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Original article

Polycyclic aromatic hydrocarbons (PAHs) in urban street dust within three land-uses of Babylon governorate, Iraq: Distribution, sources, and health risk assessment

Ruqayah Ali Grmasha[a], Osamah J. Al-sareji[a,*], Jasim M. Salman[b], Khalid S. Hashim[c,d]

[a] Environmental Research and Studies Center, University of Babylon, Al-Hillah, Iraq
[b] Department of Biology, College of Science, University of Babylon, Al-Hillah, Iraq
[c] Department of Environmental Engineering, Faculty of Engineering, University of Babylon, Al-Hillah, Iraq
[d] BEST Research Institute, Liverpool John Moores University, Liverpool, UK

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ABSTRACT

This study is considered to be the first investigation of 16 polycyclic aromatic hydrocarbons (PAHs) in terms of distribution and sources identification for three land-use in Babylon governorate, Iraq. Potential sources of 16 US EPA priority PAHs were identified by employing diagnostic ratio as well as principal component analysis (PCA) method. Additionally, Incremental Lifetime Cancer Risk (ILCR) model was determined in order to assess the risk exposure to the individual PAHs in street dust (SD). Findings in three land-use indicated that the total sixteen PAHs concentrations in the samples were 555.9, 1388, 1221.8 $\mu g\ Kg^{-1}$ for Residential Area, Industrial Area, and Commercial area, respectively, with an average of 1055 $\mu g\ Kg^{-1}$. Moreover, study findings pointed out that the percentages of both LMW and HMW (included MMW) in the street dust were accounted for 38.3% and 61.7% of the total PAHs, respectively. Two components are founded in the PCA with HMW accounted for 75.8% of the total PAHs, and PAHs LMW contributed 24.2% of the total PAHs. Ratios results in nutshell indicated the predominance of pyrogenic source for sixteen PAHs. This suggested by possible sources such as the emission from vehicles, regular gas and fuel combustion activities, as well as coal and wood, were the major cause of 16 principal PAHs in SD samples in all three land-use in Babylon governorate. Results from ILCR model stated that total cancer risk for both targeted individuals exposed to SD in all land-use is more than 10^{-4} that is referred to increase potential health risk. The PAHs contamination in Babylon governorate needs urgently to be addressed on priority. Moreover, this work is beneficial for Babylon governorate to utilize it as a benchmark for future research.

1. Introduction

Street dust (SD) is considered as an indicator of the quality of the urban environment as it represented a mixture of complex pollutants sources including polycyclic aromatic hydrocarbons (PAHs), heavy metals and other gases that result from fuel combustion (Shote et al., 2019; Gritsenko et al., 2019). Rapid urbanization causes population density and increases road improvement, which leads to altering the concentration of PAHs in the dust (Yan et al., 2005). Runoff water on the other side is playing an essential role in transporting street dust along with its pollutant to the receiving waterbody which causes negative impacts on the aquatic ecosystem (Shahir et al., 2020; Giwa et al., 2019; Shote et al., 2019). Furthermore, dust can be spread out in the atmosphere as a result of various activities such as wind, particle resuspension in tire vehicles and deposited on plant leaves, which impact the air quality (Pant and Harrison, 2013).

PAHs are considered one of the ubiquitous classes of anthropogenic organic pollutants (Larsen and Baker, 2003). The U.S. EPA has identified 16 PAHs as priority pollutants that widespread in

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* Corresponding author.

E-mail addresses: ruqayah.grmasha@uobabylon.edu.iq (R.A. Grmasha), eng.osama.jaber@uobabylon.edu.iq (O.J. Al-sareji), jasimsalman@uobabylon.edu.iq (J.M. Salman), K.S.Hashim@ljmu.ac.uk (K.S. Hashim).

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the ecosystem and pose negative impacts on human health (US EPA, 1991). These organic pollutants are carcinogenic to the skin, lungs, as well as the bladder (Boffetta et al., 1997).

Usually, PAHs compounds can be found in the ecosystem as by-products of incomplete combustion of waste, biomass burning as well as fossil fuel. The spills of petroleum-based products are also represented as a source of PAHs (Dong and Lee, 2009). Therefore, depending on the original source of PAHs, they can be categorized as pyrogenic or petrogenic (Franco et al., 2017). PAHs released from petrogenic sources comprise 2 to 3 aromatic rings structure, which refers to low molecular weight (LMW) compounds, while PAHs derived from pyrogenic origin contain dominantly 4 to 6 aromatic rings structure, namely high molecular weight compounds (HMW) (Lorenzi et al., 2011). The carcinogenic toxicity of HMW PAHs compounds is higher than that of LMW compounds (Lu et al., 2008).

There are several studies that pointed out PAHs sources in the urban environment. Franco et al. (2017) stated that atmospheric deposition is the main source of PAHs on the SD. Others reported that the vehicle's exhaust gases are the dominant sources of PAHs as a result of incomplete fuel combustion (Takada et al., 1990). On the other hand, Faure et al. (2000) stated that asphalt is the common source for PAHs.

A study conducted by Liu et al. (2017) investigated a range of factors that influencing the PAHs build-up on the urban roads. The findings of the study indicated that traffic volume was the top influenced factor followed by two factors, which were land-use as well as the roughness of the road surface. However, it was founded that distance to highway street has not shown a significant influence on PAHs build-up on urban roads. Another important finding in this study is heavily traffic volume tended to released more loads of PAHs compounds with higher than 4 ring structures.

