

Distribution and sources of polycyclic aromatic hydrocarbons in soils along the Shatt Al-Arab River delta in southern Iraq

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Abstract: The soil samples from 0–10 cm depth were collected from three areas (Center of Basrah – CB, Garmat Ali – GA, and Abu Al-Khasib – AK) located along the Shatt Al-Arab River (SR) delta in southern Iraq to estimate the distribution and sources of polycyclic aromatic hydrocarbons (PAHs). The PAH total concentrations in the soils decreased significantly from CB (72.16 ng/g dry weight (DW)), GA (36.48 ng/g DW), to AK (17.30 ng/g DW) gradually indicating the impact of pollution emissions on the distribution of PAHs in soils. The low (2 and 3 ring) and high (4, 5, and 6 ring) molecular weight PAHs accounted for 14%, 16%, 37%, 21%, and 12% respectively in CB soil, 24%, 31%, 29%, 7%, and 10% in GA soil and 40%, 29%, 17%, 8%, and 8% in AK soil. The high molecular weight PAHs predominated in CB soils and the low molecular weight PAHs dominated in GA and AK soils suggesting a difference in emission sources between the studied areas. The PAH diagnostic ratios and principal component analysis (PCA) indicated that PAHs in soils of the SR delta essentially originated from traffic and industrial emissions and biomass and grass/wood/coal combustion. The PAH atmospheric transport from CB area might impact the PAH distribution in the soils of AK area. The risk assessment of the soils has been performed. The total toxic equivalent concentrations (Bap_{teq}) of PAHs in the examined areas did not exceed the Dutch target values suggesting that no carcinogenic risk for the SR delta soils was found.

Keywords: PAHs; oil contamination; risk assessment; soil pollution

Polycyclic aromatic hydrocarbons (PAHs) are a group of environmental persistent organic pollutants. They are bioaccumulative and toxic compounds to living organisms (CHEN & CHEN 2011; ADHIKARI *et al.* 2016).

There are two origins of PAHs in the environment, natural and anthropogenic. The natural origin attributes to forest fires and volcanic activity, etc. (PAH background values). The anthropogenic one includes incomplete combustion of fossil fuels, and industrial emissions (PAH contamination levels) (MOTELAY-MASSEI *et al.* 2004; PENG *et al.* 2016).

The PAHs are of environmental interest because of their carcinogenic, mutagenic, and teratogenic impacts on living organisms and humans (OLSSON *et al.* 2010; ZHENG *et al.* 2012). The increased attention to the behaviour, toxicity, monitoring and distribution of PAHs in soils is important for assessing their risks to human health. Due to PAH hydrophobicity, low water solubility and vapour pressure, the chemicals tend to adsorb on the soil organic matter and accumulate and persist in soil for long periods (SVERDRUP *et al.* 2002; KWON & CHOI 2014). Therefore, soil is considered the final reservoir for such hydrophobic

organic contaminants. It has been well documented that most of the PAH pollutants will be present in the upper soil layer (PENG *et al.* 2016).

As the oil producer country, Iraq has the emissions of PAHs. The emitted PAHs mainly originate from the combustion of fossil fuels and biomass (FARID *et al.* 2016). The investigations on concentrations and distribution of PAHs in atmosphere, water, soils, and sediments have been scarce in Iraq. As the PAHs down in terrestrial ecosystems, soils in many areas of Iraq, for example SR delta, contain a large amount of PAHs. However, investigations on the concentrations, distribution and probable sources of PAHs in the soil have been relatively less frequent than in water and sediment.

The soil is one of the main elements which also includes the atmosphere, water and plant that can play an important role in the elimination of PAH contaminants from the environment (VÁCHA *et al.* 2010; WANG *et al.* 2015). The soil acts as an essential repository of PAH compounds (ORECCHIO 2010; HU *et al.* 2015), so the role of soil in the insulating PAHs must be considered intensively. Thus, the research on the distribution and potential sources of PAHs in soils has been essential in assessing soil segregation and managing the risks associated with soil exposure to these chemicals.

The environment of Shatt Al-Arab River (SR) is considered an industrialized and urbanized region in southern Iraq, which has deteriorated severely during the past decades. The organic contaminants including petroleum hydrocarbons and pesticides have been well documented in various regions of this environment (FARID *et al.* 2016). Therefore, the objective of this study was to determine the concentrations, profiles, and possible sources of PAHs in soils of three areas (CB – urban, GA – suburban, and AK – rural) located along the SR delta influenced by urbanization.

MATERIAL AND METHODS

The SR delta includes many regions covering an area of about 969 059 km² in Basrah governorate. The annual average temperature is 24°C and ranges from 12°C in January to 34°C in July. The annual precipitation is 140 mm and begins in October at a monthly average of less than 1 mm, up to 29.3 mm in December. In order to estimate PAH pollution, three areas representing different disturbances due to urbanization were selected along the

