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Quality, Quantity and Origin of PAHs (Polycyclic Aromatic Hydrocarbons) in Lotic Ecosystem of Al-Hilla River, Iraq

Fikrat M. Hassan[1], Jasim M.Salman[2], Atheer S.N. Al-Azawey[2], Nadhir Al-Ansari[3] and Sven Kutsson[3]

1. College of Science for Women, University of Baghdad, Baghdad, Jadiria-Baghdad 14001, Iraq

2. College of Science, University of Babylon, Babylon, Hilla 14004, Iraq

3. Department of Civil, Environmental and Natural Resources Engineering, Lulea University of Technology, Lulea 971 87, Sweden

Abstract: The Euphrates River is one of the major rivers in Iraq. When it reaches north of Hilla city, it will be divided in two branches. One of these braches flows toward Hilla city. On this branch, six locations were studied for the water quality of the Euphrates water. The present paper is aimed to fill the gap of information of the presence of PAHs (poly aromatic hydrocarbons) in water and sediment of Al-Hilla River, as well as to determine the quality and quantity of some PAHs. The depth of the river ranges from 2 m to 6 m. The quality, quantity and the origin of PAHs were studied in the water and sediment of Al-Hilla River. In addition, some physical and chemical properties were studied at six sites along the studied area, for the period March, 2010 to February, 2011. Sixteen PAHs that are listed by USEPA (US Environmental Protection Agency) as priority pollutants (Nap (naphthalene), Acpy (acenaphthylene), Acp (acenaphthene), Flu (fluorine), Phen (phenanthrene), Ant (anthracene), Flur (fluoranthene), Py (pyrene), B(a)A (benzo(a)anthracene), Chry (chrysene), B(b)F (benzo(b)fluoranthene), B(k)F (benzo(k)fluoranthene), B(a)p (benzo(a)pyrene), BbA (dibenzo(a,h)anthracene), B(ghi)P (benzo(ghi)perylene) and Ind (indeno (1,2,3-cd) pyrene)) were detected in Al-Hilla river. High concentrations of PAHs were detected in the sediment relative to that within the water. The present study revealed that the origin of PAHs in water and sediment might be the pyrogenic origin.

Key words: PAHs, food chain, water, sediment, Euphrates River.

1. Introduction

PAHs (polycyclic aromatic hydrocarbons) exist in the environment and is distributed in both aquatic and terrestrial environments. PAHs can be both natural and anthropogenic origin. It can form by several pathways: biosynthesis, pyrogenic and petrogenic [1]. PAHs are able to absorb onto sediment limiting their bio-availability [2]. The PAHs toxicity depends on physical-chemical parameters of an aquatic system, number, position and chemistry of the basic aromatic ring [3].

US-EPA [4] had identified 16 unsubstantiated PAHs as priority pollutants and benzo(a)pyrene is most common carcinogenic. PAHs in aquatic environments originate from possible sources such as pyrogenic PAHs resulting from incomplete combustion with high-temperature and short duration of organic matter [5]. Petrogenic PAHs are relatively derived from petroleum and other fossil fuels containing PAHs [6]. Diagenetic PAHs refer to PAHs formation from biogenic precursors, like plant terpenes, leading to the formation of compounds such as retene (methyl isopropyl phenanthrene or 1-methyl-7-isopropyl phenanthrene $C_{18}H_{18}$) and derivatives of phenanthrene and chrysene [7-9]. A potential fourth source of PAHs is biogenic, i.e., purely from bacteria, fungi, plants or animals in sedimentary environments without any contributions from diagnostic processes, However, this source is not significant [10].

Corresponding author: Nadhir Al-Ansari, professor, research fields: water resources and environmental engineering. E-mail: nadhir.alansari@ltu.se.

PAH inputs to the aquatic environment are primarily from two sources: water movement contains dissolved and particulate constituents derived from watersheds, and atmospheric deposition both in precipitation and dry deposition from air sheds of the coastal ocean. According to WHO (World Health Organisation) [11], concentration of individual PAHs in surface and coastal waters from highly industrially polluted rivers are generally 0.05 µg/L. Development of industry, agriculture and urbanization increases the activity and amounts of pollutants that reach the aquatic ecosystems in Iraq. There was an increase in the petroleum hydrocarbons in, Khor Al-Zubair and north west Arabian Gulf probably due to petroleum leakage [12, 13]. High level of PAHs was recorded in Shatt Al-Arab River than in the north west Arabian Gulf [14-16]. Al-Saad et al. [17] recorded a low concentration in marshland of southern Iraq, while pollution by PAHs recorded in the Tigris River due to discharge of sewage and oil waste [18]. The distribution of PAHs in the Euphrates River was studied recently by Ref. [19] while macrophytes and sediment of the Euphrates River by Mohammed et al. and Hassan et al. [20-22].

Sediment had been described as the “ultimate sink” or storage place for pollutants [23, 24]. PAHs concentrations in sediment are increasing in industrialized and urbanized areas, where many authors noted that the sediment is the source or a sink of contaminants in the aquatic environment [4, 25]. Many toxic contaminants are difficult to detect in aquatic systems due to their ability to accumulate in the sediments in higher level than in soluble form, hence it is difficult to control. Benthos are accumulated pollutants via the contaminated sediment through many ways [26].

A study of PAHs in El Menofiya governorate, Egypt revealed dominances of four rings of PAHs in aquatic systems [27]. Pahila et al. [28] found lower concentration of total PAHs and remained almost at the same level two years after oil spill in southern Guimaras in the central Philippines. A study in Niger Delta revealed that the origin of PAHs was Petrogenic and sometime from other sources [29].

The present study is aimed to fill the gap of information of the presence of PAHs in water and sediment of Al-Hilla River, as well as to determine the quality and quantity of some PAHs.