In developing counties such as Iraq, heavy traffic densities, commercial activities, burning oils, the absence of environmental regulations as well as wars including repeated internal conflict, have created huge issues associated with contamination of surface dust. Thus, the aim of this work is mainly focused on the determination of PAHs concentration and distribution in three land-use in Babylon governorate. Secondly, the present study will identify the potential PAHs sources in street dust in the governorate. Finally, the research will examine the health risks via exposure to PAHs in multi-pathways such as inhalation, ingestion, and dermal contact. Moreover, this work is useful for the local government to employ it as a benchmark for future work.

2. Experimental procedures

2.1. Babylon governorate

The present work was carried out in Babylon governorate, 100 km south of the capital city of Iraq, Baghdad. It is one of the oldest cities worldwide (Inter-Agency, 2009) with a total population of 2.15 million inhabitants (Iraqi Ministry of Planning, 2016). The governorate located between longitudes (44°2′43″E and 45°12′11″E) and latitudes (32°5′41″N and 33°7′36″N) with the total area of 5315 km^2 (IMMPW, 2009). Moreover, there are five major cities in the governorate which are Al-Musayiab, Al-Mahawil, Al-Hillah, Al-Qasim, and finally Al-Hashimiyah. The average annual wind speed in the investigated area is 7.2 km/h. Additionally, the average annual precipitation in Babylon is 102 mm (Chabuk et al., 2018). The sites in this study with different anthropogenic activities were randomly chosen with considering areas such as industrial, commercial, and residential (included schools). The traffic density in these locations varies, but vehicles with diesel and gasoline engines are dominated.

2.2. Sample collection

Three main land-use, which are industrial, commercial, and residential (included schools) areas in Babylon governorate, were examined for 16 principal PAHs with the total of seventy-two samples. The global positioning system (GPS) was utilized for site locations. Fig. 1 shows the sampling locations. Moreover, coordinates of the sampling locations were illustrated in supplementary materials Table Sl. The sampling procedures occurred during weekdays in September 2019, a summer season in Iraq. In order to collect the fine dust from impenetrable surfaces of paved street, an area of 1 m^2 was swept gently with plastic brushes along with dustpans (Shabbaj et al., 2018). Three samples in each site were taken and mixed as one constitute. Each mixed sample was contained between 12 and 18 g of street dust approximately. A total of 10 brushes were used for each day of sampling to avoid cross contaminations between the sampling sites. To remove impurities, brushes were prewashed with Nitric acid and rinsed with distilled water and then let dried overnight for the next day of sampling. Polyethylene bags with zip-lock were used to store the collected samples after wrapping the bags to remove any air prior to laboratory analysis. Samples were sieved through 1.0 mm mesh stainless steel sieves to remove coarse impurities and debris including hair, leaves, glass, stones, cigarette butts, metal scraps, plastic pieces as well as woods. Samples stored afterword in an ice chest at a temperature of 4 °C. After that, the desiccator was utilized for the samples to remove wetness. Many studies have been stated that PAHs adsorption was commonly founded in finer dust particles rather than the larger once (Franco et al., 2017). The reason for that could be clarified by the largest surface area of fine SD particles allows more PAHs deposition compared with the larger dust particles (Dong and Lee, 2009). In the meantime, the smaller dust particle (<63 μm) can have a negative health impact by adhering to human skin (Saeedi et al., 2012). For the reason explained above, the samples passed through stainless steel sieve with<63 μm mesh and stored in polyethylene bags in a refrigerator prior to analysis. The amount of fine particulate that passed through (<63 μm) mesh stainless steel sieve was around 7 to 10 g in all samples that could be categorized as respirable particulate matters. Thus, 6 g from the fine particulate was taken for analysis after wrapping and labeling with polyethylene bags with taking into consideration reducing the air contents in the bags. The labeled samples were kept in a refrigerator.

2.3. Analysis

First and foremost, the two grams of homogenized fine particulate in SD samples were taken from the 6 g of wrapped polyethylene bags to be analyzed by EPA 3550C method, ultrasonic extraction method (US EPA, 2007). In order to start the process of sample extraction, 5 ml of acetone was added to the sample and then put it in the ultrasonic bath for about 10 min in 25 °C. This step was run three times. After the end of each trial, the acetone was decanted and passed via filter paper (Whatman 41 used for this purpose) to a centrifugal class tube, and the process of extraction proceed for the remaining residues. In addition, samples were subject to a centrifuge for three trials for 15 min. Finally, at the third trial of each sample, the amount of solvent was reduced with the assistance of a rotary evaporator to 0.5 ml at 35 °C.

By employing a gas chromatography-mass spectrometry (GC–MS), 16 US EPA PAHs were detected with both EPA methods SW-846 test method 3550C (US EPA, 2007) as well as 8270D (US EPA, 1998). The carrier gas that used in GC–MS (Agilent 6890 N 5975C mass selective detector, USA) was helium at 1.5 ml.min^{-1} as flow rate with an HP-5MS gas chromatography column, which has the following dimensions (30 m × 0.32 mm × 0.25 μm). The

