene, dibenz[a,h]anthracene, indeno[1,2,3-cd]pyrene and ovalene[36].

The main objective of this study was to evaluate the level of contaminated samples with 16 PAHs from fourteen selected sites in Shatt Al-Hilla river and monitoring PAHs concentrations during one year to indicate the effect of both weather and location.

EXPERIMENTAL

Study area: Shatt Al-Hilla river is one of the important rivers for water supply and irrigation in Babylon Governorate, Iraq. The total length of this river is 97 km. Many pollution sources are present near this river like draining sewage, agriculture pumps, treated wastewater of textile factory and layout pipes of purification stations of drinking water in addition to the pollution by atmospheric deposition of PAHs and others volatiles compounds. Shatt Al-Hilla river is starting from Saddat Al-Hindya and finish southern borders of Al-Hilla city in Sadder Al-Dughara passing through a several villages and cities[37]. Fig. 1 shows the map of study area.

S1 represents the site near Saddat Al-Hindiya barrage which locate after this barrage directly about 1km on the right bank of Shatt Al-Hilla river. This site has selected to investigate the pollutant influent in Shatt Al-Hilla that located before interring the study area.

S2 represents the site near the municipal water treatment station. This station used for drinking water. About 4 km from Saddat Al-Hindiya barrage on the right bank. This station has a lay out pipe. This pipe was used to remove the slurry, sediments and impurities precipitate from crude water. which was purified in precipitation tanks and then drain the precipitants to the river again by these pipe which it content about high percent of PAH, for this reason site two was selected to indicate the pollution that came from this station in addition to that came from site locate before in. Samples have collected from 3 m from the pipe out let.

S3 represents the site near Al-Jebal treatment station about 2 km from Saddat Al-Hindiya barrage on the left bank of Shatt Al-Hilla river, in this station the sewage water is discharge through the river by pipe. Sewage water may be including PAHs, according to the assumption this site selected to indicate the total pollution for this site and others locate before it. Samples were packed in specify bottles from distance about 3 m of pollution source.

S4 represents the site near (Al-Sadda Al-Muaffa) about 6 km from Saddat Al-Hindiya barrage on the right bank of the river, at this station pollution which produced from the agriculture water pumps which use for plants irrigation, these pumps operate with oil derivatives, these type of fuels are rich with PAH compounds especially when the fuel combustion is incomplete. This site selected to investigate the affect of these pumps on pollution levels.

S5 represents the site near of Al-Batta Bridge about 2 km northern of Al-Hilla city on the left bank of Shatt Al-Hilla river. In this station the drivers are use this region for washing their cars. Often the washing water had mixed with different type oil derivatives such as gasoline, lubricates oil, gearbox oil, wax and so on, for this reason site five selected to indicate affect of these pollutants in addition to those came from before it. Sampling site was about fifteen meters from the pollution source.

S6 represents the site near Sooq Al-wardiya in the mid of Al-Hilla city on the right bank of the river. In this station, the pollution source is the drainpipe of sewage came from Al-wardiya region, which discharge the contents throw river. This site had selected to remark the pollution levels in production source and others. Samples bottles have filled about 3 m from pollution pipe.

S7 represents the site near small bridge in Al-Hilla city on the left bank of the river. The pollution source is pipe discharge water mixed with different oil derivatives and sewage drain. This pipe also carry out wastewater came from big market Hilla city (Sooq Al-Hilla). This site had selected to investigate the pollution levels in pollution source and others. Samples bottles filled about 3 m from pollution pipe.

S8 represents the site near Al-Farisy region 2 km southern from city center on the left bank of the river. The pollution source in this site is persistence the drainpipe came from treatment station for sewage water. This site selected to indicate the total pollution for this site and others locate before it. Samples bottles had filled about 3 m from pollution pipe.

S9 represents the site near Effar region about 4 km southern of Hilla city center, on the left bank of the river, in this station pollution which produced from the agriculture water pumps which use for plants irrigation, these pumps operate with oil derivatives also, therefore has been selected to indicate the effect of these pumps.

S10 represents the site is Dolab village, about 6 km southern of Al-Hilla city on the left bank. This site was selected to indicate the effect of boats, which operate with hydrocarbons fuel, which spread in this location and used by anglers. The incomplete combustion is for this fuel contributes to raise the contamination levels with PAH compounds, for this reason the site had selected.