2. Materials and Methods

2.1 Study Area

Babylon was constructed 4,100 years ago and is one of the most ancient cities in the world. Now it is known as Babylon Governorate and its capital city is referred to as Hilla. This city covers an area of about 5,229 km^2 which lies in the middle of Iraq (100 km) to the north of the capital Baghdad and its population reaches more than 1,600,000. Al-Hillah city is located adjacent to the ancient city of Babylon and consist of 60 districts. It divided in to two parts by a big branch of Euphrates River called (Shat Al-Hilla) where it passes through the city center.

The main Euphrates River, at its middle region in Iraq, is divided into Al-Hindiya River and Al-Hilla River (Fig. 1). The length of Al-Hilla River is about 102 km; it covers 102,248 acres from the agricultural area in Babylon Province. Six sites were selected along Al-Hilla River: Site 1, Al-Mussayab District before Euphrates branching (longitude 44°18'16.62" and latitude 32°40'52.32"); Site 2, Al-Shujaireia region (longitude 44°16'40.33" and latitude 32°46'26.40"); Site 3, Sinjar region near Ancient Babylon city (longitude 44°23'19.92" and latitude 32°33'13.57"); Site 4, Al-Hilla city center (longitude 44°26'22.85" and latitude 32°28'59.81"); Site 5, Al-Farisi region south of Al-Hilla city (longitude 44°29'16.15" and latitude 32°25'18.51"); Site 6, Al-Hashymiya city (longitude 44°39'10.41" and latitude 32°22'17.77").

2.2 Physical and Chemical Properties

Monthly samples were taken from six studied sites for 12 months that started in March, 2010 up to February,

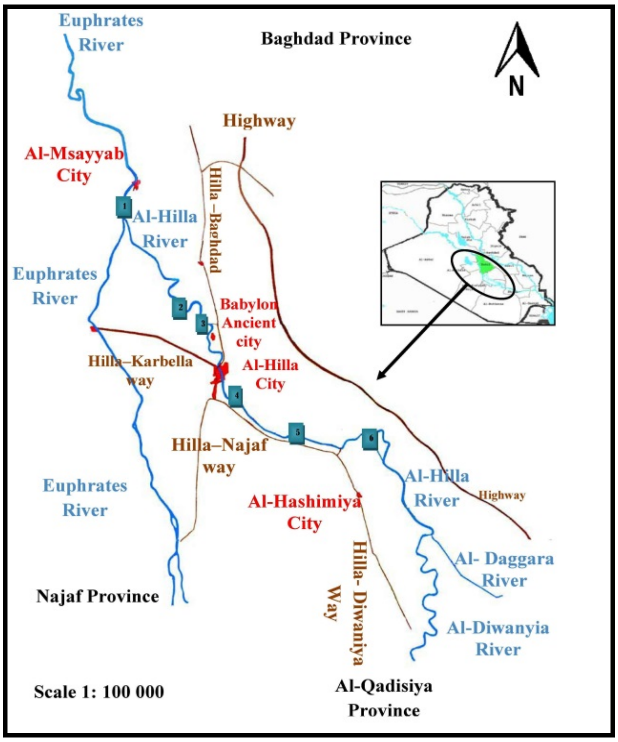

Fig. 1 The studied sites in Al-Hilla River.

2011. The temperatures of water and air, electrical conductivity, water transparency and pH, alkalinity, total hardness, calcium, magnesium, chloride and sulfate were measured according to APHA (American Public Health Association) [30]. TOC (total organic carbon) (%) was analyzed in the manner described by Gaudette et al. [31]. Sediment texture was analyzed following method described in Bouyoucos [32].

2.2.1 PAHs: A-Sample Collection

The depth of the river varies from 2 m to 6 m. Water samples at depth of 50 cm were collected using pre-cleaned dark glass bottle (1 L) in a metallic holder around the bottle connected with a rope that was lowered into the water and allows to rest briefly to ensure that it is filled with water and then transferred to the labeled dark bottle (with volume 2.5 L) containing 60 mL of carbon tetra chloride CCl_4 solvent [33]. Sediment was collected using Ekman grab sampler and stored frozen at -20 ºC before it was analyzed [34]. This was done to eliminate any mixing with materials disposed on the surface of the water and to avoid any disturbance and mixing with bed sediments of the river.

2.2.2 B-Extraction of PAHs

A 30 mL CCL_4 was added to each one liter of sample in separator funnel, then shaken for one hour, to separate organic layer, the settled organic layer was collected in tight glass container and dark. Extraction procedure was repeated with another 60 mL of CCl_4 and collected in the same container. Then organic extract was evaporated to dryness by rotary evaporator and 1 mL of acetonitrile and methanol (90:10) was added to the flask [33].

Sediment was dried under 15 ºC. A dry weight of sample (10 g) was homogenized in a stainless steel container. Then mixed with 25 mL of acetone with handle for 5 min, soak in a dark-cold place overnight. This mixture was shaken for 1 h. The solution was separated in dark glass containers and this process was repeated three times. Then the solution centrifuged at 2,500 rmp for 5 min. The supernatant solution was transferred for separation processes with a mixture of 50 mL hexane and 100 mL deionized water. The final volume of separation solution reduced to 10 mL by rotary evaporator. After that transfer it to silica gel cleanup column finally dried by rotary and dissolved in 1 mL of Acetonitrile and Methanol (90:10) and stored until measured in HPLC (high performance liquid chromatography) [34].

The PAHs extracts of water and sediment were analyzed by high performance liquid chromatography (Schimadzu) model, Japan. Recovery test for evaluation of extraction method efficiency were done according to methods of Song et al. [35] and Kumari et al. [36]. PAHs in the spiked sediments were extracted following the procedure had been used in search (recovery percentage $b - a / c \times 100$), where, b is the amount of analyte found after the addition of standard solution, a is the amount of the analyte found before the addition of standard solution, and c is the amount of standard compound added}. According to ratios (Phe/Ant, Chry/BaA, Flu/Pyr, Flu/(Flu + Pyr) and LMW (low molecular weight)/HMW (high molecular weight) can determine PAHs origins [37, 38]. The present study results were analyzed statistically by SPSS (statistical package for the social sciences) and Conoco for windows 4.5 CCA (canonical correspondence analysis).