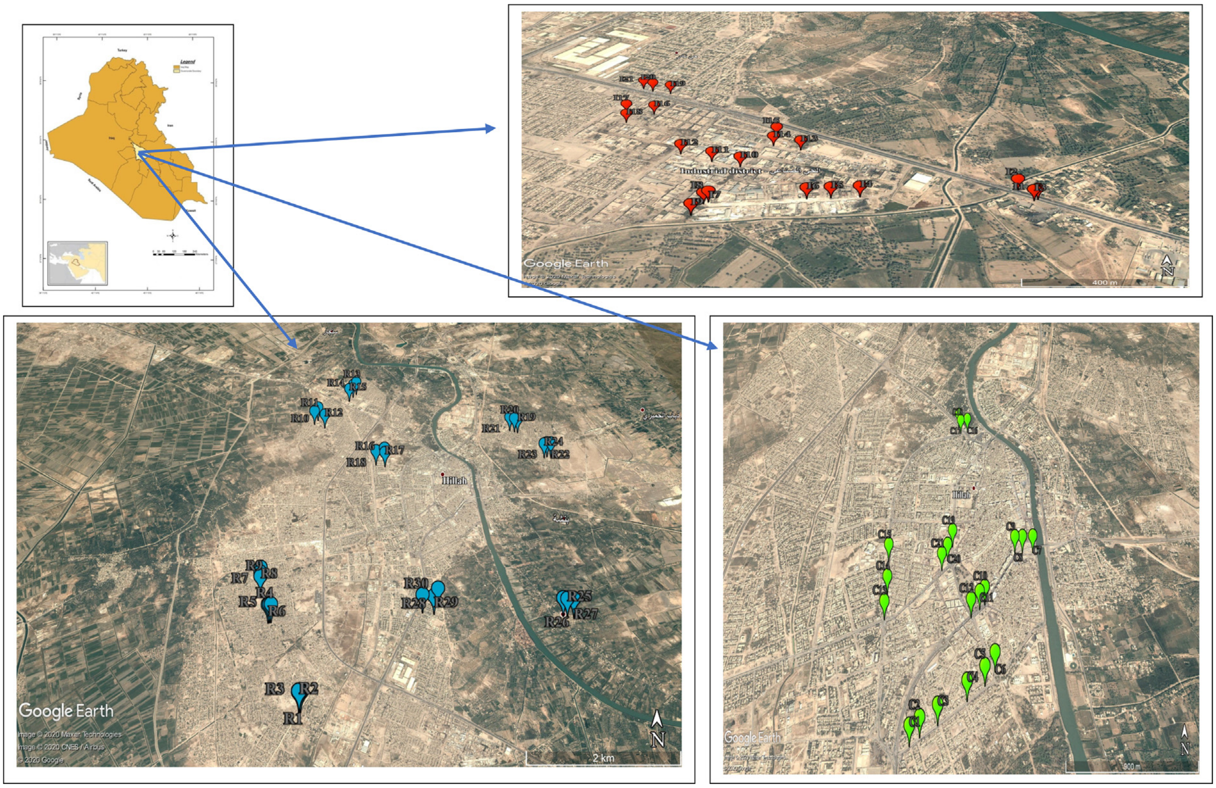

Fig. 1. The locations of the SD sampling in Babylon, Iraq, red, green, blue are industrial, commercial, and residential areas, respectively.

injector temperature was 300 °C. The mode that was run in the analyzing was full scan mode with a mass scan range of 45–600 amu. Oven temperature program was as the following: the initial degree was 100 °C for one min increased to 300 °C at a rate of 8 °C/min and was maintained at 300 °C for 39 min. Blanks and reference samples were measured to maintain accurate precision and accuracy in the experiments. In addition, triplicate runs for each SD sample was accomplished, which in turn made the relative standard deviation of <6%. The comparison of the limit of detection (LOD) with single to noise ratio was observed to be 3:1. That means the GC–MS limits of detection were maintained via diluting the standard mixture solution till single to noise ratio is equal to 3. For determination of each PAHs recoveries, about 100 μL of 1 mg/L standards added into blank sample. The measured 16 principal PAHs average recovery rate was between 92% and 100%. The regression coefficients were more than 0.92 in all PAHs calibration curves.

2.4. Statistical analysis

As reported in the literature on PAHs, different statistical analysis methods for various environmental aspects were utilized (Saeedi et al., 2012). In this work, cluster analysis and principal component analysis (PCA) were employed by using IBM SPSS® (version 25.0) to evaluate PAHs distribution in three land-use in Babylon governorate. Pearson correlation coefficients were carried out to figure out the type of relationships between the measured sixteen principles PAHs.

2.5. Pahs source identification

Diagnostic PAHs ratio method is wildly used for the evaluation of PAHs sources in SD. The following diagnostic PAHs ratios were utilized to identify PAHs sources: BaP/BghiP, BaA(BaA+Chr)$^{-1}$, Flu (Flu+Pyr)$^{-1}$, and Ant(Ant+Phe)$^{-1}$ (Franco et al., 2017; Saeedi et al., 2012).

2.6. Potential health risk assessment

The toxicities of PAHs in the SD samples were determined to depend on the toxic equivalency factor (TEF) (Nisbet and LaGoy, 1992). Among all PAHs, BaP was characterized as a reference chemical in the TEF system because of its high carcinogenic potential and assigned a value of 1 in order to quantify the carcinogenicity of each PAH relative to BaP. Other chemical compounds of PAHs have their own specific TEF values depending on their level of carcinogen when compared to BaP as reported in past literature (Lee and Dong, 2010). TEFs for 16 PAHs are illustrated in Table S3. The toxic benzo[a] pyrene equivalent (BaPeq) content for 16 principles PAHs can be utilized to calculate the carcinogenic potency (Lee and Dong, 2010). In this work, the toxic equivalent quotient (TEQ) of each SD sample was determined by following Eqs. (1) and (2) (Nisbet and LaGoy, 1992).

$$\mathrm{BaPeq_i} = \mathrm{PAH_i} \times \mathrm{TEF_i} \tag{1}$$

$$\mathrm{TEQ} = \sum\nolimits_i^n (\mathrm{PAH_i} \times \mathrm{TEF_i}) \tag{2}$$

where $\mathrm{PAH_i}$ is the concentration of each PAH and $\mathrm{TEF_i}$ stands for toxic equivalency factor.

