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Determination of Benzo[a]anthracene in Surface Water of Shatt Al-Hilla River by Solid Phase Extraction and High Performance Liquid Chromatography

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In this study, the monthly variations for the concentrations of benzo[a]anthracne [$C_{18}H_{12}$] in surface water of Shatt Al-Hilla, mid of Iraq were monitored for one year, starting from November 2011 to October 2012. The process was done by using solid phase extraction through HPLC technique with UV-visible detector. Selected samples were taken from fourteen sites on both banks of the studied river. The results showed high spatial variations in concentrations of benzo[a]anthracene and from month to month depending on human activities. The highest concentration of benzo[a]anthracene was detected in site five in November 2011. The accumulation concentration of benzo[a]anthracene in all sites during the study period was 1280.11 ppb.

Keywords: Benzo[a]anthracene, Polycyclic aromatic hydrocarbons, Shatt Al-Hilla river, HPLC.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are a class of about 10,000 compounds, representing a group of hazardous organic chemicals consisting of two or more fused aromatic rings in linear, angular or cluster arrangements[1,2]. Polycyclic aromatic hydrocarbons are mainly formed from incomplete combustion or pyrolysis of carbon-containing materials such as: wood, petroleum, coal or industrial wastes[3-5]. These compounds are occur in the aquatic environment as a result of ship traffic, oil spills, pyrolytic processes, industrial wastewater and domestic discharges[6]. Sixteen PAHs are classified as priority pollutants by US-EPA United States Environmental Protection Agency. Benzo[a]anthracene (BaA), a high molecular weight consist of four fused aromatic rings, was used as model chemical. It is considered as a human carcinogen and listed in the United State Environmental Protection Agency (US EPA, 2009) priority pollutants[7]. The main sources of benzo[a]anthracene in an environment are pyrolytic processes such as burning of gasoline and waste and it occurs in creosote. Benzo[a]anthracene and benzo[a]pyrene (BaP), are formed when tobacco, gasoline, garbage or any plant material or animal burns, are the most potent carcinogens[8-10]. They can act as promoters and initiators in the carcinogenic process[11]. The carcinogenic effects of exposure to both compounds are mediated by their metabolic conversion, which might causes DNA adduct formation and mutations[12]. The carcinogenic and mutagenic effects of individual PAH and PAH containing products such as coal tars have been well investigated in several animals and in humans. Polycyclic aromatic hydrocarbons are wide spread environmental contaminants and methods of monitoring of human exposure to PAHs as a preventive health assess are very importance. Polycyclic aromatic hydrocarbons especially those with four or more fused aromatic rings and their metabolites, are considered as hazardous contaminants due to their toxicity, carcinogenicity and mutagenicity and are classified as compounds with significant human risk[13,14]. Due to abundant of PAHs in trace level concentration and wide distribution in water environment, it is required and vital to develop efficient methods for preconcentration and high selective and sensitive separation technique and analysis instruments. Recently, the development of preconcentration steps in order to be implemented prior for determinations of trace level compounds were explored in considerable depth[15]. With a view to eliminating or at least minimizing the use of different solvents employed in conventional liquid-liquid extraction[16-18], which has been used by the Environmental Protection Agency (EPA), other methods have been developed. Among them, membrane extraction[19,20], solid phase extraction (SPE)[21,22] solid phase microextraction (SPME)[23,24] are the most common ones. The most frequent analytical methods for PAHs compounds in surface water were high performance liquid chromatography-fluorescence detection (HPLC-FLD)[25,26] or detection by ultraviolet diode-array (HPLC-UVDAD)[27,28]; gas chromatography coupled with mass spectrometry (GC-MS)[29-31], high performance liquid chromatography-electro spry ionization mass spectroscopy (HPLC-ESI-MS)[32] and GC[33], have also often been applied to measure PAHs in water.

The main objective of this study was to evaluate the level of contamination surface water samples with benzo[a]-anthracene from fourteen selected sites in Shatt Al-Hilla river and monitoring the concentrations during one year to indicate the effect of both weather and location. Structure of benzo[a]-anthracene is shown in Fig. 1.

