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Source identification of total petroleum hydrocarbons and polycyclic aromatic hydrocarbons in PM$_{10}$ and street dust of a hot spot for petrochemical production: Asaluyeh County, Iran

Sajjad Abbasi, Behnam Keshavarzi*

Department of Earth Sciences, College of Sciences, Shiraz University, Shiraz, 71454, Iran

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ABSTRACT

Total petroleum hydrocarbons (TPH) and polycyclic aromatic hydrocarbons (PAHs) are important pollutants that affect public health in urban areas, especially in developing and oil-rich countries such as Iran. This assesses the relationship between TPH and PAHs in street dust and suspended dust, and investigates toxicity level in the urban environment of the most important petrochemical center in Iran. For this purpose, 21 and 48 street dust samples were collected for TPH analysis and PAH analysis, respectively, in Asaluyeh County. Moreover, seven air dust samples were taken for PAH analysis. TPH concentrations ranged between 240 and 4400 mg kg$^{-1}$, with a mean of 1371.43 mg kg$^{-1}$. The maximum $\sum$PAH concentration (6016.3 mg kg$^{-1}$) was detected in a petrochemical complex while the minimum $\sum$PAHs content (16.93 mg kg$^{-1}$) was measured in an urban area. The mean concentrations of total PAHs in street dust particles were 491.35 mg kg$^{-1}$ in summer and 304.04 mg kg$^{-1}$ in winter. The results indicated that PAH concentration in summer was higher. PAH sources were identified using both PAHs ratios and robust statistical methods such as Generalized Estimating Equations (GEE), backward GEE, logistic regression, principal components analysis (PCA) in conjunction with multiple linear regression (MLR) and positive matrix factorization (PMF). The results showed that PAH species generally originate from pyrogenic sources and about 0.08% of TPH was typically PAHs. However, petrogenic sources of PAHs in the industrial areas were 11.2 times more abundant than in urban areas. Also, backward GEE model demonstrated that TPH is more influenced by HMW PAHs, particularly indene. Estimated incremental lifetime cancer risk (ILCR) was higher than 10$^{-4}$, showing that Asaluyeh inhabitants (especially children and indoor workers) are probably exposed to cancer risk, particularly through dermal contact and dust ingestion.

1. Introduction

Urban design and geographic location are two important factors in amplifying effects of environmental contaminants. Over the last few decades, several studies were carried out to link urban quality with urban design. For instance, Nikolopulou et al. (2004) investigated microclimate in multiple open urban spaces. Based on air ventilation assessment, the development of urban planning guidelines was considered by Ng (2009). Oke (1988) also investigated optimum street canyon characteristics according to diverse climate-related criteria in urban regions and demonstrated a number of useful relationships between the geometry and the microclimate of urban street canyons. Previous studies are potentially helpful in establishing guidelines governing street dimensions to be used by urban designers. On the other hand, rapid urbanization, population growth and consequent accumulation of contaminants pose major challenges for people and planners. For more explanation, in 2003, Hong Kong was hit by severe acute respiratory syndrome, which led to numerous fatalities. Thus, a number of focused studies were conducted with a recommendation being utilization of air ventilation systems (Ng, 2009).

Asaluyeh County is the most important industrial center in Iran. The county is limited to the Persian Gulf in the south and a mountain range in the north (Abbasi, Keshavarzi, Moore, & Mahmoudi, 2018; Abbasi, Keshavarzi, Moore, Turner et al., 2019). The northern barrier prevents the southwest-northeast wind current to disperse the pollution load and hence resulting in increasing the air pollution potential. Thus, it is important to select appropriate methods to investigate contaminants and their effects on human health. Accelerated urban and industrial development and a huge petrochemical complex are already reported to be responsible for the high level of pollutants in Asaluyeh port (Alahverdi & Savabieasfahani, 2012).

* Corresponding author.
E-mail address: bkeshavarzi@shirazu.ac.ir (B. Keshavarzi).

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Generally, atmospheric pollution is a primary concern in urban areas with particulate matter (PM) leading to the most deaths globally among environmental threats (WHO, 2006). PM10 is capable of reaching conductive tracheobronchial airways through inhalation (Harrison & Yin, 2000). On the other hand, street dust serves as both source and sink for atmospheric PM. Street dust is generated from soil, cement, sea salt (Zhai, Feng, Zhu, & Jianhui, 2006), evaporation of vehicle fuel (Duffy, Nelson, Ye, & Weeks, 1999), direct emission from vehicle exhaust (Maićić, 2007), pieces of rubbers (Abbasi et al., 2017; Abbasi, Keshavarzi, Moore, Turner et al., 2019), abrasion of the street surface and the resuspension of accumulated dust on streets (Thorpe & Harrison, 2008). Street dust thus serves as an indicator of urban life quality and reflects contamination of different environments like soil, water and air (Wong, Li, & Thornton, 2006).

TPH is a term used to describe a wide family of chemical compounds that originally derive from crude oil (Todd, Chessin, & Colman, 1999). When TPH is adsorbed by street dust, rainfall can wash TPH and transfer it to surface water. However, there are risks for shallow aquifers, which may be used for private wells for drinking water purposes (Amadi, Abbey, & Nma, 1996; Albers, 1995; Todd et al., 1999). Also, different TPH compounds may be separated from the original mixture (depending on the chemical properties), evaporated, dissolved into the groundwater or attached to soil particles. Hence, human can be exposed to these compounds through respiration, ingestion and dermal pathways (Todd et al., 1999). TPH provides an estimate of the concentration of higher molecular weight hydrocarbons, while PAHs provide an estimate of more toxic oil components (Wade et al., 2011).

PAHs are a great concern as some carcinogenic species (Chrysuite, Gemenetzis, & Samaa, 2009) are always present in the soil, air, and sediments (Giaccalone, Gianguzza, Mannino, Orecchio, & Piazzese, 2004). PAHs are introduced into the environment by both anthropogenic sources and/or natural processes (Junker et al., 2000). Anthropic sources are divided into petrogenic and pyrogenic ones. Pyrogenic PAHs often originate from incomplete combustion of fossil fuels, biomass and municipal wastes (Yunker et al., 2002). Petrogenic PAHs are spills of petroleum-derived products and the diagenesis of organic matter in anoxic environment (Lima, Farrington, & Reddy, 2005).