S11 represents the site near Al-Dabla village, which locate about 12 km southern from Al-Hilla city on the left bank of the river. This region had selected due to the pollution that produced from the treatment station for sewage water of Al-Dabla village. This site selected to indicate the total pollution for this site and others locate before it. Samples bottles filled about 3 m from pollution pipe.

S12 represents the site near Al-Ibrahimia bridge, which locate about 20 km southern from Al-Hilla city on the right bank. This site had selected to indicate the accumulation affect for the previous contamination source.

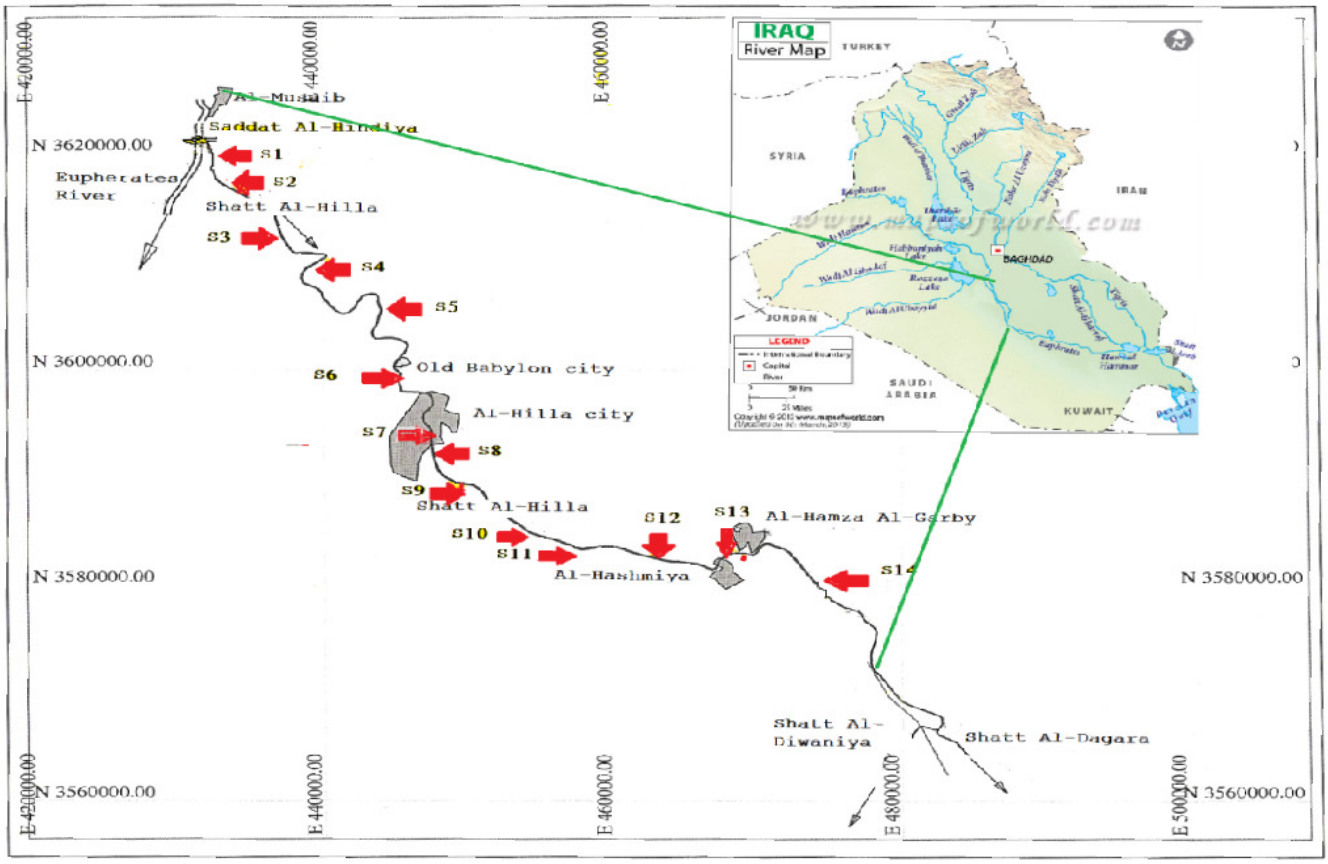

Fig 1. Map indicating the, sampling points in Shatt Al-Hilla river

S13 represents the region near Al-Hashimiya water treatment station for drinking water production, about 20 km southern of Al-Hilla city on the left bank of the river, this station has a drain pipe to remove slurry and sediments from precipitating tanks came from this station. Samples bottles filled about 3 m from pollution pipe.