3. Results and Discussion

The results of the studied physical and chemical properties of the study area were summarized in Table 1. The highest values of air and water temperatures were recorded in July 2010 at Sites 6 and 1, respectively, while the temperature of air and water through the study period was always above 5 ^{o}C. Temperature affects water physical properties [39]. The present results for both air and water temperatures were influenced by the clear changeable seasonal climate in Iraq [40, 41]. Al-Hilla River had been characterized as a fast flowing river in comparison with other Iraqi River [42]. pH values were 7.6-8.8, this indicated alkaline which is a common features in Iraqi inland water [42, 43]. Higher concentration of total hardness might be due to high evaporation rates during summer season and the availability of cations [39] might be also due to high precipitation and thus high soil leaching and high present velocities [41]. The present study indicates that the diluting effects of precipitation and rising water discharge of studied river were the reasons of lower values of hardness, and it matched with other studies [42, 43]. The present results showed that the sediment texture was composed of clay, sand and silt sequentially (Fig. 2).

The concentration of PAH in Al-Hilla River water ranged between 0.002 µg/mL for benzo(a)pyrene to 101.48 µg/mL for Acp (acenaphthene) (Table 2). This

Table 1 Physical and chemical properties of the samples.

Properties	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6
Air temperature (ºC)	5.3-37.3 22.7 ± 11.9	7.6-38.8 24.3 ± 11.3	8.1-44.3 26.4 ± 12.3	8.6-45.3 27.9 ± 12.6	11-46.6 29.2 ± 12.1	9-48 29.1 ± 13.6
Water temperature (ºC)	5-35 20 ± 10.7	6.6-35.5 21.5 ± 10	7.6-38.6 23.2 ± 10.7	8-41 24.9 ± 11.2	10-40.3 25.9 ± 10.4	8-41 26.5 ± 10.8
Water flow (cm/s)	19-70 40.7 ± 15.6	20-85 42.1 ± 14	22-85 46.5 ± 18.6	22-80 48.5 ± 16.9	25-75 49.5 ± 15.1	23-70 45.8 ± 14.5
Transparency (m)	0.25-1 0.7 ± 0.2	0.5-1.2 0.7 ± 0.2	0.5-1 0.7 ± 0.1	0.5-1 0.7 ± 0.2	0.5-1 0.6 ± 0.1	0.5-1 0.7 ± 0.1
Water pH	8.7-7.5 7.9 ± 0.2	7.6-8.8 7.9 ± 0.3	7.6-8.7 7.9 ± 0.2	7.4-8.7 7.9 ± 0.3	7.7-8.7 8 ± 0.2	7.7-8.1 7.9 ± 0.1
EC (electrical conductivity) (µs/cm)	600-788 664 ± 71.7	528-788 653.8 ± 82.4	603.6-809.6 680.5 ± 74.9	610.3-821.3 688.6 ± 78.1	622-947.6 722.1 ± 113.6	603-879.6 705 ± 98.9
DO (dissolved oxygen) (mg/L)	6-11.2 8.1 ± 1.9	6-10.7 8 ± 1.8	6-10.5 7.8 ± 1.6	6-10 7.7 ± 1.5	5-9 7.3 ± 1.4	5.1-9.5 7.3 ± 1.3
BOD (biological oxygen demand) (mg/L)	3.2-5 3.8 ± 0.5	3.3-5.5 3.9 ± 0.6	3.6-5 4.1 ± 0.3	3.8-4.9 4 ± 0.2	3-4.9 4.1 ± 0.5	3.1-4.9 4 ± 0.5
Alkalinity (mg/L)	103.3-155.3 126.5 ± 17.2	106.6-150.6 132.3 ± 14.4	103.3-157.3 132.3 ± 18.2	100.6-155.3 132.2 ± 18.1	111.3-171.3 144.2 ± 21.4	100-178 141.6 ± 25.6
Hardness (mg/L)	486.6-670 561.9 ± 68	450-656.6 553 ± 73	390-690 553.7 ± 96.6	460-683.3 568 ± 75.3	436.6-713.3 588.5 ± 87.3	430-716.6 582.4 ± 95.4
Calcium (mg/L)	276-343.3 278 ± 40.4	213.3-313.3 276.6 ± 38.9	213.3-346.6 294.3 ± 45.8	203.3-360 298.8 ± 95.1	250-370 333.9 ± 37.3	236.6-370 314.9 ± 51.5
Magnesium (mg/L)	54.2-95.5 68.9 ± 17.1	46.1-98 66.6 ± 17	42.1-85 65.7 ± 15.5	39.7-84.2 66.6 ± 14.6	29.1-94.7 64 ± 20.4	34.8-93.1 65.3 ± 20.8
Sulphate (mg/L)	548.5-979.8 778.9 ± 138	562.7-877.1 771.8 ± 117.8	562.7-877.4 779.9 ± 114.3	555.3-860.8 777.6 ± 113	593.1-957.3 809.1 ± 121.3	559.4-890.4 797.4 ± 113.6
Chlorides (mg/L)	227.3-419.8 327.9 ± 65	249.6-419.8 331.9 ± 59.7	239.3-436.5 335.4 ± 64.8	253.6-426.5 332.6 ± 58	263.2-416.2 347.7 ± 55.7	234.5-413.2 342.7 ± 56.8
TN (total nitrogen) (mg/L)	0.4-1 0.73 ± 0.2	0.42-0.97 0.71 ± 0.1	0.48-0.91 0.71 ± 0.1	0.47-0.92 0.76 ± 0.1	0.5-1.1 0.85 ± 0.1	0.5-0.99 0.83 ± 0.1
TP (total phosphorous) (mg/L)	0.01-0.098 0.061 ± 0.03	0.01-0.097 0.062 ± 0.02	0.01-0.09 0.062 ± 0.02	0.017-0.092 0.067 ± 0.024	0.02-0.1 0.07 ± 0.02	0.02-0.098 0.07 ± 0.023