In general, 2- and 3-ring PAH compounds are more volatile (molecular weight: 128–178; Kow: 3.3–4.5; Koc: 3.11–4.42) (Cui et al., 2016; Guo et al., 2009; Liu, Liu, Chen, Wang, & Cao, 2013) and mostly occur in the gas phase of the atmosphere and can deposit on the surface of particles via wet deposition, while less volatile i.e., 5–6 ring PAHs (molecular weight: 202–276; Kow: 5.18–7.1; Koc: 4.64–6.8) (Cui et al., 2016; Guo et al., 2009; Liu et al., 2013) mostly tend to deposit on the surfaces of particles via wet and dry deposition (Mannino & Orecchio, 2008). Among the hazardous contaminants, PAHs are serious because of their mutagenicity and carcinogenicity (National Research Council (NRC), 1983). Street dust contaminated with PAHs indicates a higher health risk to children (Keshavarzi, Sajjad Abbasi, Moore, Delshab, & Soltani, 2017; Krugly et al., 2014).

As already mentioned, PAH species have different characteristics and several factors, including temperature and humidity, affect their concentration. In order to identify sources, robust statistical methods such as Generalized Estimating Equations (GEE), backward GEE, logistic regression and Positive Matrix Factorization (PMF) models must be employed. Each method offers particular advantages that depend on the nature of data and the desired research focus (Hu, Goldberg, Hedeker, Flay, & Pentz, 1998). The reasons for selecting these statistical methods in the current study are given in Section 2.3.1.

The specific objectives of this study are to: (1) measure the concentrations of PAHs and TPH in street dust of urban and industrial areas in the winter and summer; (2) measure the concentrations of PAHs in the PM10 fraction of street dust samples in urban and industrial areas; (3) identify various sources of PAHs by GEE, backward GEE, logistic regression, PMF, diagnostic ratios and principal components analysis (PCA) in conjunction with multiple linear regression (MLR); (4) determine how TPH concentration is affected by different members of PAHs; and (5) evaluate human exposure risk to PAHs in the Asaluyeh street dust considering different scenarios.

2. Material and methods

2.1. Study area

Iran is located in the mid-latitudinal belt of arid and semiarid regions. Asaluyeh County is located in Bushehr province, south Iran (Fig. 1). Average annual temperature and rainfall in Asaluyeh are 25.9 °C and 35 mm, respectively. Asaluyeh is the biggest gas field in the world shared by Iran and Qatar. It contains 51,000 km³ gas in place and 56 billion barrels (8.9 × 10¹⁷ m³) condensate in place on both sides. The Iranian side accounts for 10% of the world’s and 60% of Iran's total gas reserves. Many petrochemical plants, gas powerhouses and semi-heavy industries are active in Asaluyeh. Related industries include electrical and electronic industries, instrumentation industries and chemical industries. A population of about 73,958 inhabitants live in Asaluyeh.

2.2. Sampling and analyses

Before sampling, amber glass containers were first washed with soapy water, and then with distilled water, n-hexane, and finally dried at 180 °C for 3 h in an oven. Furthermore, for more certainty, screw aluminium foil caps were used to provide a gas-tight seal. Then, 48 and 21 street dust samples, each representing an area of 5-10 m², were collected from the surface of different streets for PAHs and TPH analyses, respectively (Fig. 1, Table S1). Regarding PAH samples, 43 and 5 street dust samples were collected in summer and winter, respectively. Approximately 100 g of dust samples were collected in each site and passed through a 2-mm sieve and transferred to an ice chest, immediately. The gathered samples were rapidly transported to the laboratory of the Isfahan University of Technology.

Two sampling stations were considered for (re-)suspended dust: (i) the first four days in an industrial area within the PSEEZ (R1), and (ii) the second three days in an urban area (R2) (Fig. 1 and Table S1). In each station two samplers were used, one for PAHs analysis and the other for PM concentration. Samples of particulate matter (PM) were collected using an ECHO PM ambient filter sampler (TECORA, Italy) during almost ten successive days (seven samples) at both sites on PTFE filter papers (2 μm pore size and 46.2 mm diameter; Tisch Scientific, USA). To avoid local disturbance from, for example, automobiles, the sampler was set up at a height of 3–4 m, and in accordance with United States Environmental Protection Agency (USEPA) reference methods for PM10 the sampling flow rate was set at 16.67 L min⁻¹ (EPA, 2006). After 24 h, the filters were transferred to plastic petri dishes already washed with deionized water and covered with Al sheet and finally stored at 4 °C until being transported to the laboratory for PAHs extraction.

For the determination of PM10 PAHs, filter extracts were analyzed according to the USEPA method TO 13 A (USEPA, 1999). PM10 filters were extracted in Soxhlet with 125 mL of dichloromethane (CH2Cl2) for 18 h (USEPA, 1999). Then, for eliminating possible interferences, the extracts were separated/pre-concentrated through the cleanup procedure using a silica gel column (activated with 5% of distilled H2O) (Teixeira, Matteuzzi, Agudelo-Castañeda, de Oliveira Garcia, & Wiegand, 2013). The cleanup was accomplished for each sample with four solvent fractions with different polarities: first fraction: 20 mL of hexane (aliphatic); second fraction: 10 mL of hexane, 10 mL of dichloromethane; third fraction: 15 mL of hexane, 5 mL of dichloromethane; and fourth fraction: 20 mL of dichloromethane. Rotary evaporation followed by a mild stream of pure nitrogen gas was conducted for concentrating volumes for fractions 2 and 3. Finally, 1 mL of dichloromethane was added for subsequent analysis.
For PAH analysis of street dust, approximately 5 g of each dried sample was spiked with surrogate standards (Pyrene-D10, lot: 10,510 semi-volatile internal standards), and an ultrasonic bath (KUDOS, SK3210LHC model) was used during the extraction. Pyr-D10 was used as internal standard for the calibration of all species of PAHs. The samples were then extracted using a 30-mL mixture of organic solvents (n-hexane and dichloromethane [DCM] in a 1:1 v/v) for 30 min at room temperature. Amorphous sodium sulfate is added to the solution and then 2 mL of dried extracts were taken for the next step. A silica gel column was used to clean up the extract similar to PM10 samples. The samples were analyzed, for PAHs, following the EPA 3550B (extraction), EPA 3630C (clean up), and EPA 8310 (determination) procedures, and EPA 418 for TPH.