SR delta for soil sampling (Figure 1). The areas were CB (urban) (30°33'00.0"N, 47°47'10.0"E), GA (suburban) (30°48'10.6"N, 47°45'03.8"E), and AK (rural) (30°27'44.5"N, 48°00'06.0"E). Basrah is the third and sixth largest city in Iraq in terms of population (2.532 million people) and area (19 070 km²), respectively. The city is located on the west bank of the SR in southern Iraq and overlooks the Arabian Gulf. Economically, it has many ports, oil fields, industries, and tourist areas and is considered the main centre of agriculture and grazing. The city of Basrah is connected with its villages, towns and other cities of Iraq by a wide network of paved roads of varying lengths. The most important activities in the city of Basrah are the extraction, production and exportation of oil and gas, shipping, railways, agriculture, food industries, heavy industries such as iron, steel, fertilizers, petrochemicals, and fisheries. Therefore, its soil is heavily influenced by oil and anthropogenic activities, traffic, houses, workshops (mechanics, carpentry etc.), sale of all kinds of goods, and facilities handling petroleum products. GA lies within the administrative boundaries of Al-Hartha area, northeast of the city of Basrah, about 10 km from CB. The area of Al-Hartha is 200 km² and has a population of 154 thousand people (including 80 thousand people in GA). The area is linked by the main road between the cities of Baghdad and Basrah. The Tigris and Euphrates rivers meet in GA

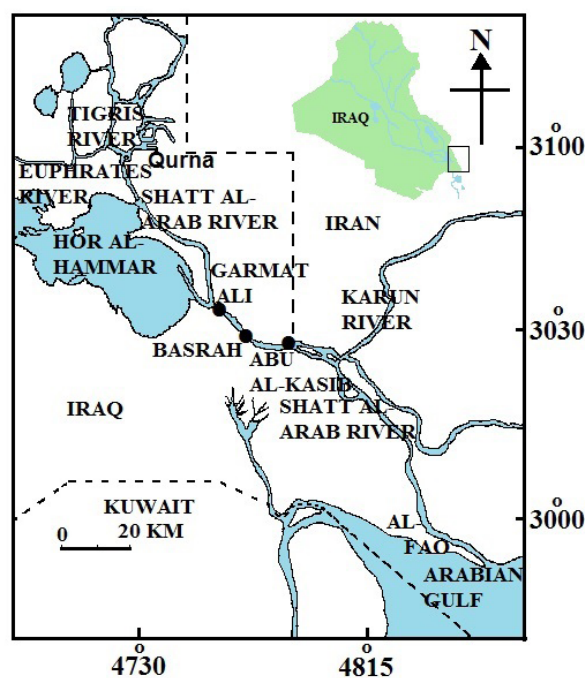


Figure 1. The Shatt Al-Arab River delta and sampling areas

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region to form the SR. Many industrial and service facilities such as thermal power station, paper mill, Basrah international airport, water injection plant to Basrah oil wells, Iraqi dates factory, and Basrah University are distributed in this area, as well as many agricultural lands and fields surrounding them. Many fishing boats can also be seen along the waters of the area. All of these activities significantly affected the soil of the region. AK is a large agricultural area located south of the city of Basrah and it has an area of 298 km² and a population of about 500 thousand people. It is about 18 km from CB and connects to the city of Basrah through a road that has orchards containing dense palm and other fruit trees. Large and small rivers pass through the AK area, which take their waters from the SR and irrigate vast agricultural lands. Geographically, AK is one of the closest areas to CB, where it is not separated from the city of Basrah by vast desert lands, large rivers or long distances. In AK area, there is one of the important Iraqi ports (Abu Floss) and the area contains a plant for the production of chemical fertilizers. AK soil is considered relatively low contaminated. A total of 50 surface soil (0–10 cm depth) samples from each area were collected from June to August (summer) 2017. To avoid the impact of pollution sources, soil samples were taken far from the sources of emission at an estimated distance of more than 200 m. Each sample comprises a mixture of soils containing more than 7 subsamples within 100 square meters and the spacing of each sample site is more than 60 m. After the transfer of the samples to the laboratory, the soils were stored frozen at –20°C until analysis.

All solvents were of analytical grade and were distilled prior to use. Sodium sulphate ashed at 400°C and silica gel and alumina (100–200 mesh) were washed using methanol and chloroform and dried before use. For PAH calibration and quantification, a standard PAH calibration mixture having 16 priority PAHs was used.

The soil samples were freeze-dried, ground to pass through a 62µ stainless steel sieve, and homogenized. The pretreatment and calibration were done using a surrogate standard mixture of 16 priority pollutants. 30 g subsamples were weighed and Soxhlet-extracted for 24 h with 250 ml dichloromethane/hexane solvent (1 : 1, V/V). The extract was then concentrated to about 2 ml by a rotary evaporator for the following cleanup. Elemental sulphur was removed from the extracts using activated elemental copper. The concentrated extract was fractionated by column

chromatography on anhydrous sodium sulphate (1 g) over alumina (10 g) and silica gel (10 g). Saturated hydrocarbons and aromatic hydrocarbons were obtained by successively eluting with hexane (25 ml) and toluene (25 ml), respectively. The aliphatic and aromatic fractions were concentrated again on a rotary evaporator, transferred to a vial, and the volume was adjusted to 1 ml exactly using a stream of nitrogen gas. An aliquot of 1 ml of aromatic hydrocarbons extract was subjected to analysis (Hu *et al.* 2015).