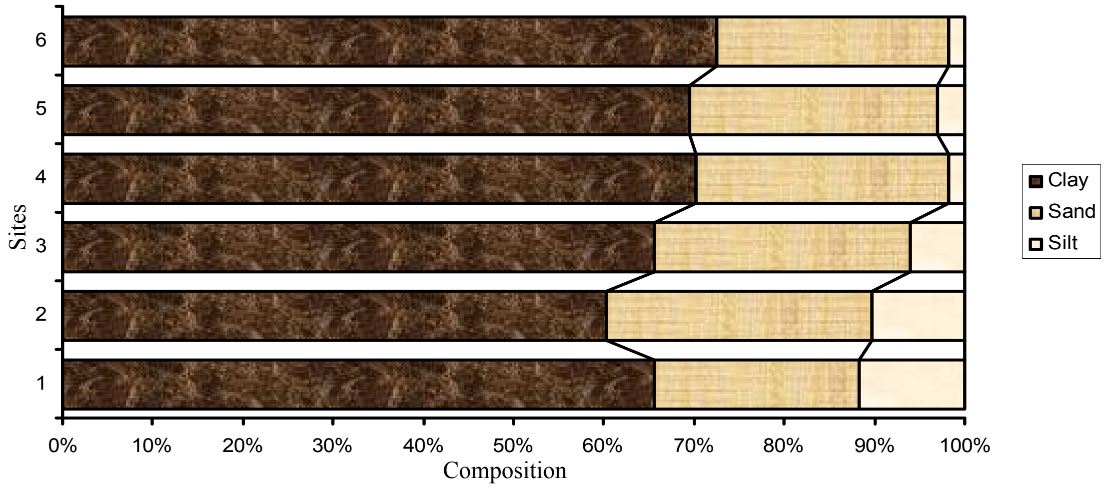

Fig. 2 Sediment texture in Al-Hilla River during the study period.

might be attributed to urban runoffs, sewage discharges, vehicle exhaust emission and intense shipping activities that were observed during the sampling. Furthermore, due to the low solubility of PAHs in water it can be found in high concentration in solid particulates [44]. The lower concentration of some high molecular weight of PAHs in the water was also observed.

This might be due to their high affinity to be adsorbed on dissolved organic matter [45, 46]. Accordingly, there is a big risk in Al-Hilla River because of PAHs characteristics (hydrophobic and easily accumulated in organisms through food chains). Other factors may be increased risks in the studied area due to their roles in the biotransformation of PAHs and synthesizing in the water column such as oxygen concentration (> 0.7 mg/L), ambient nutrient status, and presence of different types of microorganisms such as phytoplankton [47, 48]. According to the ratios of Flur/(Flur + Py), Phe/Ant, Chry/BaA, Flur/Py and LMW/HMW, the PAHs in water samples indicates that they are of different sources including pyrolytic and petrogenic sources. The ratios of phenanthrene to anthracene (Ph/An) and fluoranthene to pyrene (Fl/Py) have been widely used to distinguish petrogenic and pyrogenic sources of PAHs [49]. All ratios of the current research indicate that the source of PAH is pyrolytic [50, 51]. The concentration of PAHs in sediment ranged (0.58-89.27), (2.84-89.89), (2.13-83.91), (2.99-86.56), (6.44-103.63) and (0.90-120.70) μg/g in stations 1, 2, 3, 4, 5 and 6 respectively.

The fluctuation of PAH compounds concentrations might depend on PAHs characteristic as lipophilic compounds while the low concentration related to their ability tend to adsorb to sediment [52, 53].

High concentrations of PAHs in sediment were noticed as compared with that in water (Table 3). It is well known that the concentration of PAHs in the sediment is usually found to be higher than concentrations in the water due to their physical and chemical properties [54]. The present results agree with Refs. [55, 56]. PAHs concentration in sediment were ranged (0.13-3.5 μg/g) for (Ph/An), based on this result the origin of PAHs is considered as pyrolytic sources because the values of less than 10 μg/g [57].

To detect the sources of PAHs in an ecosystem the isomer ratios (Flu/Flur + Pyr) were used and to imply the sources for PAHs. Yunker et al. [58] promulgated that < 0.4 indicated as petrogenic sources while ratios between 0.4 to 0.5 explained the source from the burning of natural material.

According to the results of this study, it showed that the ratios of isomer in the range of (0.508-0.551) that demonstrated the pyrolytic sources [59].

Table 2 Values of PAHs compounds in the water during March, 2010-February, 2011.