The samples were analyzed for PAHs using a Hewlett-Packard (HP) 1090 high-performance liquid chromatography (HPLC) system equipped with a HP-1046 fluorescence detector. Considering the recommendation by the International Agency for Research on Cancer (IARC), the sixteen most hazardous PAHs were measured, including Naphthalene (Nap), Acenaphthene (Ace), Acenaphthylene(Ac), Fluorine (Fl), Phenanthrene (Phe), Anthracene (Ant), Fluoranthene (Flu), Pyrene (Pyr), Benzo[a]anthracene (BaA), Chrysene (Chr), Benzo[b]fluoranthene (BbF), Benzo[k]fluoranthene (BkF), Benzo[a]pyrene (BaP), Benzo[e]pyrene (BeP), Dibenzo[a,h]anthracene (DbahA), Benzo[g,h,i]perylene (BghiP), Indene (Ind). The extracts were concentrated to 1 ml by a rotary vacuum evaporator. 20 μl of each extract was used for PAHs analysis. The mobile phase was acetonitrile/water in gradient mode at a flow rate of 1 ml/min and the temperature was set at 35 °C. Generally, average recoveries for PAHs and TPH in dust were approximately 88–95% for all 16 measured PAHs and TPH. The detection limit (DL) of PAHs for dust ranged from 0.05 to 0.4 μg/kg and precision was 4–8%. Reagent blanks, analytical duplicates/replicates, and analysis of the standard reference material (Dr. Ehrenstorfer GmbH Alkanes-Mix 10, and Sigma-Aldrich Co. LLC EPA 525 PAH Mix A and EPA 525 PAH Mix B) were processed.

Fig. 1. Street dust collection sites: red points indicate samples collected in summer, green points signify samples collected in winter and yellow stars are air dust stations.
2.3. Statistical analyses

EPA’s Positive Matrix Factorization (PMF) Model is a mathematical receptor model that provides scientific support for the development and review of environmental contaminations such as PAHs. The current study employed EPA PMF v5.0.14.

Generally, the descriptive statistics, PCA-MLR, GEE, backward GEE and logistic regression were done using SPSS version 19.0 software. PCA-MLR is a statistical procedure that uses an orthogonal transformation to convert a set of observations of possibly correlated variables (entities of which take on various numerical values) into a set of values of linearly uncorrelated variables called principal components. Also, MLR was used to quantify source contributions to samples based on pollutants. The primary function of PCA was a reduction in the number of variables while retaining as much as possible of the original information; therefore, variables with similar characteristics were grouped into factors (Fang et al., 2004). When PCA was performed with Varimax normalized rotation, each principal component score contained information on all PAHs combined into a single number, while the loadings indicated the relative contribution for PAHs species made to that score (Kong et al., 2012; Yongming, Peixuan, Junji, & Posmentier, 2006).

Regarding the GEE and backward GEE, the variables in this research were the response (dependent) variable. Also, the variables (PAH species) , and their interaction effects were continuous predictor (independent) variables. For example, if we have five variable, such as A, B, C, D and E, the general equation of GEE is as in Eq. (1).

\[
\hat{F}_i = \hat{\beta}_0 + \hat{\beta}_A A_i + \hat{\beta}_B B_i + \hat{\beta}_C C_i + \hat{\beta}_D D_i + \hat{\beta}_E E_i + \hat{\beta}_{AB} A_i B_i + \hat{\beta}_{AC} A_i C_i + \hat{\beta}_{AD} A_i D_i + \hat{\beta}_{AE} A_i E_i + \hat{\beta}_{BC} B_i C_i + \hat{\beta}_{BD} B_i D_i + \hat{\beta}_{BE} B_i E_i + \hat{\beta}_{CD} C_i D_i + \hat{\beta}_{CE} C_i E_i + \hat{\beta}_{DE} D_i E_i + \epsilon_i,
\]

where \( \hat{\beta} \)'s are model parameters (coefficients) and \( \epsilon \) is the random component of the model, which follows a random distribution with a mean value of 0.

As can be seen in Eq. (1), this model contains the main effects and all 2-way interaction effects of the predictors A, B, C, D, and E. However, wherever the effects were not significant (Sig > 0.05), backward GEE and GEE were used to remove ineffective parameters. The final model had maximum accuracy.

Logistic regression analysis was carried out to compare petrogenic and pyrogenic sources of PAHs in industrial and urban areas. All statistical analyses were performed using the SPSS statistical package software (version 19). A probability of Sig < 0.05 was considered statistically significant. Generally, based on Sig, one can find if the relation between parameters is significant or not. When the level of Sig is lower than 0.05 it indicated significant correlation and as such (Sig < 0.5), beta (B) is used to determine the relationship intensity.

2.3.1. Comparison of statistical methods

Each statistical method has its own advantages and disadvantages and in the current study several methods were considered to get more accurate results. For this purpose PCA-MLR, PMF and GEE were performed. Generally, PCA’s key advantages are (i) its low noise sensitivity, (ii) the decreased requirements for capacity and memory, and (iii) increased efficiency given the processes taking place in a smaller dimensions (Karamizadeh et al., 2013). Other advantages of PCA include: (i) Lack of redundancy of data given the orthogonal components; (ii) Reduced complexity in images’ grouping with the use of PCA; (iii) Smaller database representation since only the trainee images are stored in the form of their projections on a reduced basis; (iv) Reduction of noise since the maximum variation basis is chosen and so the small variations in the background are ignored automatically (Phillips et al., 2005; Srinivasulu Asadi et al., 2010); (v) Results cannot be weighted to account for uncertainties in the measured data; (vi) PCA models cannot properly handle missing data or values below the detection limit (both of which commonly occur in environmental measurements); and (vii) MLR analysis of the factor scores was used to quantify source contributions to samples based on pollutants (Larsen & Baker, 2003; Ashayeri et al., 2018). PCA’s key disadvantages of PCA are: (i) The covariance matrix is difficult to be evaluated in an accurate manner (Phillips et al., 2005); (ii) Even the simplest invariance could not be captured by the PCA unless the training data explicitly provides this information (Li et al., 2008); and (iii) PCA is not as powerful as other statistical methods in small datasets (Karamizadeh et al., 2013).

It is worth mentioning that weaknesses and limitations of PMF method according to EPA reports are important and include: 1) PMF models require large datasets on measured concentrations (preferable > 100 samples), 2) Analysis is limited by the accuracy, precision, and range of species measured at the receptor (e.g. ambient monitoring) sites, 3) A determination must be made of how many ‘factors’ to retain, 4) Emission sources have to be deduced by interpreting these factors, 5) Information is needed on source profiles or existing profiles in order to verify the representativeness of the calculated source profiles and uncertainties in the estimated source contributions, 6) The method relies on many parameters and initial conditions and model input; results are sensitive to the pre-set parameters.