Another widely used model to quantitatively measure the exposure risk of targeted individuals to SD bound PAHs is the incremental lifetime cancer risk (ILCR), and it is widely utilized in literature (Jiang et al., 2014; Soltani et al., 2015). In this model, three estimated exposure pathways of dermal contact, oral ingestion, and inhalation were taken into consideration in which dust bound PAHs can enter the human body. ILCR determination is mainly dependent on the detection of PAHs contents as BaP equivalent concentration with employing TEF of each PAHs relative to BaP, which is assigned as the reference chemical compound with TEF equal to one. Afterward, total ILCR refers to the summation of three routes of SD uptake, namely, dermal contact, oral ingestion as well as inhalation. If ILCR (unitless) less than $1/10^{6,}$ it is considered negligible, whereas there is a significant concern if the value exceeds $1/10^4$. Moreover, in the case of ILCR values were between $1/10^6$ and $1/10^4$, it is considered potentially carcinogenic to humans. The following equations (Eqs. (3)–(6)) were widely employed to calculate ILCR for the three exposure routes (US EPA, 2011).

$$\mathrm{ILCR_{ingestion}} = \mathrm{CS} \times \mathrm{IR_{ingestion}} \times \mathrm{EF} \times \mathrm{ED} \times \left(\mathrm{CSF_{ingestion}} \times \sqrt[3]{\frac{\mathrm{BW}}{70}}\right) \times \left(\mathrm{BW} \times \mathrm{AT} \times 10^6\right)^{-1} \tag{3}$$

$$\mathrm{ILCR_{inhalation}} = \mathrm{CS} \times \mathrm{IR_{inhalation}} \times \mathrm{EF} \times \mathrm{ED} \times \left(\mathrm{CSF_{inhalation}} \times \sqrt[3]{\frac{\mathrm{BW}}{70}}\right) \times (\mathrm{BW} \times \mathrm{AT} \times \mathrm{PEF})^{-1} \tag{4}$$

$$\mathrm{ILCR_{dermalcontact}} = \mathrm{CS} \times \mathrm{SA} \times \mathrm{AF} \times \mathrm{ABS} \times \mathrm{EF} \times \mathrm{ED} \times \left(\mathrm{CSF_{dermalcontact}} \times \sqrt[3]{\frac{\mathrm{BW}}{70}}\right) \times \left(\mathrm{BW} \times \mathrm{AT} \times 10^6\right)^{-1} \tag{5}$$

$$\mathrm{Carcinogenicrisk} = \mathrm{ILCR_{ingestion}} + \mathrm{ILCR_{dermalcontact}} + \mathrm{ILCR_{inhalation}} \tag{6}$$

where CS is PAHs concentration of SD sample ($\mu g.kg^{-1}$), CSF stands for the carcinogenic slope factor, which measured by the following unit $(mg\ kg^{-1}day^{-1})^{-1}$. The CSF of BaP values as reported by the US EPA are 25, 7.3, and 3.85 $(mg\ kg^{-1}day^{-1})^{-1}$ for the selected routes in this study, which are dermal contact, oral ingestion as well as inhalation respectively (Chen et al., 2013). Table 1 describes other parameters in the ILCR formula.

3. Results and discussion

PAHs concentration level in SD varied significantly worldwide. The 16 PAHs were obtained using GC–MS based on both the PAH characteristic ions as well as the retention time of the standard solution (Peters and Harlin, 1995) as illustrated in Fig. S1. The average concentration of ∑16 PAHs in three types of land-use in Babylon governorate was presented in Table 2 along with a comparison to other cities worldwide. As illustrated in Table 2, the mean ∑16 PAHs in Babylon governorate is higher than ∑16 PAHs mean concentration in Korea (Ulsan), Iran (Bandar, and Abbas), China (Guangzhou) and Serbia (Novi Sad). However, the determined mean of ∑16 PAHs in Babylon governorate was noticed lower than those detected mean of ∑16 PAHs in the USA (Tampa and Orlando), Iran (Bushehr) as well as China (Chang-Zhu-Tan).

Table 2
Sixteen PAHs average concentration (μg/ kg) in urban topsoil from selected cities.

Country (City)	Mean	Inhabitant (million)	References
Iraq (Babylon)	1055	2.15	This Study
Korea (Ulsan)	**960**	1	(Kwon and Choi, 2014)
USA (Tampa)	4562	0.37	(Liu et al., 2019)
USA (Orlando)	3227	0.27	
China (Guangzhou)	**480**	10	(Wang et al., 2011)
China (Chang-Zhu-Tan)	8760	13.1	(Long et al., 2013)
Serbia (Novi Sad)	**363**	0.25	(Škrbić et al., 2017)
Iran (Bandar Abbas)	**362.33**	0.68	(Keshavarzi et al., 2018)
Iran (Bushehr)	1116.02	0.3	(Keshavarzi et al., 2017)

The PAHs findings indicated that the percentages of LMW and HMW (included MMW) in the Babylon street dust were accounted for 38.3% and 61.7% of the total average, respectively. As presented in Fig. 2, that showed the ring profile of PAHs in SD in Babylon governorate, the largest percentage of HMW (included MMW) in the selected land-use were in industrial, commercial, and then a residential area with 71.6%, 57.9%, and 44.9% respectively. On the other hand, PAHs compounds with LMW were observed to be higher in the residential area, followed by the commercial and industrial areas with a percentage of 55.1%, 42.1%, and 28.1%, respectively.