S14 represents the endpoint of study area about 45 km southern of Al-Hilla city on the right bank of the river, this site had selected to evaluate the effect of all pollutants sources and before it from S1 to S13 at this point.

Sampling and pretreatment: Fourteen samples of surface water from Shatt Al-Hilla river are collected once per month. Various sensors including temperature, pH, dissolve oxygen and conductivity deployed for obtaining these master variables. The depth of surface water samples were collected are ranged between 0.5 to 0.25 m using pre-cleaned amber glass bottle.

TABLE-1
RANGE OF MEAN CONCENTRATIONS IN ppb, FOR PARENT PAHS,
IN WATER FROM FOURTEEN SITES DURING ONE YEAR ARE DESCRIBED

Site / PAHs µg/L)	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	S13	S14
NA	1.20	1.97	3.89	0.11	7.73	ND	1.05	6.39	0.36	0.02	0.15	7.13	0.63	0.54
Aceph	0.47	2.90	11.22	5.13	5.57	3.03	1.21	10.90	1.40	0.51	2.51	3.85	1.14	3.16
AC	2.95	0.37	1.97	1.80	0.08	1.49	0.72	2.99	10.86	0.72	0.04	0.57	0.13	0.26
Fluor	3.90	6.59	14.80	10.88	6.01	18.99	10.57	14.83	13.79	9.42	5.61	11.43	5.13	9.33
Phen	6.70	1.01	0.87	1.30	2.36	3.58	3.27	0.40	2.88	7.37	0.29	0.24	4.25	17.14
AN	6.64	6.32	0.47	1.62	7.88	1.06	3.05	1.51	0.08	5.39	10.26	1.16	4.19	1.13
Flur	3.26	5.77	9.35	3.13	7.42	3.81	1.31	5.73	2.50	9.99	3.29	17.46	7.24	15.20
Pye	0.24	8.53	30.11	0.37	1.57	4.42	ND	0.27	0.40	0.54	ND	5.44	2.66	6.21
BaA	2.23	6.81	12.54	1.59	18.16	2.75	8.28	9.12	17.41	12.16	7.90	1.75	3.41	2.50
Chry	1.48	15.43	1.49	0.82	0.20	3.10	1.06	3.82	0.01	0.01	1.52	0.20	0.01	3.90
BbF	4.91	3.68	13.45	6.19	6.74	2.87	1.56	1.98	4.50	15.30	3.58	11.74	4.52	2.56
BkF	2.62	0.38	1.71	0.75	9.01	6.72	0.35	9.67	8.39	9.90	6.46	6.03	17.25	8.99
B(a)P	ND	4.56	5.70	0.68	0.08	50.17	2.44	0.33	2.31	0.85	0.35	1.36	3.06	0.69
DB(a,h)A	24.34	2.37	3.73	1.31	3.60	15.27	0.69	0.44	6.50	1.82	0.03	ND	6.79	ND
B(g,h.i)P	25.02	5.56	1.47	3.13	1.53	14.29	2.32	0.55	5.17	1.32	2.60	2.43	3.37	2.07
I(1,2,3-cd)P	11.88	8.82	0.36	1.33	0.73	7.32	6.06	0.96	1.00	0.06	ND	4.83	11.41	6.70

ND: not detected

The capacity for these bottles is 2.5 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.

The standard mixture solution of polycyclic aromatic hydrocarbons (16) compounds: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, 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 Supelco EPA 525 PAH Mixture. This standard was stored at 4 °C, protected from light. HPLC grade of dichloromethane and acetonitrile purchased from Sigma Aldrich.

Extraction procedure: All glassware's were pre cleaned with washing acids, solvents, detergents, hot water, rinsed with distilled water and then dried for 1 h at 180 ºC. Water samples extracted by Supelco, Supelclean™ ENVI-18 solid phase extraction Tube bed wt. 500 mg, volume 6 mL, pkg of 30 ea. These tubes conditioned with 5 mL of ethyl acetate and then conditioned with 5 mL of methanol followed by 2 × 5 mL of deionized water[38]. One liter of water sample passed through the extraction column with flow rate 2 mL/min. Suspended PAHs eluted of extraction column by dichloro methane. The passed solution concentrated to 1 mL by rotary evaporator. The concentrated sample collected in small dark isolated glassy container.