A specific advantage of GEE is its ability to robustly estimate variances of the regression coefficient for data exhibiting high correlation between repeated measurements (Abbasi, Keshavarzi, Moore, Mahmoudi, 2018; Ballinger, 2004; Ghsisletta & Spini, 2004; Hu et al., 1998). Other advantages include: 1) The GEE algorithm has been incorporated into many major statistical software packages, including SAS, STATA, R, and S-PLUS, 2) the model is robust to the mis-specification of correlation structure, because the parameter estimate remain consistent, 3) when the working correlation structure is correctly specified, the parameter estimates from GEE are efficient (Liang & Zeger, 1986; Khajeh-Kazemi et al., 2011). GEE’s limitations include: 1) in the case mis specification of the working correlation matrix the parameter estimates from GEE can be inefficient (Liang & Zeger, 1986), 2) the consistency of the estimated parameter depends only on the correct specification of the mean model; but there is no universally accepted test for goodness-of-fit for mean model in GEE that extends beyond binary dependent variable (Barnhart & Williamson, 1998), 3) GEE parameter estimates are sensitive to outliers or contaminated data and in that cases GEE fails to give consistent estimators and more seriously will lead to incorrect conclusion (Preiser & Qaqish, 1996, 1999; Qu & Song, 2004), 4) In GEE due to lack of an objective function it is complicated to use model selection criterion (Pan, 2001), 5) if the correlation parameters are not consistently estimated, GEE fails to produce consistent estimators (Crowder, 1986, 1995).

2.4. Exposure and risk assessment

The incremental lifetime cancer risk (ILCR) resulting from exposures to PAHs in Asaluyeh’s street dust was calculated using the USEPA standard model (residential/ Commercial and industrial scenarios) (USEPA, 1991). This model is used in the current study to assess exposure risk of adults and children to PAHs in street dust. The following assumptions underlie the model applied in this study: (a) Human beings are exposed to urban surface dust through three main pathways: ingestion, inhalation, and dermal contact with dust particles; (b) Intake rates and particle emission can be approximated by those developed for soil particles; (c) Some exposure parameters of people in the observed areas are similar to those of reference populations; (d) The total carcinogenic risk could be computed by summing the individual risks calculated for the three exposure ways; (e) The cancer risk is assessed based on exposure under a specific type of land use pattern over the entire lifetime. The doses received through the ingestion (ing), inhalation (inh) and dermal contact (der) of PAHs were calculated following the guidance (USEPA, 1989).
Table 1
Descriptive statistics of TPH and PAHs (μg kg⁻¹) in street dust of Asaluyeh County.

| Compounds | Aromatic ring | Molecular weight | Mean    | S.D.    | Skewness | Minimum | Maximum |
|-----------|---------------|------------------|---------|---------|----------|---------|---------|
| TPH       | -             | -                | 1371429 | 1304992 | 1.52     | 240000  | 440000  |
| Napthalene (Nap) | 2        | 128              | 9.85    | 7.05    | 6.03     | 0.73    | 240     |
| Acenaphthene (Ace) | 3        | 154              | 35.39   | 72.63   | 4.38     | 1.8     | 430     |
| Fluorine (Fl) | 3          | 165              | 16.48   | 33.65   | 5.02     | 1.8     | 210     |
| Phenanthrene (Phe) | 3       | 178              | 128.55  | 438.79  | 6.29     | 1.3     | 2900    |
| Anthracene (Ant) | 3          | 178              | 15.23   | 48.65   | 6.15     | 1.3     | 320     |
| Fluoranthene (Flu) | 4        | 202              | 48.38   | 87.48   | 5.32     | 1.7     | 570     |
| Pyrene (Pyr) | 4           | 202              | 57.36   | 195.25  | 6.43     | 0.9     | 1300    |
| Benz[a]anthracene (BaA) | 4       | 228              | 19.30   | 39.43   | 3.48     | 0.3     | 190     |
| Chrysene (Chr) | 4           | 228              | 28.17   | 33.37   | 3.17     | 0.4     | 170     |
| Benzo[b]fluoranthene (BFB) | 5      | 252              | 10.72   | 31.61   | 1.70     | 1       | 48      |
| Benzo[k]fluoranthene (BkF) | 5      | 252              | 26.81   | 31.29   | 1.93     | 1.2     | 130     |
| Benz[a]pyrene (BaP) | 5         | 252              | 31.81   | 66.15   | 4.78     | 1.2     | 410     |
| Benzo[e]pyrene (BeP) | 5         | 252              | 42.26   | 48.20   | 2.86     | 1.4     | 260     |
| Dibenz[a,h]anthracene (DahA) | 5       | 278              | 8.66    | 7.62    | 1.66     | 0.13    | 32      |
| Benzo[g,h,i]perylene (BghiP) | 6       | 276              | 7.79    | 6.94    | 1.61     | 0.13    | 28      |
| Indene (Ind) | 6           | 276              | 4.59    | 4.36    | 1.45     | 0.13    | 18      |

S.D.: Standard deviation.

∑PAHs: total PAH concentration, sum of individual mass concentration of 16 PAH congeners.
LMW PAHs: low molecular weight 2–3 ring PAHs.
HMW PAHs: high molecular weight 4–6 ring PAHs.
COMPAHs: combustion derived PAH concentration.
CANCANPAHs: non-carcinogenetic PAHs.
NCANPAHs: carcinogenetic PAHs.
TEF: PAHs toxic equivalency factor with respect to BaP.

3. Result and discussion

3.1. Total petroleum hydrocarbons (TPH) in street dust

As shown in Table 1, large variability in TPH concentrations of sampling sites was observed. Urban areas typically exhibited higher TPH concentrations than industrial sites. The maximum, minimum and mean TPH are 4400, 240 and 1371.43 mg/kg, respectively. The high concentration of TPH is probably related to petroleum products, oil carrier trucks and automobiles. The TPH concentrations in refineries and petrochemical units are lower than those of the urban areas and far from the authors’ expectation (Fig. S1). This can be the result of many factors such as washing the connecting roadways. Such roadways in refineries and petrochemical units (industrial areas) are regularly washed, and hence pollutants adsorbed to street dust are removed (Kennedy, 2003; Zhang, Zhang et al., 2008; Zhang, Dou et al., 2008). Consequently, the concentration of pollutants in such places is lower than in regions where street dust remains on the street surface for a long time. According to Adeniyi and Afolabi (2002), street dust pollution can be identified when TPH concentration is higher than 10–100 mg/kg, indicating that all collected samples in Asaluyeh are polluted. Hence, measuring TPH subunits such as PAHs seemed reasonable (Fig. S1).