The determination of PAHs was performed on an Agilent capillary gas chromatograph (GC) (Agilent, USA) with flame ionization detector (FID) (Agilent, USA). The fused silica capillary column (10 m × 250 µm × 0.5 µm) used was wall-coated open tubular (methyl silicone) (Agilent US2463233H DB-petrp, Agilent, USA), with helium as a gas carrier at a flow rate of 1.5 ml/min. The operating temperatures for detector and injector were 300°C and 320°C, respectively. The temperature of the column was held at 50°C for 8 min, then 8°C/min to 350°C. Prior to GC analysis, a standard PAH mixture was injected for calibration and their quantification. The PAH standards consisted of 16 priority PAHs; naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorine (Flo), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), pyrene (Pyr), benzo(a)anthracene (Baa), chrysene (Chr), benzo(b)fluoranthene (Bbf), benzo(k)fluoranthene (Bkf), benzo(a)pyrene (Bap), dibenzo(a,h)anthracene (Dia), indeno(1,2,3-cd)pyrene (Inp), and benzo(g,h,i)perylene (Bpe). Individual PAHs were quantified based on the retention time of an authentic PAH mixed standard, and concentrations of each PAH were calibrated based on the standard calibration curve. The concentrations based on individually resolved peaks were summed to obtain the total PAH concentrations. The PAH concentrations were reported in ng/g DW.

The procedural blank, spiked blanks (solvent spiked with 16 PAHs) and matrix spiked (soil spiked with 16 PAHs) samples were processed for the limit of quantification analysis. At every successive sample, calibration was done by analysing the standard PAH calibration mixture. The relative standard deviation of each replicate was less than 13%. The average recoveries of 16 PAHs in spiked blanks and matrix spiked samples were 112.45 ± 20% and 54.37 ± 12%, respectively. The procedural blank contained no detectable amounts of target analytes. The method detection limits of PAHs ranged from 0.15 to 0.7 ng/g DW.

To determine the carcinogenic potency associated with exposure to a given PAH, the Bap toxic equivalent quantity (Bap_{teq}) was calculated. The toxic equivalent factor (TEF) was used to calculate the Bap_{teq} for each individual PAH. In order to compare the carcinogenic potencies associated with the total PAH concentrations at examined areas, the sum of each individual Bap_{teq} (i.e., total Bap_{teq}) was calculated and then used as a surrogate indicator. The total Bap_{teq} was calculated using the following equation:

$$Bap_{teq} = \sum TEF_i \times CPAH_i$$

where:

TEFi – toxic equivalent factor of each PAH relative to Bap congener i

CPAHi – concentration of individual PAH congener i

The PAH concentrations were statistically analysed using standard deviation (SD). The sum of PAHs in soil samples represents total PAHs. The sum of high molecular weight (HMW) and low molecular weight (LMW) PAHs, and the ratio of Phe/Ant, Fla/Pyr, Ant/Ant+Phe, Fla/Fla+Pyr, Inp/Inp+Bpe and Baa/Baa+Chr were used to identify possible PAH sources. The results of soil samples were analysed by multivariate statistics like PCA. PCA with varimax rotation method was used to obtain significant blueprint and relationships between individual PAHs.

RESULTS AND DISCUSSION

The total PAH concentrations in the CB, GA, and AK soils were 72.16, 36.48 and 17.30 ng/g DW, respectively (Table 1). The PAH concentrations showed an obvious gradient from CB, GA, to AK indicating a considerable impact of urbanization on the soil. The highest total PAH concentration was found in the CB soil. The concentration of total PAHs in the GA soil was about one half of that in the CB soil and twofold of that in the AK soil. The level of PAH concentrations in the soils of the present areas was lower or moderate compared to those soils around the world of urban areas (BANGER *et al.* 2010; WANG *et al.* 2013; HU *et al.* 2015), suburban areas (TSIBART *et al.* 2014; DI *et al.* 2016; PENG *et al.* 2016) and rural areas (RAY *et al.* 2012; KWON & CHOI 2014), respectively. According to the classification system of MALISZEWSKA-KORDYBACH (1996), the PAH concentration of 200–600 ng/g in soil represents weak contamination and the concentration of less than 200 ng/g indicates no contamination. This suggests

that the concentration of total PAHs of SR delta soils fell within the range of low levels. However, the total PAH concentration in the AK soil was much higher than those of endogenous sources (1–10 ng/g) resulting from plant synthesis and natural fires, suggesting that anthropogenic PAHs from CB area might contribute to the contamination of AK soils through atmospheric transport. None of the PAH concentrations of soil samples in recent study was more than 600 ng/g, and the GA and CB soils were weakly contaminated.

The PAH profile analysis in the soils of CB, GA and AK areas revealed the predominance of HMW-PAHs (4, 5, and 6 rings) in the CB soil and LMW-PAHs (2 and 3 rings) in GA and AK soils. The HMW-PAH profile diminished in soils along the gradient from CB,

Table 1. Concentrations of polycyclic aromatic hydrocarbons (PAHs) (ng/g DW $\pm$ standard deviation) in soils of three areas located along Shatt Al-Arab River delta