Station	Season	PAHs compounds (µg/mL)															
		Nap	Acpy	Acp	Flu	Phen	Ant	Flur	Py	B(a)A	Chry	B(b)F	B(k)F	B(a)P	BbA	B(ghi)P	Ind
1	Spring	18.063	ND	44.252	20.804	2.946	1.138	10.037	1.143	6.880	2.272	0.150	1.213	ND	21.677	51.356	1.600
	Summer	ND	ND	18.931	3.257	0.425	0.785	1.251	1.781	4.336	0.724	0.005	ND	ND	ND	22.881	ND
	Autumn	23.698	4.587	40.257	22.361	3.904	3.671	9.511	3.224	10.225	ND	1.200	2.997	ND	ND	54.691	1.553
	Winter	22.112	ND	41.670	16.552	3.027	3.083	10.889	2.667	7.339	3.012	1.024	ND	0.008	12.337	50.025	1.125
	M ± SD	15.9 ± 10.90	1.146 ± 2.29	36.277 ± 11.68	15.743 ± 8.67	2.575 ± 1.49	2.169 ± 1.42	7.922 ± 4.48	2.203 ± 0.92	7.195 ± 2.41	1.502 ± 1.38	0.594 ± 0.60	1.052 ± 1.41	0.002 ± 0.004	8.503 ± 10.53	44.738 ± 14.70	1.069 ± 0.74
2	Spring	19.212	ND	34.353	19.883	3.820	1.427	ND	2.565	16.209	8.444	ND	3.932	ND	13.172	20.371	0.218
	Summer	2.390	ND	17.751	2.347	0.478	0.018	ND	0.879	2.784	1.218	ND	0.929	ND	1.207	ND	ND
	Autumn	20.847	9.007	51.510	ND	5.001	2.280	8.276	5.991	ND	ND	1.105	4.051	0.013	15.578	15.258	ND
	Winter	21.696	ND	39.292	0.756	0.210	0.172	13.253	1.437	4.038	2.667	0.109	ND	ND	10.626	172.626	2.899
	M ± SD	16.03 ± 9.15	2.251 ± 4.50	35.726 ± 13.98	5.746 ± 9.47	2.377 ± 2.39	0.974 ± 1.07	5.382 ± 6.53	2.718 ± 2.29	5.757 ± 7.16	3.082 ± 3.73	0.303 ± 0.53	2.228 ± 2.07	0.003 ± 0.006	10.14 ± 6.29	52.063 ± 80.83	0.779 ± 1.41
3	Spring	ND	18.410	70.387	1.5174	0.115	0.030	7.642	ND	15.341	0.129	0.075	ND	ND	21.044	34.049	1.023
	Summer	ND	0.087	31.330	0.836	0.083	0.081	1.027	0.057	2.308	ND	0.024	0.099	ND	ND	10.290	ND
	Autumn	18.937	ND	55.991	2.539	1.328	1.221	8.367	3.058	ND	3.228	1.991	ND	0.058	0.589	40.587	0.781
	Winter	45.572	ND	14.210	6.644	4.413	1.655	6.509	11.028	7.780	11.606	1.409	8.822	ND	28.264	98.773	9.585
	M ± SD	16.12 ± 21.56	4.624 ± 9.19	42.979 ± 25.05	2.884 ± 2.60	1.484 ± 2.03	0.746 ± 0.81	5.886 ± 3.32	3.535 ± 5.19	6.357 ± 6.82	3.740 ± 5.45	0.874 ± 0.98	2.230 ± 4.39	0.014 ± 0.02	12.47 ± 14.37	45.924 ± 37.56	2.847 ± 4.51
4	Spring	28.378	23.476	91.100	ND	ND	ND	16.652	2.158	1.670	2.557	8.427	0.089	2.837	25.337	42.270	2.406
	Summer	1.367	1.015	12.118	ND	ND	0.259	7.009	ND	1.183	1.083	7.651	0.147	ND	0.519	8.008	0.072
	Autumn	40.687	19.121	91.222	9.258	2.024	0.014	17.897	13.051	3.129	4.258	ND	11.029	ND	20.111	ND	0.028
	Winter	43.822	20.898	96.5561	27.429	5.1811	1.5511	15.105	16.874	44.197	16.225	1.874	16.388	ND	18.837	169.361	38.7148
	M ± SD	28.56 ± 19.31	16.127 ± 10.23	72.749 ± 40.50	9.171 ± 12.93	1.801 ± 2.44	0.456 ± 0.73	14.16 ± 4.90	8.020 ± 8.21	12.544 ± 21.11	6.030 ± 6.91	4.488 ± 4.18	6.9133 ± 8.14	0.709 ± 1.41	16.20 ± 10.82	54.909 ± 78.47	10.30 ± 18.97
5	Spring	48.632	48.450	110.964	23.197	1.747	1.549	24.384	ND	10.287	14.448	15.711	4.971	ND	44.262	61.403	11.272
	Summer	4.097	7.685	31.647	27.088	ND	0.736	9.810	ND	5.683	7.278	1.172	2.449	ND	5.001	18.847	2.093
	Autumn	62.525	40.438	138.786	13.980	2.688	ND	21.1516	27.974	ND	ND	12.488	15.605	3.709	40.016	40.277	7.780
	Winter	33.766	38.497	124.561	32.019	2.538	0.898	19.929	28.4930	58.4241	37.946	11.398	14.508	ND	60.915	178.729	47.674
	M ± SD	37.25 ± 25.03	33.767 ± 17.91	101.48 ± 47.92	24.071 ± 7.63	1.743 ± 1.23	0.795 ± 0.63	18.81 ± 6.29	14.116 ± 16.30	18.598 ± 26.88	14.981 ± 16.44	10.192 ± 6.28	9.383 ± 6.64	0.927 ± 1.85	37.54 ± 23.49	74.814 ± 71.42	17.20 ± 20.66
6	Spring	34.456	31.818	69.233	ND	0.683	1.311	20.714	17.333	7.028	11.855	7.497	1.980	2.470	28.181	ND	ND
	Summer	5.227	9.366	10.678	0.0247	ND	ND	6.240	0.892	6.025	ND	10.257	ND	1.025	9.364	4.087	0.243
	Autumn	35.689	29.371	61.325	1.367	2.015	ND	17.292	19.258	15.223	28.856	12.557	ND	7.291	22.004	12.789	ND
	Winter	29.737	22.861	67.360	18.829	0.997	0.885	12.910	ND	30.596	ND	0.2082	12.284	ND	22.026	104.057	30.284
	M ± SD	26.22 ± 14.26	23.345 ± 10.06	52.149 ± 27.85	5.055 ± 9.20	0.923 ± 0.83	0.549 ± 0.65	14.28 ± 6.24	9.370 ± 10.34	14.718 ± 11.35	10.177 ± 13.64	7.629 ± 5.362	3.566 ± 5.88	2.696 ± 3.22	20.39 ± 7.90	30.233 ± 49.50	7.631 ± 15.10

M: mean; SD: standard deviation; spring-summer-autumn: 2010; winter: 2010-2011; ND: not detected.