3.2. Polycyclic aromatic hydrocarbons (PAHs) in street dust

Descriptive statistics of PAH concentrations in summer are presented in Table 1. The highest ∑PAHs (6016.3 μg/kg) was found in P3 (a
sampling site in a petrochemical company), while minimum ∑PAHs (16.93 μg/kg) occurred in P42 (a sampling site in an urban area). During summer and winter, the mean concentration of total PAHs in street dust particles was 491.35 and 304.04 μg/kg, respectively. In general, ∑PAHs concentrations at petrochemical stations are higher compared to urban stations. Contrary to many previous studies that show a higher concentration of PAHs in winter, in the current study, total PAHs are higher in the summer (Fig. 2a). As already mentioned during winter, meteorological conditions like shorter daylength, lower temperatures, lower atmospheric mixing height, reduced vertical dispersion due to thermal inversion, increased use of heaters, enhanced sorption to particles at lower temperature and low photochemical reactivity of PAHs would increase PAHs content during winter (Baalbaki et al., 2018; Gope, Masto, George, & Balachandran, 2018; Liu, Cheng, Hou et al., 2007; Liu, Cheng, Ou et al., 2007; Periera-Netto, Krauss, Cunha, & Rego, 2006). Nonetheless, this is not the case everywhere and depends on many other factors. For example, in the current study, heating devices are not frequently used and the weather is not that cold in winter. It was also found that PAHs concentration during monsoon season is lower than summer because the heavy washout and runoff can wash street dust and their adsorbed PAHs (Gope et al., 2018). Therefore, rainfall and runoff are important for washing street dust in the winter, rather than PAHs themselves. According to Nowak, Crane, Stevens, Hoehn, and Walton (2008), precipitation helps wash away some surface contaminants, but PAHs are not readily washable. For example, Škrbić, Durišić-Mladenović, Živančev, and Tadić (2019) reported similar results to those of the current study. The higher concentrations of PAHs in street dust sampled in summer might be attributed to the additional pollution sources in summer such as the emission from numerous motorcycles that are not driven during the cold months (Škrbić et al., 2019). It is worth mentioning that PAHs emission from motorcycles was about 10 to 16 times greater than those from vehicles equipped with catalyst and low emission automobiles (Pham, Kameda, Toriba, & Hayakawa, 2013). In addition, natural gas and diesel fuel are used in Asaluyeh for generating electricity. Considering hot and humid weather in the summer, a sharp increase in power consumption by coolers cause higher emission of PAHs mass.

Comparison of PAH species revealed that the highest concentrations of naphthalene (P7 station), acenaphthene (P3 and P7 stations), fluorine (P3 and P7 stations), phenanthrene (P3 station), anthracene (P3 station), fluoranthene (P3 station), pyrene (P3 station), benzo[a]anthracene (P3 and P12 stations) and chrysene (P3, P12 and P17 stations) mostly occur at petrochemical areas. However, maximum benzo[b]fluoranthene (P9, P3, P6, P15, P17, P38 and P41 stations), benzo[k]fluoranthene (P9, P3, P16 and P17 stations), benzo[a]pyrene (P41, P39, P9, P17 and P16 stations), benzo[c]pyrene (P13, P9 and P23 stations), dibenzo[a,h]anthracene (P41, P38, P26, P17 and P16 stations), benzo[g,h,i]perylene (P41, P16, P39, P38, P17 and P26 stations) and indene (P41, P39, P26 and P16 stations) often occur in urban areas with high traffic load (Keshavarzi et al., 2017). Both petrochemical and other industrial areas indicated high average concentrations of low molecular weight (LMW) PAHs (2 and 3 rings), while only urban areas demonstrated remarkable mean content of high molecular weight (HMW) PAHs (4 rings and above). The main pollution source of PAHs is believed to be motor vehicles in urban areas of the current study. Generally, the LMW PAH species are produced by crude oil products at low to moderate temperatures, such as wood and coal combustion (Wang et al., 2011), but the HMW compounds are generated, for instance, when fuel is burned in engines at high temperatures (Mastral & Callen, 2000). Molecular weight of 4 rings PAHs lies between those of LMW and HMW PAHs and their characteristics are comparable to the properties of HMW and LMW PAHs (Table 1). Therefore, they may occur both in industrial regions (with high potential for generating LMWPAs) and in urban areas (with high potential for producing HMWPAs).

On average, the percentage of PAHs with 2, 3, 4, 5 and 6 rings are 1.98, 30.90, 29.81, 33.27 and 4.04%, respectively (Table 1 and Fig. 3). The abundance of PAHs based on ring numbers in the street dust of Asaluyeh follows the order of 5 rings > 4 rings > 3 rings > 4 rings > 6 rings > 2 rings. The 5 ring compounds indicated that industrial and traffic pollutants are more abundant (Wlcke, Amelung, Martius, Garcia, & Zech, 2018).
PAH compounds with 2 and 3 rings have less molecular weight and hence are more volatile than PAHs with 4 to 6 rings (Liu, Cheng, Hou et al., 2007; Liu, Cheng, Ou et al., 2007). Therefore, the greater concentration of PAH compounds with 2 and 3 rings at the mentioned stations indicates their recent release from pollution sources in the environment. High concentration of the 5 and 6 ring species probably reflects incomplete fuel combustion in industry and petroleum carrier trucks. These compounds have a strong tendency to deposit and bond to soil or dust particles (Khalili, Scheff, & Holsen, 1995). Also, the mean of combustion PAHs (the sum of Flu, Pyr, BaA, Chr, B(b + k)F, and BaP (Rogge, Hildemann, Mazurek, Cass, & Simoneit, 1993; Rajput & Lakhani, 2009)) to total PAHs in the street dust samples is 0.64 μg kg⁻¹ and constitutes a significant proportion of the total PAHs concentration. According to International Agency for Research on Cancer (IARC), carcinogenic PAHs include Nap, BaA, Chr, B(b + k)F, DbahA, and Ind. The mean ratio of carcinogenic PAHs to total PAHs (CANPAHs/PAHs) is lower than the mean ratio of the non-carcinogenic PAHs to total PAHs (NCANPAHs/PAHs) indicating higher abundance of the non-carcinogenetic PAHs (Table 1). Furthermore, considering Fig. 2c, the concentration of carcinogenic PAHs is higher than the value of non-carcinogenic PAHs, especially in regions with high traffic load. The carcinogenic PAHs concentration is also higher in summer (Fig. 2c). Fig. 2b depicts lower LMW PAHs concentration in winter because as already pointed out LMW PAHs are easily washed by surface runoff in this season. In previous studies the bioavailable fractions of organic pollutants are reported as the sum of water-soluble and acid-soluble fractions that which negatively correlate with the log Kow of organic pollutants. Therefore, HMW PAHs are more stable than LMW PAHs and rainfall washes LMW more efficiently (Wang, Zhu, & Zhang, 2015) (Fig. 2b).