PAHs	Area		
	CB	GA	AK
Nap	10.21 ($\pm$ 0.20)	8.60 ($\pm$ 0.10)	6.88 ($\pm$ 0.60)
Acy	0.47 ($\pm$ 0.10)	0.35 ($\pm$ 0.40)	0.15 ($\pm$ 0.80)
Ace	0.46 ($\pm$ 0.40)	0.33 ($\pm$ 0.50)	0.20 ($\pm$ 0.30)
Flo	0.75 ($\pm$ 0.10)	1.27 ($\pm$ 0.30)	0.84 ($\pm$ 0.20)
Phe	7.92 ($\pm$ 0.20)	7.89 ($\pm$ 0.00)	2.90 ($\pm$ 0.40)
Ant	1.55 ($\pm$ 0.30)	1.47 ($\pm$ 0.40)	0.84 ($\pm$ 0.80)
Fla	9.59 ($\pm$ 0.20)	3.52 ($\pm$ 0.30)	0.79 ($\pm$ 0.50)
Pyr	8.04 ($\pm$ 0.10)	2.86 ($\pm$ 0.70)	0.62 ($\pm$ 0.50)
Baa	3.27 ($\pm$ 0.40)	1.20 ($\pm$ 0.40)	0.53 ($\pm$ 0.20)
Chr	5.90 ($\pm$ 0.50)	2.80 ($\pm$ 0.80)	0.89 ($\pm$ 0.30)
Bbf	6.72 ($\pm$ 0.20)	1.40 ($\pm$ 0.00)	0.92 ($\pm$ 0.00)
Bkf	5.03 ($\pm$ 0.80)	0.43 ($\pm$ 0.40)	0.16 ($\pm$ 0.20)
Bap	2.29 ($\pm$ 0.20)	0.37 ($\pm$ 0.10)	0.13 ($\pm$ 0.30)
Dia	1.48 ($\pm$ 0.20)	0.22 ($\pm$ 0.50)	0.10 ($\pm$ 0.10)
Inp	4.06 ($\pm$ 0.40)	1.90 ($\pm$ 0.70)	0.99 ($\pm$ 0.00)
Bpe	4.42 ($\pm$ 0.80)	1.87 ($\pm$ 0.30)	0.36 ($\pm$ 0.40)
Total PAHs	72.16	36.48	17.30
Total of 7 carcinogenic PAHs	28.75	8.32	3.72

CB – urban; GA – suburban; AK – rural; Nap – naphthalene; Acy – acenaphthylene; Ace – acenaphthene; Flo – fluorine; Phe – phenanthrene; Ant – anthracene; Fla – fluoranthene; Pyr – pyrene; Baa – benzo(a)anthracene; Chr – chrysene; Bbf – benzo(b)fluoranthene; Bkf – benzo(k)fluoranthene; Bap – benzo(a)pyrene; Dia – dibenzo(a,h)anthracene; Inp – indeno(1,2,3-cd)pyrene; Bpe – benzo(g,h,i)perylene

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GA, to AK, while the LMW-PAH profile increased along the previous gradient. The 4, 5 and 6 ringed PAHs ranged from 37%, 21% and 12% respectively in CB soil to 17%, 8% and 8% respectively in AK soil, whereas the 2 and 3 ringed PAHs varied from 14% and 16% respectively in CB soil to 40% and 29% respectively in AK soil (Figure 2). The same conclusion was also reported by RIBES *et al.* (2003), ORECCHIO (2010) and WANG *et al.* (2013) where the researchers demonstrated the dominance of LMW-PAHs in low pollution areas (tropical, mountain, agricultural, and non-industrial soils) and HMW-PAHs in urban and industrial soils.

Typically, LMW-PAHs were generated from biomass and grass/wood/coal combustion (combustion processes of low or moderate temperature) and HMW-PAHs from vehicular exhausts and industrial fuel combustion (combustion processes of high temperature) (ZHANG *et al.* 2007; MORILLO *et al.* 2008; GENNADIEV & TSBART 2013). The dominance of LMW-PAHs in the GA and AK soils suggests the contribution from combustion processes of low or moderate temperature while the abundance of HMW-PAHs in the CB soil is an indicator of combustion processes of high temperature. The traffic and industrial emissions were the main sources of PAHs in CB area causing significant PAH accumulation in soil, while atmospheric transmission and PAH deposition also contribute to the soil PAHs of AK area. This was in agreement with conclusions of other reports such as RAY *et al.* (2012) and WANG *et al.* (2015).

Nap was the most dominant PAH in CB (14%), GA (24%), and AK (40%) soils. Nap, Phe, Fla, and Pyr were dominant PAHs in CB soil (49%) while Nap, Phe, and Fla were dominant PAHs in GA soil

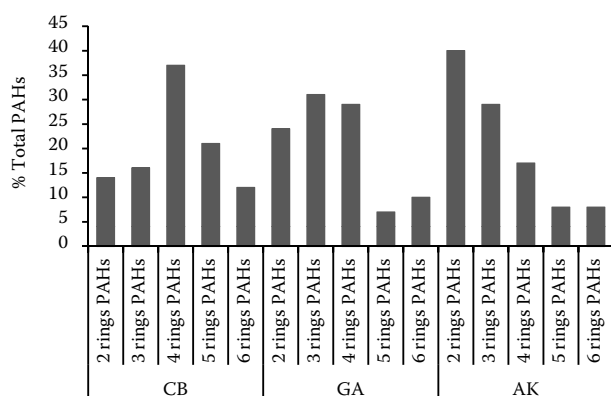


Figure 2. Composition profile of polycyclic aromatic hydrocarbons (PAHs) in soils of the Shatt Al-Arab River delta CB – urban; GA – suburban; AK – rural

(56%). Nap and Phe were dominant PAHs in AK soil (57%) (Figure 3). Nap may be of biogenic origin particularly in rural areas (NADAL *et al.* 2004; KWON & CHOI 2014), which partly explained the dominance of LMW-PAHs in AK area. Moreover, the coal and biomass combustion are the main sources of PAH contamination in rural areas, and the emission factors for low-ringed PAHs from biomass combustion are higher than those for coal combustion (ZHANG *et al.* 2007). In addition, the LMW-PAHs in urban areas are exposed to photochemical degradation more than in rural areas because of hydroxyl radicals (OH) (WANG *et al.* 2009), which further explained the presence of high concentrations of LMW-PAHs in the soil of AK area than CB area.