The major contamination was in the industrial area, followed by commercial and residential areas. In light of this, street dust composition in Babylon was dominated by HMW PAHs where these compounds are derived from various combustion processes that indicated vehicular emissions.

3.1. PAHs geographical distribution

The average concentrations of PAHs in the three types of land-use presented in Table 3. In addition, PAHs full names can be found in Fig. S1. As illustrated in Table 3, the average concentration of the sixteen priority PAHs in the areas is 1055 $\mu g\ kg^{-1}$. The average concentration of the sixteen PAHs for residential land-use was 555.9 $\mu g\ kg^{-1}$ which was the lowest value followed by commercial and industrial areas with the amount of 1221.8 μgkg^{-1} and 1388 μgkg^{-1} respectively. Several factors affect the geographical distribution of PAHs concentration in SD in different land-use (Franco et al., 2017). In fact, the highest concentration of 16 PAHs in the industrial points sample in this study can be mainly explained by the repeated oil combustion and spills in addition to heavy traffic density that this area exposure repeatedly every day. The commercial area also noticed to have high 16 PAHs concentration, which increased by many factors such as insignificant air dispersion, low wind speed due to buildings as well as narrow streets. However, the lower values

Table 1
Parameters descriptions used for ILCR model.

Parameter	Description	Unit	Adults	Children	References
ABS	Dermal-Absorption-Factor	unitless	0.13	0.13	(US EPA, 2011)
AF	Dermal-Adherence-Factor	mg/cm^2	0.07	0.2	(US EPA, 2011)
AT	Average-Time (70years_365 days/year)	Days	25,550	25,550	(Soltani et al., 2015)
BW	Body-Weight	Kg	70	15	(US EPA, 2014)
ED	Exposure-Duration	Years	20	6	(US EPA, 2014)
EF	Exposure-Frequency	days/year	350	350	(US EPA, 2014)
IR ingestion	Ingestion-Rate	mg/day	100	200	(US EPA, 2011)
IR inhalation	Inhalation-Rate	m^3/day	20	10	(Soltani et al., 2015)
PEF	Particular-Emission-Factor	m^3/kg	1.36×10^9	1.36×10^9	(US EPA, 2014)
SA	Dermal-Surface-Area-Exposure	cm^2	5700	2800	(US EPA, 2014)

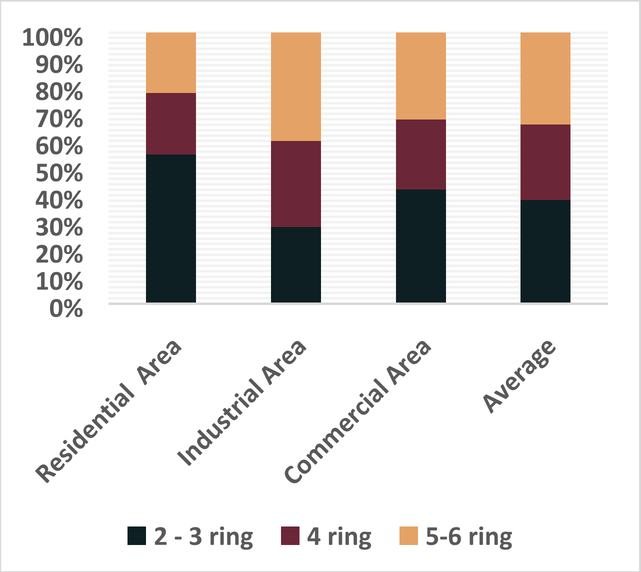

Fig. 2. PAHs ring profiles in SD for three areas in Babylon.

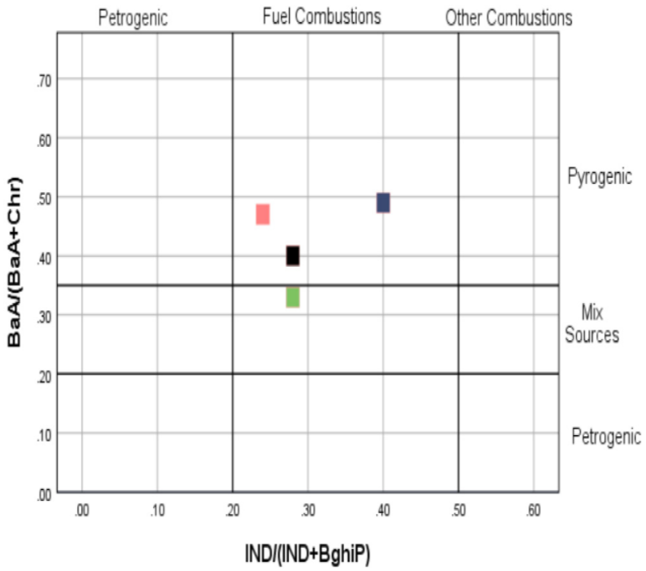

Fig. 3. Diagnostic ratios IND(IND+BghiP)$^{-1}$ versus BaA(BaA+Chr)$^{-1}$ where pink (commercial), black (average), green (industrial), blue (residential).

of 16 PAHs in the residential land was due to low traffic density as well as lower oil and coal combustion in the point samples.