Table S3 reveals that the concentrations of PAHs in Asaluyeh street dust are more varied and higher than Isfahan (Iran), Beijing (China), Cairo (Egypt) and Ulsan (South Korea), and lower than Tehran and Bushehr (Iran), Manchester (UK), Guangzhou (China), New Delhi (India) and Istanbul (Turkey). Generally speaking, comparison of contamination in different regions and sampling sites is almost impossible. The reason is that many factors (including climatically and geological) can greatly affect the results. Hence, one must always bear in mind that origin of pollution may also be geogenic rather than anthropogenic. Furthermore, the intensity of precipitation varies in different locations and thus may wash street dust and pollutants differently. Finally, different sampling and analytical methods must be taken into account when a comparison is made. It is worth noting that similar studies were conducted in Asaluyeh, Bushehr and Bandar Abbas cities (south of Iran) with almost the same climate, weather, and sampling methods. The main reason for differing concentrations of PAHs in Bandar Abbas are anthropogenic activity such as traffic load and industrial activity. More specifically, the industrial activity (petroleum units) and traffic load in Asaluyeh are higher than Bushehr and Bandar Abbas resulting in higher PAHs concentration in Asaluyeh. Thus, traffic load and industrial activity are two important factors that affect contamination of street dust. As mentioned, Asaluyeh is limited to the Persian Gulf in the south and mountains to the north. Thus, the sweeping effect of wind blowing from sea toward mountains (the northern barrier) highlights air and street dust pollution due to lack of dispersion. This sweeping effect of wind can be severely reduced in areas surrounded by mountains. Short and long-term exposure to PM10 in outdoor and indoor environments can result in respiratory and cardiovascular diseases placing an economic burden on society due to medical expenses or even death of experienced workers (Martins & da Graça, 2018).

### 3.3. Polycyclic aromatic hydrocarbons (PAHs) in PM10

The PM fraction was obtained by subtracting the pre-sampling weight of filter from the post-sampling weight using an analytical microweigh (Model LIBROR AEL-40SM; SHIMADZU Co., Kyoto, Japan) with a 1 μg sensitivity. Since PAHs were not investigated in Asaluyeh where the weather is warm and humid, for more certainty in PAHs results, sampling campaign was conducted in winter over approximately a ten-day period (27/1/2018 to 6/2/2018). The results revealed that the PM concentration varies in different days depending on weather condition. For example on 28/1/2018, high wind speed increased resuspended dusts. However, PM concentration and temperature generally had a positive correlation. Furthermore, it is evident that increasing temperature decreases soil moisture and consequently increases resuspended dust (Figs. 4 and S2). The maximum (6.25 μg/m³), minimum (0.72 μg/m³) and average (2.38 μg/m³) concentrations of PM10 did not exceed the USEPA (100 μg/m³) and WHO (50 μg/m³) air quality standards. Also, according to PM10 concentration, calculated air quality indices (AQIs) ranged from 0.66 to 5.78 with an average of 2.2 indicating “good” category.

Fig. 4 shows variations of the PAH concentrations in the (re-)suspended dust samples collected daily in industrial and urban areas. The highest ΣPAHs is 4.73 ng/m³ in N4 sampling site (a petrochemical company), while the minimum ΣPAHs was 2.84 ng/m³ in U1 station (an urban area). The average air dust PAH content in the study area is 3.75 ng/m³ with non-carcinogenetic PAHs being more abundant than carcinogenetic ones. The results indicate higher total PAHs and LMW PAHs concentrations in the industrial areas (petrochemical units) compared with urban areas. Among combustion-derived PAHs, HMW-PAHs are abundantly generated at high temperature (automobile motors), while the petroleum-derived residues have relatively high LMW-
PAHs content (Mai et al., 2003). Figs. 3 and 4 reveal that the decreasing trend of LMW PAHs concentrations is: air dust > winter street dust > summer street dust. This clearly shows that two major factors affecting LMW PAHs concentration include (i) temperature (ii) volatility. It is no surprise that the filter dust has relatively high levels of LMW. LMW (2–3 rings) PAHs are known to be relatively more volatile resulting in their less abundance in settled dust compared to air particles. Also, given the lower temperature in winter, higher LMW PAHs concentration was observed. PAH concentration and temperature have a negative relationship since PAHs (especially LMW PAHs) are temperature sensitive and with increasing temperature, PAHs volatilize. It is interesting to know that PM and PAHs concentrations have a negative correlation owing to dilution of the PAHs concentration by increased suspended dust concentration (Figs. 4 and S2).

### 3.4. Statistical source identification

The skewness, standard deviation and Sig value (< 0.05) of Shapiro–Wilk test confirmed non-normality of PAHs (Table 1). Thus, considering the non-normal distribution of PAH compounds, nonparametric statistical tests were chosen to conduct statistical analyses.

Factor analysis is an appropriate statistical method for determining the relationship between components. In this study, PCA as an extraction method, Varimax rotation for better representation of data and eigenvalues greater than 1 were used to extract factors. By using this statistical test, the number of variables can be reduced and presented in several main components, each containing several variables. The data were also analyzed by KMO test for evaluating the number of samples and Bartlett test for measuring similarity of data prior to performing factor analysis. The KMO and Bartlett values were more than 0.6 and 0.97 respectively, while the total variance of the components was more than 70% of the total data variance. Hence, suitability of factor analysis was approved for reducing the number of variables and identifying hidden structures between the data. Regarding the results of PCA (Table 2), the first component represented 67.6% of the total variance and included LMW PAHs (naphthalene, acenaphthene, fluorine, phenanthrene and anthracene) that mostly originate from oil leaks that evaporate and degrade rather easily (Liu, Cheng, Hou et al., 2007; Liu, Cheng, Ou et al., 2007). The second component comprises 22% of the total variance. fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[e]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenzo[a,h]anthracene, benzo[g,h,i]perylene and indene that fall in this component are HMW PAHs mainly coming from fuel combustion and are hard to evaporate and degrade (Liu, Cheng, Hou et al., 2007; Liu, Cheng, Ou et al., 2007). The presence of pyrene and chrysene in this group indicates that their origin is petroleum burning. Burning fossil fuels commonly leads to the formation of a large amount of pyrene, benzo[a]pyrene, benzo[b]fluoranthene and benzo[k]fluoranthene, all included in the second component (Hwang, Kusch, Barral, & Huffaker, 2003; Rajput & Lakhani, 2009).