HPLC conditions: After sample extraction a portion of extract were injected by micro syringe reversed-phase HPLC. The experimental parameters were for HPLC Shimadzu LC-10 AVP, PAH column 250 × 4.6 mm I.d, with guard column 5.0 × 4.6mm I.d, Flow rate 1.5 mL/min detected by UV detector. Absorbance at 254 nm with high sensitivity results have detected. Polycyclic aromatic hydrocarbons compounds were eluted using water/acetonitrile gradient[37].

RESULTS AND DISCUSSION

One hundred and sixty eight samples collected from fourteen sites located on the both banks of Shatt Al-Hilla river during 12 months from November 2011 to October 2012. The results exhibit high variety between the concentrations of PAHs from site to site and from month to month.The average concentrations during one year for each site of individual PAHs in water samples are shown in Table-1. The mean concentrations of PAHs in water samples ranged from 0.01 µg/L of chrysene at site 13 to 50.17 µg/L of benzo[a]pyrene at site 6. It is clear that the five-ring PAHs {benzo[b]fluoranthene, benzo[k]-fluoranthene, pyrene, benzo[a]anthracene and chrysene} are the most abundant in all water samples, whereas the two ring represented by naphthalene is the lowest in all water samples and not determines in all samples of site six. Four-ring PAHs include pyrene, fluoranthene, benzo[a]anthracene and chrysene, five-ring PAHs include benzo[k]fluoranthene, benzo[b]fluoranthene, benzo[a]pyrene and dibenzo(a,h)-anthracene and six-ring PAHs include benzo(g,h,i)perylene and indeno(1,2,3-cd)pyrene were variant in the mean concentrations. Much research has dealt with PAH compounds in water of several rivers[39-44], they reported that the concentrations of PAHs in those polluted areas ranged from 10-1000 ng/L in water samples.

Azad *et al.*[45] was reported the highly industrially polluted river, those which the individual PAHs concentration in water exceeded to 10 g/L. Polycyclic aromatic hydrocarbons do not show high level of toxicity as far as aquatic organisms' presents in surface water, the lower molecular weight of PAHs tend to exhibit higher lethal toxicity for aquatic organisms than the larger PAHs[46]. It is clear in Table-1 that the concentrations of three-ring PAHs are exhibit pollution in different sites such as: Acenaphthylene in sites S3 and S8; acenaphthene in S9; fluorene in S3, S4, S6, S7, S8, S9 and S12; phenanthrene in S14 and anthracene in S11.

The composition patterns of PAHs by number of rings are shown in Fig. 2. It is clear that five-ring PAHs are the most abundant in most surface water samples, whereas the less abundant is two-ring PAHs.

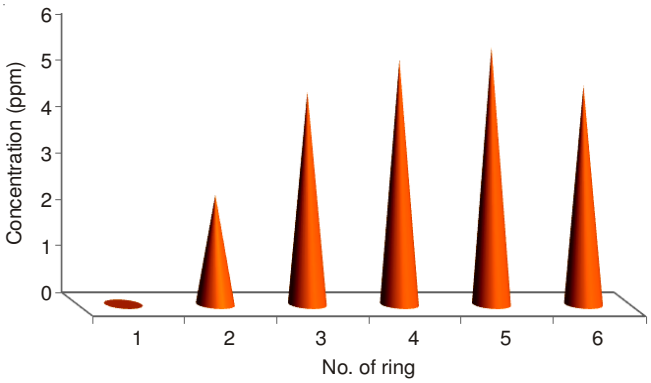

Fig. 2. Distribution of 2,3,4,5 and 6-ring in the surface water of fourteen sites of Shatt Al-Hilla, Iraq for PAH compounds

During the study period, the concentration of ΣPAHs in surface water of Shatt Al-Hilla at the different sampling sites in the period November-2011 to October-2012 was 13115.52 ppb. The minimum value was 300.102 ppb for acenaphthene while the maximum value was for fluorene 1690.608 ppb. The both compounds are consisting of three fused aromatic rings. that confirm the work of Nagy *et al.*[14].

Conclusion

This study presents the first comprehensive survey of PAHs in surface water of Shatt Al-Hilla river. This paper provides an important data on PAHs concentration along this important river. One hundred and sixty eight samples of Shatt Al-Hilla river collected from fourteen selected sites of Al-Hilla city-Iraq from November 2011 to October 2012 and analyzed by HPLC. Benzo[a]pyrene was highest concentration (601.81) ppb in site six in November 2011 among sixteen compounds were analyzed. The results showed high variations in concentrations of PAHs from site to site and from month to month subject to the human activities per each site every month.

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