Table 3 Values of PAHs compounds in the sediments during March 2010-February 2011.

Station	Season	PAHs compounds (μg/g)															
		Nap	Acpy	Acp	Flu	Phen	Ant	Flur	Py	B(a)A	Chry	B(b)F	B(k)F	B(a)P	BbA	B(ghi)P	IND
1	Spring	ND	ND	57.565	18.5	ND	4.415	28.1	17.879	22.473	11.028	9.057	6.187	8.091	75.69	117.378	2.858
	Summer	10.007	20.717	10.449	ND	0.137	0.364	ND	8.571	11.874	1.494	3.406	3.172	ND	ND	23.3	0.674
	Autumn	ND	ND	60.557	17.102	2.218	7.339	24.887	19.699	20.942	9.148	13.245	ND	ND	93.178	105.677	2.2401
	Winter	42.626	25.405	65.878	15.061	ND	5.233	22.722	19.503	ND	ND	12.782	6.852	9.561	113.883	110.756	2.79
	M ± SD	39.946 ± 21.21	11.530 ± 13.45	48.612 ± 25.67	12.665 ± 8.56	0.588 ± 1.08	4.337 ± 2.92	18.927 ± 12.81	16.413 ± 5.29	18.783 ± 4.73	5.417 ± 5.481	9.622 ± 4.54	6.272 ± 2.36	6.139 ± 4.23	70.687 ± 49.643	89.277 ± 44.24	2.140 ± 1.01
2	Spring	ND	ND	ND	11.502	4.51	5.769	19.926	14.293	20.604	9.354	ND	ND	8.448	68.973	103.593	3.274
	Summer	7.048	9.538	11.549	1.75	0.044	ND	ND	ND	4.247	1.327	0.196	2.885	ND	ND	23.602	1.49
	Autumn	ND	ND	53.348	14.16	7.938	1.021	22.091	18.518	11.392	9.288	1.966	4.502	ND	ND	114.252	2.592
	Winter	64.63	27.764	57.578	ND	ND	5.188	18.357	21.178	ND	ND	2.625	6.278	6.847	79.257	118.135	2.505
	M ± SD	46.116 ± 26.50	9.325 ± 13.08	30.618 ± 29.12	9.835 ± 5.51	3.123 ± 3.84	4.063 ± 2.11	15.093 ± 10.17	13.497 ± 9.43	11.319 ± 6.86	4.992 ± 5.02	2.842 ± 2.69	3.416 ± 2.66	6.145 ± 2.94	37.057 ± 42.99	89.895 ± 44.62	2.465 ± 0.73
3	Spring	59.994	12.301	66.157	19.84	ND	ND	22.361	24.152	28.343	13.064	9.0713	ND	ND	72.107	121.177	7.4819
	Summer	10.172	7.179	23.249	5.746	2.32	ND	ND	ND	9.434	2.494	1.1479	2.856	ND	ND	26.315	1.419
	Autumn	55.935	9.807	ND	ND	ND	ND	20.932	10.802	9.845	ND	ND	3.238	6.386	69.434	84.809	ND
	Winter	50.617	28.943	ND	ND	18.541	10.091	19.453	22.061	13.912	14.81	4.798	ND	ND	57.466	103.377	10.628
	M ± SD	44.179 ± 22.99	14.557 ± 9.81	55.597 ± 21.64	6.396 ± 9.36	8.870 ± 6.92	3.502 ± 4.76	15.686 ± 10.52	14.253 ± 11.16	15.383 ± 8.87	9.995 ± 5.44	3.754 ± 4.09	3.821 ± 3.37	2.136 ± 3.01	49.751 ± 33.77	83.919 ± 41.17	4.882 ± 5.02
4	Spring	65.982	18.197	77.777	26.341	ND	ND	23.917	36.36	20.783	14.892	ND	ND	ND	83.599	123.799	8.189
	Summer	ND	ND	16.249	ND	ND	ND	9.264	10.751	7.247	3.661	2.1	2.885	6.839	24.774	31.173	1.561
	Autumn	ND	ND	ND	ND	12.333	8.246	27.953	8.848	11.918	9.113	5.206	9.099	8.041	78.494	95.286	2.679
	Winter	62.813	30.122	70.778	ND	ND	8.347	22.913	24.944	14.725	18.642	ND	ND	13.478	73.883	95.999	9.921
	M ± SD	51.307 ± 26.20	12.079 ± 14.77	60.153 ± 29.41	13.704 ± 13.86	7.896 ± 9.54	4.148 ± 4.79	21.011 ± 8.12	20.225 ± 12.93	13.668 ± 5.656	11.577 ± 6.57	8.622 ± 5.90	2.996 ± 4.28	7.089 ± 5.53	65.187 ± 27.23	86.564 ± 39.24	5.587 ± 4.091
5	Spring	ND	ND	90.917	30.244	23.414	11.499	37.313	49.131	29.095	ND	ND	ND	ND	112.928	144.1822	9.635
	Summer	ND	ND	12.8491	2.675	ND	ND	8.2648	12.751	10.247	10.986	2.1	3.459	12.268	21.774	41.659	2.517
	Autumn	79.753	26.128	ND	ND	19.823	13.156	37.799	18.481	19.579	18.631	14.213	13.629	11.76	101.172	117.838	ND
	Winter	71.747	31.302	89.078	ND	ND	12.858	38.566	37.359	22.856	21.968	ND	ND	20.263	102.091	110.857	13.628
	M ± SD	69.417 ± 20.50	14.357 ± 16.71	68.711 ± 37.43	17.713 ± 19.19	11.122 ± 12.21	9.378 ± 6.29	30.485 ± 14.82	29.430 ± 16.82	20.444 ± 7.86	18.003 ± 4.87	7.880 ± 7.94	8.758 ± 8.424	11.072 ± 8.34	84.491 ± 42.15	103.634 ± 43.73	6.445 ± 6.29
6	Spring	156.712	11.310	166.462	10.787	1.242	0.643	16.459	13.017	21.086	19.916	ND	ND	ND	ND	132.174	ND
	Summer	ND	ND	ND	ND	0.973	0.148	4.803	4.741	8.621	11.824	1.576	2.885	11.589	93.953	83.015	1.490
	Autumn	100.655	15.344	100.641	20.776	1.453	1.0467	27.829	ND	ND	ND	2.782	5.382	9.974	106.656	122.908	2.139
	Winter	91.829	30.122	124.178	ND	ND	5.407	29.200	36.476	28.791	25.302	4.790	4.3125	18.906	105.674	90.213	ND
	M ± SD	107.311 ± 33.99	14.194 ± 12.44	120.707 ± 33.45	13.249 ± 10.08	0.917 ± 0.64	1.811 ± 2.42	19.572 ± 11.38	15.936 ± 14.10	14.624 ± 12.81	14.260 ± 11.00	2.771 ± 1.43	3.144 ± 2.33	11.186 ± 6.02	76.570 ± 51.37	107.077 ± 24.10	0.907 ± 1.080