The PAH contamination can be related to pyrolytic or petrogenic origins. The petrogenic origin includes ordinarily higher concentrations of LMW-PAHs, whereas the HMW-PAH dominance refers to the pyrolytic origin (combustion origin) (RAY *et al.* 2008; TSBART *et al.* 2016). In addition, some diagnostic ratios such as Phe/Ant, Fla/Pyr, Ant/Ant+Phe, Fla/Fla+Pyr, Inp/Inp+Bpe, and Baa/Baa+Chr were utilized to differentiate between petrogenic and pyrolytic PAH origin (MORILLO *et al.* 2008; QUIROZ *et al.* 2011; PENG *et al.* 2016). The Phe/Ant ratio > 3 indicates pyrolytic origin and < 3 indicates petrogenic origin (ZRAFI *et al.* 2013; FARID *et al.* 2016). Whereas the Fla/Pyr ratio < 1 is characteristic of a petrogenic source and the ratio indicates a pyrolytic source when it is > 1 (SAFO-ADU *et al.* 2014). The ratio of Ant/Ant+Phe < 0.1 is characteristic of a petrogenic source and > 0.1 characterizes a combustion source (PENG *et al.* 2016). The Fla/Fla+Pyr ratio < 0.4 indicates a petrogenic source, while this ratio indicates a combustion source when it is > 0.5 and the ratio between 0.4 and 0.5 indicates the combustion of liquid fossil fuel (SAFO-ADU *et al.* 2014). The Inp/Inp+Bpe ratio < 0.20 is generally associated with petrogenic source, and > 0.50 indicates biomass and coal combustion, whereas this ratio between 0.20 and 0.50 refers to the combustion of liquid fossil fuel (TOBISZEWSKI & NAMIE'SNIK 2012; HU *et al.* 2015). Furthermore, the Baa/Baa+Chr ratio > 0.2 indicates a petrogenic source, and the value between 0.2 and 0.35 refers to petroleum combustion, while the ratio > 0.35 suggests the combustion of coal, grass and wood (CHEN & CHEN 2011). In our study, the values of Phe/Ant (3.45–5.36%), Fla/Pyr (0.19–1.27%), Ant/Ant+Phe (0.15–0.22%), Fla/Fla+Pyr (0.54–0.56%), Inp/Inp+Bpe (0.47–0.73%) and Baa/Baa+Chr (0.30–0.37%) ratios