3.2. Diagnostic ratio

Several ratios have been extensively employed in literature as markers to identify various apportionment source categories of 16 PAHs in many environmental compartments (Najmeddin and Keshavarzi, 2018; Ravindra et al., 2008; Saeedi et al., 2012). In IND(IND+BghiP)$^{-1}$ ratio, the value of 0.2–0.5 represents petroleum and petrogenic source (Zhang et al., 2006) and petrogenic origin according to Yunker et al. (2002). The analysed data from this ratio indicated that all the land-use belong petroleum and petrogenic source. Regarding BaA(BaA+Chr)$^{-1}$ ratio, SD samples up to 0.2 indicate petrogenic sources, whereas those higher than 0.35 represent pyrogenic sources. Moreover, those between the range of 0.2 to 0.35 referred as mixed of both petrogenic as well as pyrogenic sources (Yunker et al. 2002). Hence, all the land-use lie in the pyrogenic sources with value more than 0.35 except the industrial area that lies in mixed petrogenic-pyrogenic sources (about 0.33). A scatter plot between IND(IND+BghiP)$^{-1}$ and BaA(BaA+Chr)$^{-1}$ in Fig. 3 showed that the land-use lie in the pyrogenic and mixed sources zones where commercial (pink), residential (blue), and average (Balck) fall into pyrogenic and the industrial (green) located in the mixed zone.

For pollution level identification for PAHs in a Babylon governorate, other ratios were employed, as illustrated in Table 4. If the ratio of (LMW/HMW) is <1, this represents pyrogenic sources, which include the incomplete combustion of fossil fuels as well as biomass. However, the ratio of (LMW/HMW) with more than 1 represents petrogenic sources, which included different examples such as spilled oil or other petroleum products. By applying the ratio of (LMW/HMW), the majority of land-use indicate the pyrogenic sources, which considered the main path of PAH pollutions in Babylon governorate. However, the industrial land-use record more than 1, which illustrates petrogenic sources.

Another widely employed ratio to identify the source of PAHs is Flu(Flu+Py)$^{-1}$. The majority of the land-use have Flu(Flu+Py)$^{-1}$ value with <0.5, which indicates that PAHs originate from gasoline combustion. However, the industrial area has a value (0.57) with more than 0.5, which clearly illustrated that PAHs compounds were mainly from diesel combustion. Moreover, by applying the BaP/BghiP ratio, it can be found that all the land-use are more than

Table 3
The average concentrations of 16 PAHs in Babylon, Iraq in three land-use: Residential, Industrial, Commercial areas, respectively.

PAH abbreviation	Residential area	Industrial area	Commercial area	Average
Nap	13	15	15	14
Acy	15	6	3	8
Ace	98	202	264	188
Fl	84	68	95	82
Phe	58	67	89.8	72
Ant	38	36	47	40
Flu	41	96	83	73
Pyr	30.5	128	89	83
BaA	27	72	68	56
Chr	27.9	143	77	83
BbF	12	117	65	65
BkF	26	95	69	63
BaP	32	138	114	95
DBA	11	21	24	19
BghiP	25.5	132	90	83
IND	17	52	29	33
Summation	555.9	1388	1221.8	1055

Table 4
PAHs ratios in Babylon governorate.

PAH ratio	Land-use type	Value	Value range (source)	References
LMW/HMW	Res.[*]	1.22	<1(Pyrogenic)	(Zhang et al., 2008)
	Ind.[**]	0.40	>1 (Petrogenic)	
	Com. [***]	0.73		
	Av. [****]	0.62		
BaP/BghiP	Res.	1.25	<0.6 (Non-traffic)	(Katsoyiannis et al., 2007)
	Ind.	1.05	>0.6 (Traffic)	
	Com.	1.27		
	Av.	1.15		
IND/BghiP	Res.	0.67	<0.4 (Gasoline)	(Caricchia et al., 1999)
	Ind.	0.39	~1 (Diesel)	
	Com.	0.32		
	Av.	0.4		
Pyr/BaP	Res.	0.95	~10 (Diesel)	(Ravindra et al., 2008)
	Ind.	0.93	~1 (Gasoline)	
	Com.	0.78		
	Av.	0.87		
Flu/(Flu+Py)	Res.	0.57	>0.5 (Diesel)	(Ravindra et al., 2008)
	Ind.	0.43	<0.5 (Gasoline)	
	Com.	0.48		
	Av.	0.47		
IND/(IND+BghiP)	Res.	0.40	< 0.2 (Petroleum and petrogenic)	(Zhang et al., 2006)
	Ind.	0.28	>0.2 – <0.5 (Petrogenic source and petroleum)	
	Com.	0.24	>0.5 (Grass, coal, and wood)	
	Av.	0.28		

[*] Res. = Residential
[****] Ind. = Industrial
[***] Com. = Commercial
[****] Av. = Average

0.6, with an average of 1.15, which indicated the traffic emissions (Katsoyiannis et al., 2007). Caricchia et al. (1999) conducted a study to classify the level of IND/BghiP. Taking into consideration applying the study results into the suggested classifications, most of the land-use are lie around gasoline dominant source while the residential area indicates diesel emission sources.