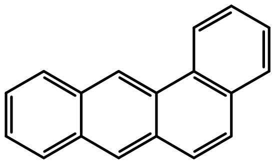

Fig 1. Structure of benzo[a]anthracene

EXPERIMENTAL

Study area: Shatt Al-Hilla river is the main source for water supply and irrigation in Babylon Governorate mid of Iraq. The total length of this river is about 97 km[34]. A lot of contamination sources are distributed randomly near this river such as treated wastewater of textile factory, agriculture pumps, draining sewage and layout pipes of purification stations for drinking water in addition to the pollution by atmospheric deposition whichtransfer several PAHs compounds. Fourteen sites were selected on the both banks of Shatt Al-Hilla river, these sites were described in our previous study[34].

Sample collection: Fourteen samples of water from Shatt Al-Hilla river were collected once monthly. Water samples have been collected in pre-cleaned dark glass bottle 2.5 L with screw cap and lined with foil to prevent matching of benzo[a]-anthracene with plastic cap and kept in cooler box with 4 °C to ensures that no degradation will happen when they are expose to the light or high temperatures degree through transferring the samples to laboratory.

The standard solution of benzo[a]anthracene was purchased from Supelco. This standard was stored at 4 °C, protected from light. Solvents such as dichloromethane and acetonitrile were purchased from Sigma Aldrich. All chemicals were used without further purification.

Extraction procedure: All glassware's which used 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 were extracted by Supelco, Supelclean™ ENVI-18 SPE Tube bed wt. 500 mg, volume 6 mL, pkg of 30 ea. These tubes were conditioned with isopropanol, acetonitrile, dichloromethane, methanol ethanol and distilled water before extraction process[35]. One liter of water sample was passed through the extraction column with flow rate 2 mL/min. Benzo[a]anthracene was eluted from column of extraction by dichloromethane. The passed solution were concentrated to 1 mL by rotary evaporator. The concentrated sample was collected in small dark isolated glassy container.

HPLC conditions: After sample extraction, a portion of extract, (20 µL) were injected by micro syringe reversed-phase HPLC. The detailed experimental parameters for HPLC Shimadzu LC-10 AVP, PAH column (250 × 4.6 mm I.d) with guard column (5 × 4.6 mm I.d) (Flow rate: detected by UV detector). Absorbance at 254 nm with high sensitivity using background correction method. Benzo[a]anthracene was eluted using water/acetonitrile gradient described in our previous study[36].

RESULTS AND DISCUSSION

One hundred and sixty eight samples are measured during 12 months from November 2011 to October 2012. The results exhibit high variety between the concentrations of benzo[a]-anthracene from site to site and from month to month. Table-1 shows the variation in the concentrations level of benzo[a]-anthracene for twelve months. The maximum value of this compound was appear in site five as shown in Fig. 2.

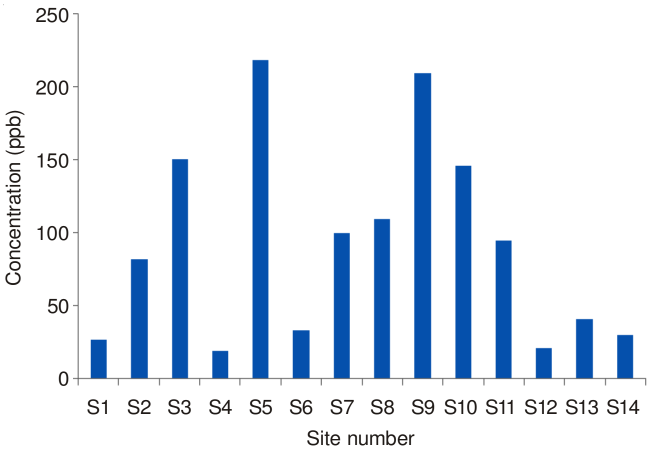

Fig. 2. Distribution of benzo[a]anthracene summations for 12 months for every site