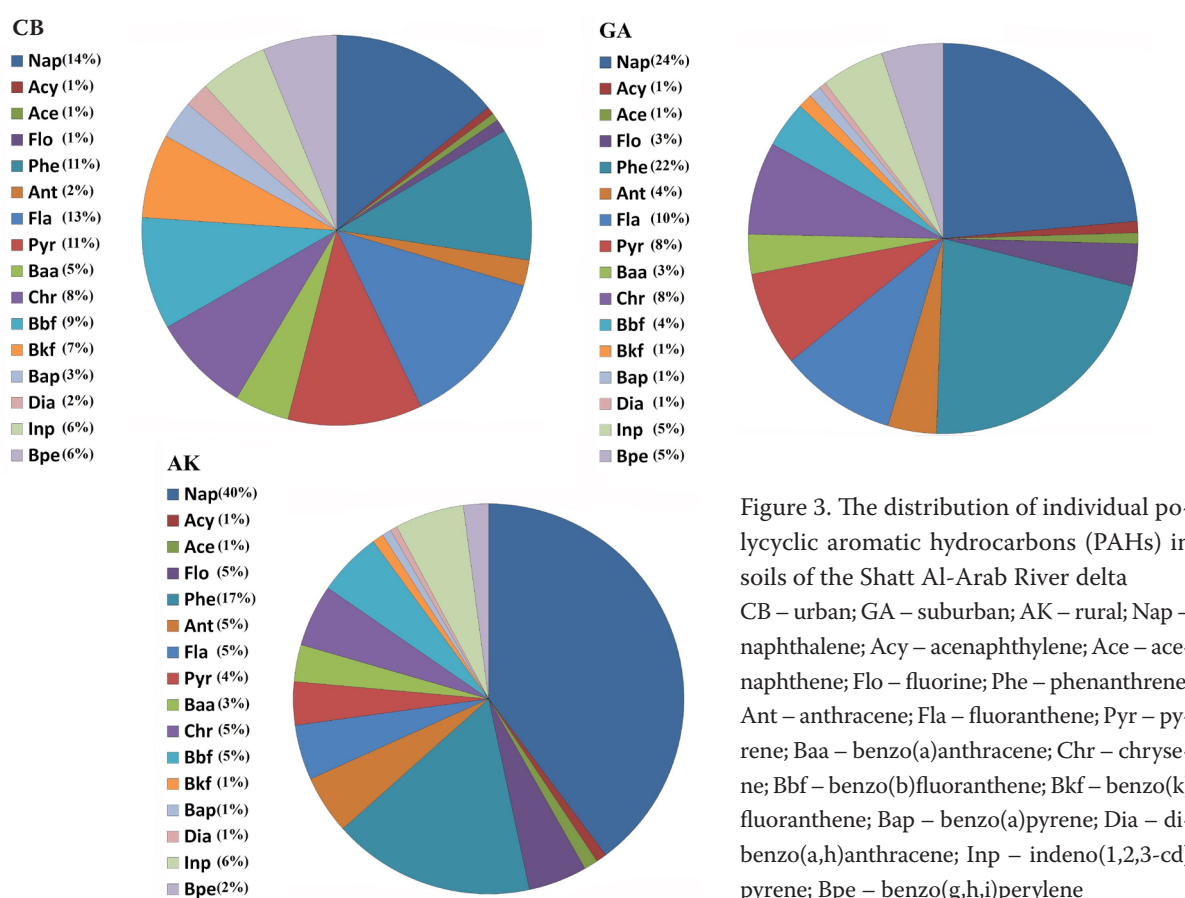


Figure 3. The distribution of individual polycyclic aromatic hydrocarbons (PAHs) in soils of the Shatt Al-Arab River delta
CB – urban; GA – suburban; AK – rural; Nap – naphthalene; Acy – acenaphthylene; Ace – ace-naphthene; Flo – fluorine; Phe – phenanthrene; Ant – anthracene; Fla – fluoranthene; Pyr – pyrene; Baa – benzo(a)anthracene; Chr – chrysene; Bbf – benzo(b)fluoranthene; Bkf – benzo(k)fluoranthene; Bap – benzo(a)pyrene; Dia – di-benzo(a,h)anthracene; Inp – indeno(1,2,3-cd)pyrene; Bpe – benzo(g,h,i)perylene

(Table 2) indicate that the traffic emission and fuel combustion might contribute to the occurrence of PAHs in CB soil, while biomass and grass/wood/coal combustion might contribute to the soil PAHs at AK area. The results were similar to reports of SALTENE *et al.* (2002) and PENG *et al.* (2016).

In the present study, the Ant/Ant+Phe and Baa/Baa+Chr ratios were plotted against Fla/Fla+Pyr and Inp/Inp+Bpe, respectively (Figure 4) in order to show the PAH distribution relative to their potential sources in soil samples. It can be seen that CB soil exhibited evidence of petroleum derived pollution, while the contamination of AK soil may be derived primarily from biomass and grass/wood/coal combustion. Petroleum derived PAHs may also be a source for PAHs in AK soils through atmospheric transport and deposition from CB area. Such inference had also been reported for urban and rural areas by TOBISZEWSKI and NAMIE'SNIK (2012); HILLER *et al.* (2015) and DI *et al.* (2016).

To promote the reliability of source identification and quantitatively partition the percentage of contribution for each source of PAH, PCA was applied to analyse the data set. The two principal components

were obtained from the PCA results of soils of the present areas, PC1 and PC2 (Table 3). It is well known that the LMW-PAHs are emitted from sources such as coke ovens (Nap, Phe, Ant and Flo), high roads (Nap), gasoline engines (Nap), and combustion of

Table 2. Diagnostic ratios of polycyclic aromatic hydrocarbons (PAHs) in the Shatt Al-Arab River delta soils

Ratios	Area		
	CB	GA	AK
Phe/Ant	5.10	5.36	3.45
Fla/Pyr	0.19	1.23	1.27
Ant/Ant+Phe	0.16	0.15	0.22
Fla/Fla+Pyr	0.54	0.55	0.56
Baa/ Baa+Chr	0.35	0.30	0.37
Inp/Inp+Bpe	0.47	0.50	0.73
Carcinogenic PAHs/PAHs	0.39	0.22	0.21
LMW/HMW	0.42	1.20	2.15

CB – urban; GA – suburban; AK – rural; Phe – phenanthrene; Ant – anthracene; Fla – fluoranthene; Pyr – pyrene; Baa – benzo(a)anthracene; Chr – chrysene; Bap – benzo(a)pyrene; Inp – indeno(1,2,3-cd)pyrene; Bpe – benzo(g,h,i)perylene; LMW – low molecular weight; HMW – high molecular weight

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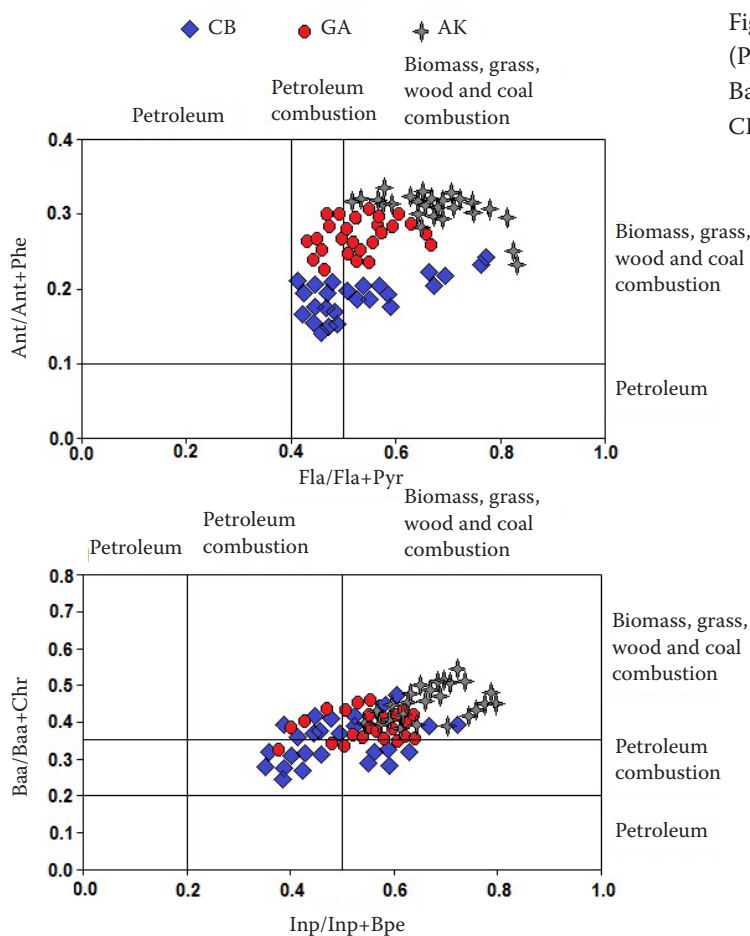