(M: mean; SD: standard deviation; spring-summer-autumn: 2010; winter: 2010-2011; ND: not detected).

The pyrolytic source of PAHs in the area might be due to the low molecular weight of some PAHs such as naphthalene and phenanthrene which are degraded rapidly in sediment. While the high molecular weight of other PAHs such as pyrene, fluoranthene, Benzo(a)anthracene and Benzo(a)pyrene are more recalcitrant, thus that leads to decrease their concentration [60].

The seasonal variation of PAHs concentrations was clear. The highest concentration of PAHs was recorded in spring and winter, while the lowest concentration was recorded in summer. That may be due to the processes of photo-oxidation, volatilization and high degradation during the summer [50, 55].

The total of PAHs compounds ranged 26.668-900.042 ug/g in sediment of the studied area and this result agrees with Al-Taee [9]. The concentration of TOC (%) in sediment is an important factor affecting PAHs concentration [51, 61, 62]. In current work, TOC (%) ranged (0.4%-2.2%) and the lowest values were recorded on Site 3 might be due to few human activities and lack of flow of sewage at this site throughout the study period. The highest values were in Site 6 [41]. There is an obvious relation between PAH and TOC observed in the current study that indicates the positive relation between TOC and PAHs [62, 63]. This relation might be due to many characterized of PAHs such as, tendency to organic compounds, anhydrous characters, or might be the fraction of TOC in the sediment [19, 64].

The results showed negative correlation between PAHs and the grain size of sediment (silt), while a positive correlation with clay due to heterogeneity deposition of PAHs in the sediment and there is an appositive correlation between clay and TOC (%) was noticed. This correlation explains the positive correlation between PAHs and clay, in contrast to this correlation, there was a negative and positive correlation between sand and some PAHs individual according to their adsorption and affinity between PAHs and sand [64, 65].

CCA for PAHs (in water) indicated that negative relationships were found between air temperature, water temperature, water flow and EC (electrical conductivity) (Fig. 3). The present results were also observed in another study on urban stream [66]. Different relationships between dissolved oxygen and individual compounds of PAHs were observed in CCA for PAHs in water, positive relationships with phenanthrene, flurene, B(ghi)A, B(a)P and ND, while a negative relationship with other studied compounds. Research carried out in Iraq indicates there are high concentrations of total PAHs in some aquatic systems (Shatt Al-Arab River and north west Arabian Gulf) compared with the present study due to the effects of industrial activities study as well as, from direct domestic, industrial discharge and burning of wood for different purposes [16]. In the Euphrates River, the study of the hydrocarbons indicates that the low concentration was recorded in B(a)A, but the high concentration was recorded in B(a)P [55], hence, it in contrast to the results of current study, where low concentration for B(a)P and high concentrations were recorded for Acep.

CCA explains the negative correlation between PAHs and the grain size of sediment (silt) (Fig. 4). While a positive correlation with clay due to heterogeneity deposition of PAHs in the sediment and there is an appositive correlation between clay and TOC (%). This correlation explains the positive correlation between PAHs and clay, in the contrast to this correlation, there is a negative and a positive correlation between sand and some PAHs individual according to their adsorption and affinity between PAHs and sand [64, 65].

The PAHs concentrations in sediment samples are several times higher than those in water, there is a strong correlation between PAHs in sediment and TOC (%) due to affinity to organic matter.