Ravindra et al. (2008) set up a value of 1 for Pyr/BaP ratio to indicate gasoline combustion for PAHs compounds and a value of 10 to represent diesel combustion. Hince applying the ratio of (Pyr/ BaP) for the obtained results, all land-use fall within a value around 10, which indicates diesel combustion is the main source for PAHs in Babylon.

Overall ratios results indicated the predominance of pyrogenic source in the sixteen PAHs generation in Babylon governorate. This can be explained by several possible sources that can be observed on the lands, which are emission from heavy traffic load, gas and fuel combustion, as well as coal and wood.

The relationships between the 16 PAHs in this study were identified by applying Pearson's correlation coefficients by utilizing SPSS software version (25.0). Table S2 illustrates the results of Pearson's correlation coefficient analysis. From the correlation coefficients matrix, it clearly noticed that a very high positive correlation between 4 rings PAHs with each other ($r > 0.8$, $p < 0.001$). In addition to 4 rings PAHs, there is a high correlation between 5 and 6 rings PAHs individuals, including BbF, BkF, BaP, DBA, BghiP, and IND with r more than 0.6 and $p < 0.001$. Furthermore, the correlation coefficients between both 4 ring PAHs and (5–6) rings PAHs were clearly founded to be highly positive with r more than 0.6 and $p < 0.001$. It is also noticed from the findings that there were very strong relationships between PAHs compounds with more than 4 aromatic ring structure and Nap. Additionally, Nap and Ace have indicated a presence of high correlation with r equal to 0.92 and $p < 0.001$. Moreover, Ace was highly correlated with DBA, BaA, Phe, Flu, Pyr, BkF, BaP, and BghiP ($r > 0.7$, $p < 0.001$). Phe observed to has a positive correlation coefficient with both Ant and DBA. Both Fl and Ant had a positive correlation. However, Acy showed negative with other investigated PAHs.

Overall results indicated that there would be similar sources for individuals of PAHs that own more than 4 ring structure. Nap and Ace might originate from a common source. The finding also indicated that Fl and Ant might be generated from the same source. Finally, Phe has also had a highly positive correlation with Ant and DBA, which may have common sources.

3.3. 3.3.Cluster analysis

This was performed in SPSS software version 25 by employing a between-groups linkage cluster method as it represented in the

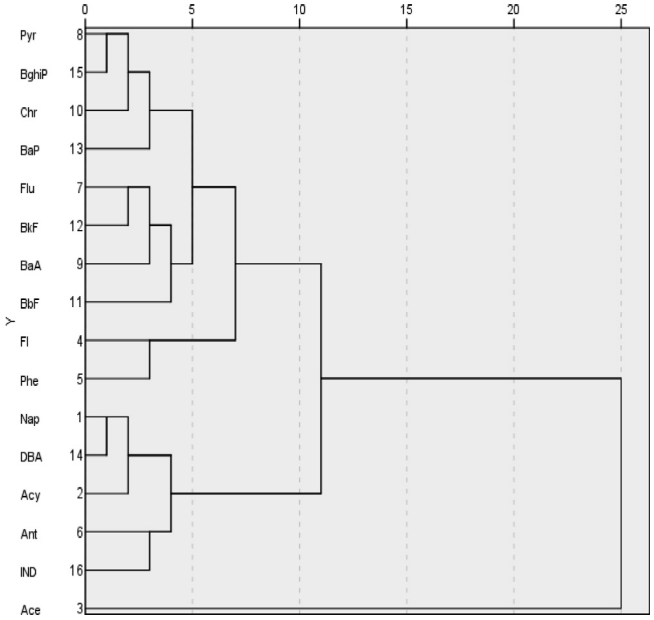

Fig. 4. Dendogram resulting from cluster analysis of PAHs concentration in Babylon.

dendrogram in Fig. 4. It can be divided into four clusters in terms of distances. The first cluster is considering the lager one, which included Pyr, BghiP, Chr, BaP, Flu, BkF, BaA, and BbF. The first cluster, which included HMW PAHs, is considered as a marker of vehicle emissions (Larsen and Baker, 2003; Kwon and Choi, 2014). BghiP in the first cluster is typically derived from vehicles run by gasoline (Larsen and Baker, 2003).

The literature on PAHs stated that both BbF, as well as BkF are considered as markers for the usage of Diesel-powered vehicles (Larsen and Baker, 2003). The second cluster is moderately associated with cluster 1 involved Fl and Phe. The third cluster contained Nap, DBA, Acy, Ant and IND. This assumed to be mixed sourced between LMW PAHs, which emitted from purified oil products as well as petroleum and its products (Jiang et al., 2014) and HMW PAHs, which come from vehicles emissions. The last cluster, which is the smallest one, includes just Ace as LMW PAHs, suggesting incomplete combustion.

3.4. 3.4.Principal component analysis (PCA)

In order to determine the relationships between the sixteen PAHs compounds, PCA was conducted for this purpose. PCA can reduce the number of variables and presented into main components. In this statistical method, Varimax rotation with Kaiser normalization was chosen to represent the 16 PAHs data, and eigenvalues are retained when it is equal and more than one to extract the factors. Table 5 illustrated PCA of 16 PAHs in street dust. Babylon, Iraq. The component plot resulted from PCA analysis presented in Fig. S2.