Figure 4. Plots of polycyclic aromatic hydrocarbon (PAH) ratios: Ant/Ant+Phe versus Fla/Fla+Pyr and Baa/Baa+Chr versus Inp/Inp+Bpe
CB – urban; GA – suburban; AK – rural

wood and coal (Acy and Ace) (CHAHAL *et al.* 2010; WANG *et al.* 2013). While the HMW-PAHs refer to sources such as incomplete combustion (Fla, Pyr, Baa, Chr, Bbf, Bkf, Bap, Inp and Bpe), coal combustion (Fla, Pyr, Baa, Chr and Bap), fossil fuel and its combustion (Bbf and Bkf), diesel and natural gas combustion (Baa and Chr) and traffic emission (Inp and Bpe) (BUCHELI *et al.* 2004; ZHENG *et al.* 2012). PC1 and PC2 interpreted 84.54% and 10.32%, 68.46% and 36.68%, and 77.51% and 18.27% of total variances of CB, GA and AK areas, respectively. In CB soil, the PC1 was heavily loaded on Fla, Pyr, Baa, Chr, Bbf, Bkf, Bap, Dia, Inp and Bpe, which were identified from traffic and industrial emission (pyrogenic source). The PC2 was dominated by Nap, Ace, Acy, Flo, Phe and Ant, suggesting mixed sources of petroleum and low temperature combustion. In GA soil, the PC1 had high loadings on Nap, Acy, Flo, Phe, Ant, Fla, Pyr, Baa, Chr and Bap, which were probably a pyrogenic source. The PC2 was characterized by loadings on Flo, Phe, Bbf, Bkf, Dia, Inp and Bpe, which indicated traffic emission and coke oven origins. In AK soil, the PC1 was dominated by Nap, Ace, Flo, Phe, Ant,

Fla, Dia, Inp and Bpe, which mainly originated from wood and coal combustion sources. The PC2 showed high loadings on Phe, Pyr, Baa, Chr, Bbf and Bkf, indicating a coal combustion source. These results are in agreement with previous papers in urban, suburban and rural soils (CRNKOVIC *et al.* 2007; HILLER *et al.* 2015; WANG *et al.* 2015).

The TEF method is widely used by many investigators to evaluate the different types of toxic PAH mixtures (ORECCHIO 2010; WANG *et al.* 2015). Bap is the only PAH having sufficient toxicological data for derivation of carcinogenic PAHs (HU *et al.* 2015). The TEFs were used in a recent study to determine the risk of other PAHs relative to Bap and to calculate Bap_{teq} . For the purpose of comparison of a hazard related to the total PAH concentrations at the studied areas, the total Bap_{teq} is used as an alternative indicator. To date, several suggestions for TEFs have been found. In this study, the TEFs reported by WANG and LANG (2010) were adopted. These TEFs are as follows: Nap = 0.001, Acy = 0.001, Ace = 0.001, Flo = 0.001, Phe = 0.001, Ant = 0.01, Fla = 0.001, Pyr = 0.001, Baa = 0.1, Chr = 0.01, Bbf = 0.1, Bkf = 0.1, Bap = 1, Dia =

Table 3. Principal component analysis (PCA) after varimax rotation for polycyclic aromatic hydrocarbons (PAHs) in the Shatt Al-Arab River delta soils

PAHs	Area					
	CB		GA		AK	
	PC1	PC2	PC1	PC2	PC1	PC2
Nap	0.23	0.88	0.9	0.42	0.72	0.13
Acy	0.31	0.82	0.91	0.39	0.84	0.36
Ace	0.43	0.77	0.73	0.18	0.88	0.28
Flo	0.33	0.83	0.81	0.77	0.93	0.17
Phe	0.14	0.74	0.72	0.76	0.9	0.71
Ant	0.24	0.76	0.86	0.35	0.82	0.27
Fla	0.79	0.15	0.79	0.42	0.87	0.38
Pyr	0.78	0.22	0.73	0.33	0.28	0.84
Baa	0.79	0.41	0.92	0.29	0.31	0.7
Chr	0.74	0.19	0.89	0.12	0.39	0.88
Bbf	0.86	0.32	0.33	0.92	0.32	0.77
Bkf	0.87	0.23	0.11	0.87	0.23	0.87
Bap	0.78	0.42	0.81	0.16	0.21	0.43
Dia	0.89	0.21	0.15	0.89	0.22	0.41
Inp	0.89	0.13	0.18	0.78	0.17	0.32
Bpe	0.82	0.14	0.28	0.86	0.18	0.37
Variance (%)	84.54	10.32	68.46	36.68	77.51	18.27