Benzo[g,h,i]perylene and indene have both similar molecular weight and tendency to be absorbed into dust particles. Generally, the MLR results indicated that the first and second components include 74.05% and 25.95% of the total PAHs concentration in Asaluyeh, respectively (Table 2). A fact that reflects LMW PAHs being usually generated in petrochemical units in the industrial areas probably make the main proportion of PAHs in the study area.

The results of GEE analysis confirmed PCA-MLR analysis (Table 3). According to the Sig and B of PAHs in GEE analysis, no strong positive correlation exists between LMW and HMW PAH subgroups reflecting their different origins and physicochemical characteristics. LMW compounds have high atmospheric mobility and may have been transported from remote sites via atmospheric transportation, while coming from fuel combustion and are hard to evaporate and degrade.

### Table 2
Principal component analysis-multiple linear regression (PCA-MLR) of PAHs concentration in Asaluyeh County.

| PAH species       | PC1     | PC2     |
|-------------------|---------|---------|
| Naphthalene       | 0.6     | −0.264  |
| Acenaphthene      | 0.52    | −0.137  |
| Fluorine          | 0.954   | −0.07   |
| Phenanthrene      | 0.97    | 0.024   |
| Anthracene        | 0.963   | 0.006   |
| Fluoranthene      | 0.2     | 0.935   |
| Pyrene            | 0.087   | 0.949   |
| Benzo[a]anthracene| 0.167   | 0.743   |
| Chrysene          | 0.369   | 0.775   |
| Benzo[e]pyrene    | 0.078   | 0.224   |
| Benzo[b]fluoranthene| 0.462  | 0.695   |
| Benzo[k]fluoranthene| 0.363  | 0.801   |
| Benzo[a]pyrene    | −0.063  | 0.929   |
| Dibenzo[a,h]anthracene| −0.041 | 0.945   |
| Benzo[g,h,i]perylene| −0.04  | 0.945   |
| Indene            | −0.013  | 0.902   |
| Contribution percent | 74.05 | 25.95   |

Bold value signifies: P value < 0.05.
Table 3
GEE matrix for PAHs concentration.

| Effecting parameters | Nap | Ace | Fl | Phe | Ant | Flu | Pyr | BaA | Chr |
|----------------------|-----|-----|----|-----|-----|-----|-----|-----|-----|
| Wald                 | 9.723 | 4.741 | 4.741 | 1.069 | 1.069 | 0.424 | 0.069 | 0.069 | 0.069 |
| Sig                  | 0.002 | 0.337 | 0.002 | 0.337 | 0.337 | 0.002 | 0.337 | 0.337 | 0.337 |
| B                    | 0.474 | 0.424 | 0.474 | 0.424 | 0.424 | 0.474 | 0.424 | 0.474 | 0.424 |

(continued on next page)
| Effecting parameters | Nap | Ace | Fl | Phe | Ant | Flu | Pyr | BaA | Chr |
|----------------------|-----|-----|----|-----|-----|-----|-----|-----|-----|
| **Wald**             | 4.702 | 1.16 | 0.011 | 0.028 | 0.282 | 3.379 | 2.48 | 1.868 | 3.202 |
| **Sig**              | 0.03 | 0.281 | 0.918 | 0.867 | 0.595 | 0.066 | 0.115 | 0.172 | 0.074 |
| **B**                | -0.018 | -0.006 | -0.001 | 6.688E-05 | 0.002 | 0.015 | 0.002 | 0.015 | 0.041 |
| **Wald**             | 0.956 | 0.612 | 0.299 | 1.773 | 3.206 | 0 | 2.945 | 0.554 | 0.529 |
| **Sig**              | 0.086 | 0.434 | 0.611 | 0.161 | 0.071 | 0.994 | 0.407 | 0.467 | 0.467 |

| Effecting parameters | BeP | BbF | BkF | BaP | DbahA | BghiP | Ind | TPH |
|----------------------|-----|-----|-----|-----|-------|-------|-----|-----|
| **Wald**             | 0.479 | 0.516 | 0.844 | 1.168 | 1.109 | 0.988 | 1.069 | 1.464 |
| **Sig**              | 0.489 | 0.472 | 0.358 | 0.28 | 0.292 | 0.32 | 0.301 | 0.226 |
| **B**                | -0.031 | -0.229 | -0.115 | -0.043 | -0.814 | -0.85 | -1.315 | -4.62E-06 |
| **Wald**             | 0.659 | 1.273 | 0.932 | 1.185 | 0.182 | 0.206 | 0.266 | 0.217 |
| **Sig**              | 0.471 | 0.249 | 0.418 | 0.93 | 0.608 | 0.65 | 0.606 | 0.641 |
| **B**                | -0.073 | 1.151 | 0.287 | 0.006 | -0.702 | -0.688 | -1.225 | -4.21E-06 |
| **Wald**             | 0.052 | 1.146 | 0.83 | 1.985 | 0.723 | 0.593 | 0.062 | 0.148 |
| **Sig**              | 0.819 | 0.284 | 0.362 | 0.298 | 0.395 | 0.441 | 0.803 | 0.7 |
| **B**                | -0.017 | 1.02 | 0.28 | -0.034 | -0.244 | -0.247 | -0.137 | -2.00E-06 |
| **Wald**             | 0.172 | 1.812 | 1.369 | 0.707 | 0.261 | 0.163 | 0.082 | 0.413 |