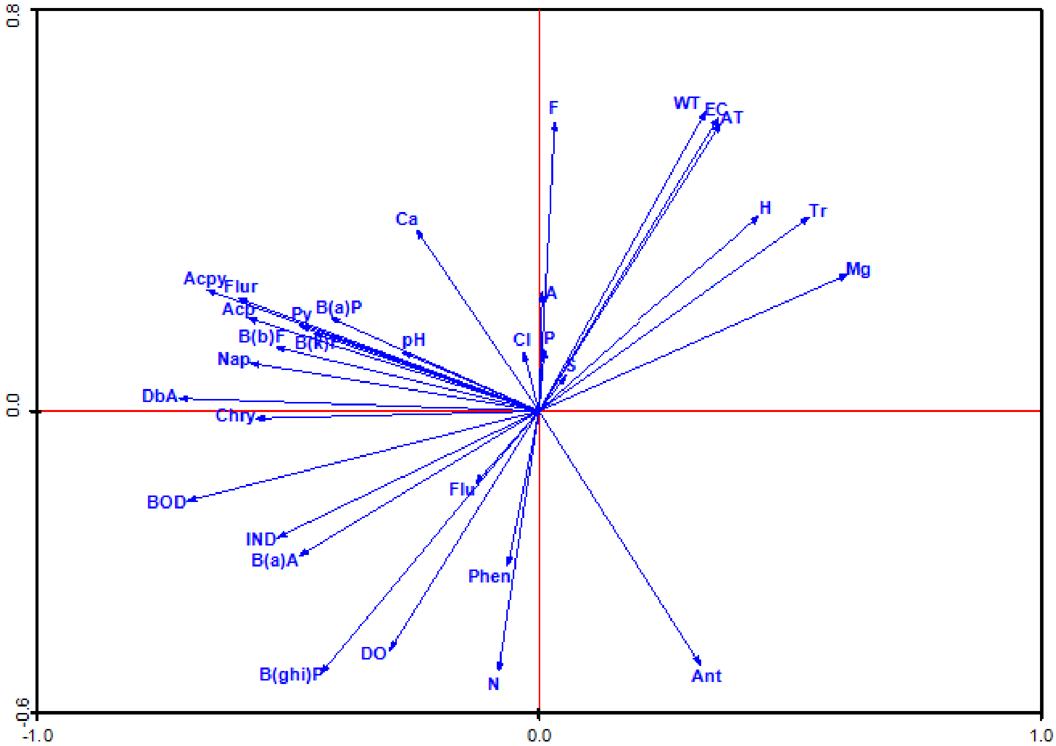

Fig. 3 CAA for some physical and chemical properties of water and PAHs in water during the study period.

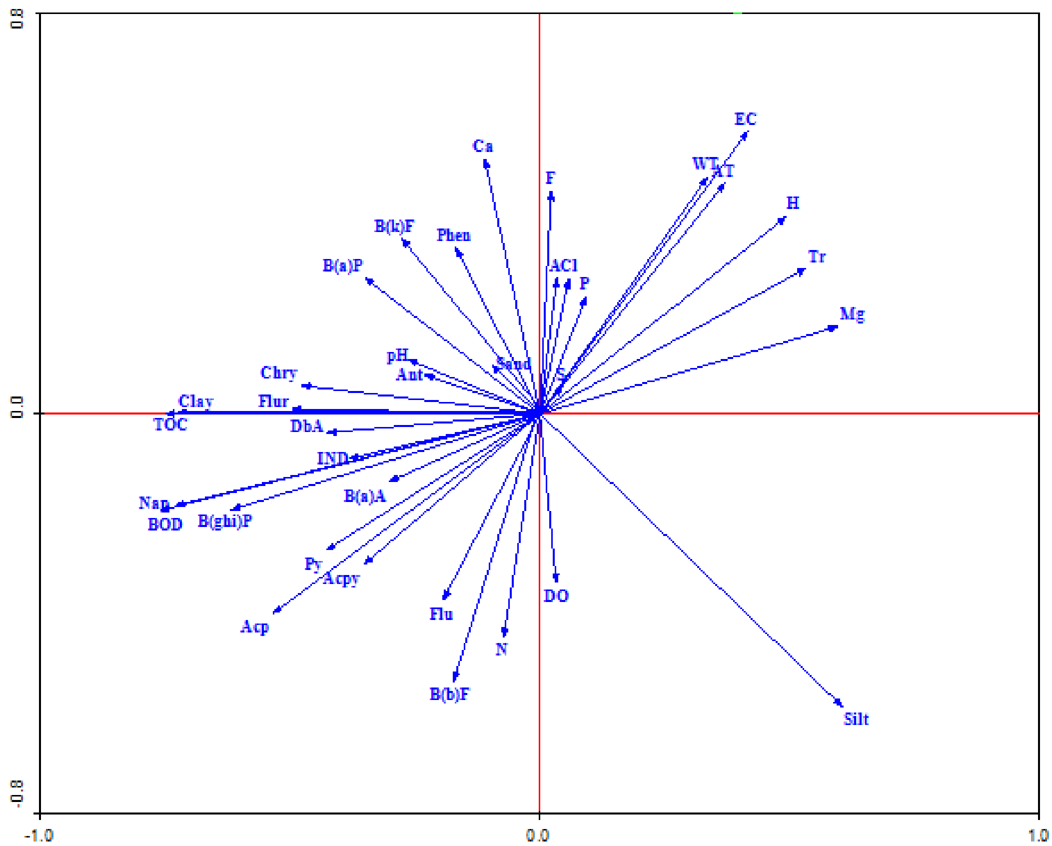

Fig. 4 CAA for some physical and chemical properties of water and PAHs in sediments during the study period.

4. Conclusions

Hilla city, the capital of Babylon Governorate is divided in two parts by a branch of the Euphrates River called Shat Al-Hilla. About 1.6 million people occupy this area. In this research, PAHs were studied for the first time in this river.

PAHs were studied within part of the Euphrates River at Babylon. Monthly samples were taken from six studied sites for 12 months that started in March, 2010 up to February, 2011.

CCA for PAHs (in water) indicated that negative relationships found among air temperature, water temperature, water flow and EC. PAHs were observed in CCA for PAHs in water, positive relationships with phenanthrene, flurene, B(ghi)A, B(a)P and ND, while a negative relationship with other studied compounds. The results indicated that PAHs concentrations in sediment samples are several times higher than those in water. There is a strong correlation between PAHs in sediment and TOC (%) due to affinity to organic matter. Also, the distribution of PAHs in sediment correlated with texture especially with clay content in sediment. A positive correlation with clay due to heterogeneity deposition of PAHs in the sediment was noticed and there is an appositive correlation between clay and TOC (%). This correlation explains the positive correlation between PAHs and clay, in contrast to this correlation, there is a negative and a positive correlation between sand and some PAHs individual according to their adsorption and affinity between PAHs and sand.

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