CB – urban; GA – suburban; AK – rural; Nap – naphthalene; Acy – acenaphthylene; Ace – acenaphthene; Flo – fluorine; Phe – phenanthrene; Ant – anthracene; Fla – fluoranthene; Pyr – pyrene; Baa – benzo(a)anthracene; Chr – chrysene; Bbf – benzo(b)fluoranthene; Bkf – benzo(k)fluoranthene; Bap – benzo(a)pyrene; Dia – dibenzo(a,h)anthracene; Inp – indeno(1,2,3-cd)pyrene; Bpe – benzo(g,h,i)perylene

1, Inp = 0.1 and Bpe = 0.01. The total Bap_{teq} values of PAHs in soils of CB, GA and AK areas are shown in Figure 5. The calculated Bap_{teq} values of PAHs varied from 0.000 15 ng/g in AK for Acy to 2.290 ng/g in CB for Bap. The total Bap_{teq} values of PAHs in soils of CB, GA, and AK areas were 5.834 14, 1.161 48, and 0.523 28 ng/g, respectively, with an average of 2.5063 ng/g. The highest value of total PAH Bap_{teq} was found at CB (5.834 14 ng/g), followed by the value of 1.16148 ng/g at GA. The soil of AK area had the lowest total PAH Bap_{teq} value of 0.523 28 ng/g (Table 4). The average value of Bap_{teq} (2.5063 ng/g) in soils of the SR delta was very much lower in comparison with those in soils reported by RAY *et al.* (2008) in India (1021 ng/g) and WANG and LANG (2010) in China (93.6 ng/g). Bap is one of the most important carcinogenic PAH compounds. Bap accounts for 32% of total Bap_{teq} with a total con-

Table 4. The total toxic equivalent concentrations (Bap_{teq}) of polycyclic aromatic hydrocarbons (PAHs) in soils of the studied areas

PAHs	Bap_{teq}			Average
	CB	GA	AK	
Nap	0.01021	0.00086	0.00688	
Acy	0.00047	0.00035	0.00015	
Ace	0.00046	0.00033	0.0002	
Flo	0.00075	0.00127	0.00084	
Phe	0.00792	0.00789	0.0029	
Ant	0.0155	0.0147	0.0084	
Fla	0.00959	0.00352	0.00079	
Pyr	0.00804	0.00286	0.00062	
Baa	0.327	0.12	0.053	
Chr	0.059	0.028	0.0089	
Bbf	0.672	0.14	0.092	
Bkf	0.503	0.043	0.016	
Bap	2.290	0.370	0.130	
Dia	1.480	0.220	0.100	
Inp	0.406	0.19	0.099	
Bpe	0.0442	0.0187	0.0036	
Total	5.83414	1.16148	0.52328	2.5063

CB – urban; GA – suburban; AK – rural; Nap – naphthalene; Acy – acenaphthylene; Ace – acenaphthene; Flo – fluorine; Phe – phenanthrene; Ant – anthracene; Fla – fluoranthene; Pyr – pyrene; Baa – benzo(a)anthracene; Chr – chrysene; Bbf – benzo(b)fluoranthene; Bkf – benzo(k)fluoranthene; Bap – benzo(a)pyrene; Dia – dibenzo(a,h)anthracene; Inp – indeno(1,2,3-cd)pyrene; Bpe – benzo(g,h,i)perylene

centration of only 1.7% in the soil samples. The reference total carcinogenic potency was calculated by the sum of multiplied Dutch target concentrations of non-polluted soil with appropriate Bap_{teq} . The carcinogenicity of the studied areas was evaluated

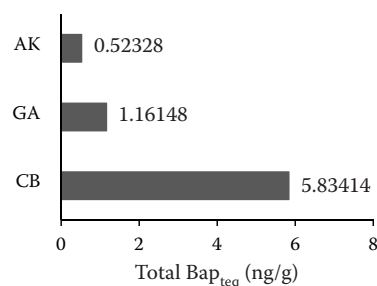


Figure 5. Total Bap_{teq} values of polycyclic aromatic hydrocarbons (PAHs) in soils of the investigated areas
CB – urban; GA – suburban; AK – rural

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by comparing the total carcinogenic potency with the reference total carcinogenic potency. The total Bap_{teq} values of the investigated areas did not exceed the Dutch target value indicating no carcinogenic risk for the SR delta soils.

CONCLUSIONS

The PAH concentrations in soils of the SR delta ranged from 17.30 to 72.16 ng/g DW, when a strong gradient of the concentrations from CB, GA to AK area was observed. The HMW and LMW-PAHs were revealed in all studied areas. The HMW-PAHs dominated in CB soil, whereas the LMW-PAHs dominated in GA and AK areas. This revealed a difference in emission sources between the studied areas and indicated the impact of urbanization on the PAH distribution in the SR delta soils. The diagnostic ratios of PAHs indicated that the PAHs in the SR delta soils originated from traffic and industrial emissions, mixed sources and grass/wood/coal combustion in the CB, GA and AK areas. The traffic and industrial emissions and biomass and grass/wood/coal combustion were the basic contributors to PAHs in soils of the SR delta. The soils in the CB and GA areas of SR delta were weakly contaminated by PAHs. The atmospheric transport from CB area can impact soils in AK area. The soil PAH risk assessment indicated that the surface soils of the SR delta do not pose any carcinogenic ecological risk. Therefore, the SR delta soils should be routinely monitored since PAHs may cause adverse effects on soil ecosystems and organisms.

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