This site as described in study area, the source of pollution in this site is that the drivers are use this region for washing their cars. Often the washing water which drain to the river are mixed with different types of oil derivatives such as gasoline, lubricates oil, gearbox oil, wax and fuel. Site nine also appear high contamination level of benzo[a]anthracene, the main pollution source in this site is related to use boats by anglers. These boat are operate with hydrocarbons fuel. In addition to the deposition by atmosphere and the pollution that came from previous sites locate before this site. Table-1. illustrate the concentrations of benzo[a]anthracene in all sites for twelve months and some statistical parameters such as summation, average and standard deviation for every site also was maintained in this table. The summation of benzo[a]-anthracene in all sites for one year was 1280.11 ppb. Bright and Healey[37] found 65 % of 4-6 ring PAHs in sludge's from a urban area, Vancouver, Canada. Crepineau *et al.*[38] concerning the contribution of motor traffic contamination to the atmosphere, data from literature are controversed. Fromme *et al.*[39], in Berlin, found a major emission of fluoranthene and pyrene from diesel engines. Lim *et al.*[40] in the center of Birmingham (UK), found 80-82 % of 4-7 ring PAHs from traffic emissions to the urban air whereas they were only 61-67 % in the background area. In contrast, Tsai *et al.*[41] at a highway toll station of Northern Taiwan, reported a ratio of 4-7 ring PAHs of only 6.9 %.

TABLE-1
CONCENTRATIONS OF BENZO[a]ANTHRACENE FOR ONE YEAR DISTRIBUTED ON FOURTEEN SITES

Site No.	Nov. 2011	Dec. 2011	Jan. 2012	Feb. 2012	Mar. 2012	Apr. 2012	May 2012	Jun. 2012	Jul. 2012	Aug. 2012	Sept. 2012	Oct. 2012	Summation	Average	ST DEV
S1	15.92	0.00	10.14	0.02	0.00	0.73	0.00	0.00	0.00	0.00	0.00	0.00	26.81	2.23	5.19
S2	0.00	21.95	19.12	40.63	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.07	81.78	6.81	13.28
S3	103.82	0.00	8.18	8.87	0.92	18.75	9.54	0.00	0.34	0.15	0.00	0.00	150.57	12.54	29.35
S4	0.00	0.00	0.00	0.00	0.00	19.09	0.00	0.00	0.00	0.00	0.00	0.00	19.09	1.59	5.51
S5	151.11	3.09	4.46	24.01	0.00	0.00	33.35	0.00	0.00	0.01	0.00	1.99	218.02	18.16	43.27
S6	0.00	3.04	12.66	14.27	3.06	0.00	0.00	0.00	0.00	0.00	0.00	0.00	33.03	2.75	5.14
S7	63.77	1.06	0.00	32.96	0.00	0.00	0.00	1.56	0.00	0.00	0.09	0.00	99.44	8.28	19.84
S8	0.00	1.45	47.91	43.41	0.00	0.00	14.26	0.00	0.00	2.42	0.00	0.00	109.45	9.12	17.56
S9	42.07	0.00	40.22	58.57	33.59	0.00	32.96	0.00	0.00	1.58	0.00	0.00	208.99	17.41	22.14
S10	66.12	0.00	0.00	18.61	17.56	0.00	43.41	0.00	0.00	0.11	0.00	0.15	145.96	12.16	21.60
S11	0.00	0.00	0.00	20.53	0.35	0.00	73.95	0.00	0.00	0.01	0.00	0.00	94.84	7.90	21.61
S12	0.00	0.00	0.00	0.00	0.00	0.00	18.61	0.00	0.00	2.42	0.00	0.00	21.03	1.75	5.35
S13	0.00	0.00	0.82	0.00	0.00	0.00	40.21	0.00	0.00	0.00	0.00	0.00	41.03	3.41	11.58
S14	0.00	0.00	0.00	1.16	0.00	0.00	0.00	0.00	15.57	0.13	13.21	0.00	30.07	2.50	5.58
Summation of benzo[a]anthracene in all sites during twelve months														1280.11	

Conclusion

One hundred and sixty eight samples of Shatt Al-Hilla river were collected from fourteen selected sites of Al-Hilla city-Iraq from November 2011 to October 2012 and were analyzed by HPLC. The highest concentration of benzo[a]anthracene was 151.11 ppb in site five in November 2011. The results showed high variations in concentrations of benzo[a]anthracene from site to site and from month to month subject to the human activities per each site every month.

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