The first component in PCA represented 75.8% of the total variance. This component was highly loaded on medium, and HMW PAHs, which are mainly originated from fuel combustion, and they are difficult to evaporate and degraded (Liu et al., 2007). It can be noticed that both Pyr and Chr are presented in these components, which are evidence that these chemical compounds are originated from petroleum burning. In fact, burning fossil fuels can lead to forming a large number of Pyr, BaP, BbF, and BkF that are founded in the first component (Rajput and Lakhani, 2009; Hwang et al., 2003). It is suggesting that the primary component emissions from traffic sources as it is well known that IND, BghiP, BaP, Flu, and Pyr are markers for vehicle emissions (Keshavarzi et al., 2017).

Table 5
Rotated Component Matrix of 16 PAHs in Babylon, Iraq.

PAHs	Component	
	1	2
Nap	**0.873**	0.487
Acy	−0.731	−0.683
Ace	0.631	0.775
Fl	−0.577	0.817
Phe	0.289	**0.957**
Ant	−0.156	**0.988**
Flu	**0.961**	0.277
Pyr	**0.995**	0.100
BaA	**0.910**	0.415
Chr	**0.995**	−0.099
BbF	**1.000**	−0.009
BkF	**0.992**	0.126
BaP	**0.958**	0.287
DBA	**0.745**	**0.668**
BghiP	**0.994**	0.106
IND	**0.981**	−0.193
Total Variance	75.8	24.2

The second component comprises 24.2% of the total variance that was containing LMW PAHs that have the ability to evaporate and degraded easily. These compounds derived mostly from petroleum spills such as crankcase oil, crude, and fuel oil that have the ability to evaporate and degraded easily (Liu et al., 2009; Liu et al, 2007). Changing engine oil along roadsides along with fuel filling for vehicles is seen regularly every day in Babylon governorate, which is the major cause of oil spillage. Scree Plot was illustrated in Fig. S3.

3.5. 3.5.Health risk assessment

Distinguishing the carcinogenic risk of sixteen PAHs compounds and the total PAHs in SD of Babylon was determined by employing Benzo[a]pyrene total potency equivalency (BaP TPE). The BaP TPE findings presented in Table S3 where it showed that residential, Industrial, and Commercial have values of 52.45, 196.29 and 163.88 ng g^{-1}, respectively. The summation of carcinogenic PAHs in terms of BaP TPE was found to be dangerous in street dust of Babylon as they composed more than 98% of the total investigated PAHs in selected lands, including the average. This high level of PAHs carcinogenicity in SD of Babylon can be explained by heavy traffic emissions near the sample sites. From Table S3, it can be noticed the predominance of the following PAHs compounds: BaA, BbF, BkF, BaP, DBA, and IND in the Babylon SD. Thus, these carcinogenic PAHs need to be urgently monitored by the local government with immediately applying contamination mitigation plans to reduce the possibility of cancer between individuals who regularly exposure to PAHs in Babylon street dust.

US EPA proposed ILCR model to determine cancer risk exposure to PAHs through multi-routes, which are ingestion, dermal as well as inhalation (US EPA, 2011) that are illustrated in Table 6. In general, total cancer risk in all land use for the three exposure routes observed a higher level for children when compared with adults, but it is not noticeable. Moreover, the highest total cancer risk was founded in the industrial, followed by both commercial and residential areas. The residential area has the lowest cancer risk, which is also reported in other literature (Gope et al., 2018).

Table 6 showed that the calculated ILCR for the selected three land-use by considering the three exposure pathways, ingestion, dermal, as well as inhalation. The findings revealed that the cancer risk for both targeted individuals in all lands is more than 10^{-4} that possesses a negative impact on the public health (Liao and Chiang, 2006). Thus, the local government should regularly monitor the

Table 6
ILCR for 16 principal PAHs exposure cancer risk in Babylon street dust.

Land-use type	Adult					Children				
	CS	ILCR				CS	ILCR			
		Ingestion route	Dermal route	Inhalation route	Cancer risk		Ingestion route	Dermal route	Inhalation route	Cancer risk
Commercial	163.88	4.682E−04	8.317E−04	3.632E−08	1.300E−03	163.88	7.845E−04	9.779E−04	1.521E−08	1.762E−03
Residential	52.45	1.498E−04	2.662E−04	1.162E−08	4.160E−04	52.45	2.511E−04	3.130E−04	4.867E−09	5.641E−04
Industrial	196.29	5.608E−04	9.962E−04	4.350E−08	1.557E−03	196.29	9.396E−04	1.171E−03	1.822E−08	2.111E−03
Average	137.54	3.930E−04	6.980E−04	3.048E−08	1.091E−03	137.54	6.584E−04	8.207E−04	1.276E−08	1.479E−03

PAHs concentration with emphasizing on applying pollution mitigation plans. Fig. S4 shows the 95% confidence interval for children and adults.

4. Conclusion

This study reports distribution, sources, and health risk assessment of 16 PAHs for 72 SD samples in three land-use in Babylon governorate, Iraq. The total PAHs in SD were 555.9, 1388, 1221.8 μg/Kg for Residential area, Industrial area, and Commercial area, respectively, with an average of 1055 μg/Kg. The findings revealed that the percentages of LMW and HMW (included MMW) in the street dust were accounted for 38.3% and 61.7% of the total PAHs, respectively. The major source of 16 PAHs in the three land-use is pyrogenic, mainly traffic emission. Furthermore, individuals total cancer risk exposed to SD is more than 10^{-4}, which is indicating negative health impacts on adults and children. The presented data could be a vital baseline for future monitoring and research. This work shows that the level of PAHs pollution needs immediate

mitigations plan from the local government of Babylon.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jksues.2020.11.002.

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