| Effecting parameters | BeP | BbF | BkF | BaP | DbahA | BghiP | Ind | TPH |
|----------------------|-----|-----|-----|-----|-------|-------|-----|-----|
| **Wald**             | 0.678 | 0.178 | 0.242 | 0.4 | 0.609 | 0.687 | 0.774 | 0.521 |
| **Sig**              | 0.471 | 0.259 | 0.334 | 0.276 | 0.67 | 0.703 | 0.687 | 0.456 |
| **B**                | -0.082 | 1.667 | 0.457 | -0.049 | -0.101 | -0.106 | 0.266 | -5.10E-06 |
| **Wald**             | 0.902 | 0.039 | 0.047 | 0.594 | 0.054 | 0.055 | 0.061 | 0.968 |
| **Sig**              | 0.421 | 1.938 | 1.604 | 0.105 | 3.176 | 3.132 | 2.372 | 0.522 |
| **B**                | -0.017 | 1.02 | 0.28 | -0.034 | -0.244 | -0.247 | -0.137 | -2.00E-06 |
| **Wald**             | 0.516 | 0.164 | 0.205 | 0.746 | 0.075 | 0.077 | 0.124 | 0.47 |
| **Sig**              | 1.44 | 2.643 | 3.529 | 0 | 1.913 | 0 | 1.28 | 1.959 |
| **B**                | 0.23 | 0.104 | 0.06 | 0.985 | 0.167 | 0.258 | 0.062 | 0.162 |
| **Wald**             | 0.071 | 1.178 | 0.425 | -0.001 | 0.608 | 0.654 | 1.233 | 7.46E-06 |
| **Sig**              | 0.781 | 5.308 | 6.751 | 1.795 | 12.454 | 10.709 | 9.267 | 1.677 |
| **B**                | 0.377 | 0.021 | 1.498 | 1.541 | 0.079 | 1.398 | 5.427 | 6.80E-06 |
| **Wald**             | 2.653 | 7.524 | 0.884 | 0.051 | 0.196 | 0.153 | 3.475 | 0.002 |
| **Sig**              | 0.103 | 0.006 | 0.347 | 0.822 | 0.658 | 0.696 | 0.062 | 0.062 |
| **B**                | 1.061 | 0.576 | 0.085 | 0.166 | 0.329 | 0.481 | 1.41E-05 | 0.195 |
| **Wald**             | 3.262 | 66.329 | 6.43 | 82.141 | 51.943 | 28.609 | 1.022 | 2.89 |
| **Sig**              | 0.071 | 0 | 0.011 | 0 | 0 | 0 | 0 | 0.312 |
| **B**                | 0.062 | 0.322 | 0.085 | 0.829 | 0.883 | 1.256 | 2.08E-06 | 0.195 |
| **Wald**             | 4.214 | 78.155 | 2.17 | 18.888 | 57.688 | 21.306 | 1.981 | 0.159 |
| **Sig**              | 0.04 | 0 | 0.141 | 0 | 0 | 0 | 0 | 8.97E-06 |
| **B**                | 0.243 | 2.344 | 0.215 | 2.556 | 2.814 | 4.329 | 2.716 | 0.099 |
| **Wald**             | 2.406 | 5.726 | 16.272 | 8.027 | 13.179 | 19.228 | 2.89 |
| **Sig**              | 0.121 | 0.017 | 0 | 0.005 | 0 | 0 | 0 | 0.089 |
| **B**                | 0.16 | 2.774 | 0.963 | 6.487 | 6.974 | 9.301 | 1.44E-05 | 0.099 |
| **Wald**             | 0.046 | 7.297 | 8.184 | 16.397 | 4305.402 | 293.471 | 2.89 |
| **Sig**              | 0.83 | 0.007 | 0.004 | 0 | 0 | 0 | 0 | 0.089 |
| **B**                | 0.004 | 0.358 | 0.152 | 0.086 | 1.09 | 1.632 | 2.555E-06 | 2.08E-06 | 1.677 |

(continued on next page)
Table 3 (continued)

| Effecting parameters | BeP | BbF | BkF | BaP | DbahA | BghiP | Ind | TPH |
|----------------------|-----|-----|-----|-----|-------|-------|-----|-----|
|                       |     |     |     |     |       |       |     |     |
| Wald                 | 0.147 | 0.702 | 0.097 | 0.077 | 0.056 | 0.504 | 0.04 | 0.141 |
| Sig                  | 0.702 | 0.006 | 0.006 | 0.006 | 0.004 | 0.534 | 0.066 | 0.066 |
| BghiP               | 0.011 | 0.138 | 0.006 | 0.006 | 0.004 | 0.534 | 0.066 | 0.066 |
| B  | 0.316 | 0.904 | 0.918 | 0.918 | 0.918 | 0.918 | 0.918 | 0.918 |
| BkF         | 1.512 | 3.374 | 7.42  | 14.365| 3819.582 | 356.486 | 3.374 | 3.374 |
| BaP                 | 2.41E-06 | 0.007 | 0.077 | 0.077 | 0.077 | 0.077 | 0.077 | 0.077 |
| DbahA            | 2.77E-06 | 0.006 | 0.006 | 0.006 | 0.006 | 0.006 | 0.006 | 0.006 |
| TPH                | 1.04E-06 | 0.004 | 0.004 | 0.004 | 0.004 | 0.004 | 0.004 | 0.004 |

Bold value signifies: P value < 0.05.

Due to the fact that the transport and fates of PAHs of street dust and (re-)suspended dust in urban ecosystems such as Asaluyeh County should be identified, an estimation of the partitioning of PAHs between street dust and (re-)suspended dust may give beneficial insights. Generally, three scenarios may occur that include (i) direct PAHs attachment to air dust, (ii) street dust PAHs evaporate and then attach to air dust, (iii) resuspension of street dust as air dust. In the first two scenarios, LMW PAHs concentration is expected to be higher than HMW PAHs concentration. Hence, Fig. 6 reveals that the LMW PAHs concentration in the air dust is higher than street dust. The atmospheric LMW PAHs (2 and 3 rings) mainly occur in the vapour phase, while HMW PAHs (5 rings or more) are often limited to particles. Regarding atmospheric temperature MMW PAHs (4 rings) partition between the particulate and vapour phases (Srogi, 2007). Therefore, according to Fig. 6, PAH species display different transmission values in street dust and air dust, respectively. In terms of street dust, Benzo(k)fluoranthene, Benzo(a)pyrene, Dibenzo(a,h)anthracene, Benzo(ghi)perylene and Indene are grouped in the first factor with high factor loading values which feasibly originated from urban sources and include HMW PAHs. HMW compounds have similar chemical and physical properties and originate from vehicle motors. In the second factor which can be considered as representing industrial sources (refinery and petrochemical units), most LMW compounds constitute the main PAHs. On the other hand, the third factor demonstrates characteristics of 4 ring PAHs which are similar to HMW and LMW PAHs and are classified as moderate molecular weight (MMW) PAHs. They probably originated from mixed pyrogenic and petrogenic sources.

Regarding air dust, three geogenic, pyrogenic and petrogenic factors were identified. The first factor includes PM (geogenic). The second and third factors include petrogenic and pyrogenic sources, respectively. HMW PAHs are mostly pyrogenic and originate from fossil fuel combustion (often in urban areas) and LMW PAHs are mostly petrogenic and originate from oil leaks (often petrochemical units in industrial areas). Also, the temperature is effective on all three factors, which is due to the effect of temperature on (re-)suspended dust generation and sensitiveness of PAHs to temperature.
### Table 4
Backward GEE matrix indicating PAHs species effect on TPH concentration.

| Parameter          | Parameter B | Std. Error | 95% Wald Confidence Interval | Hypothesis Test |
|--------------------|-------------|------------|------------------------------|-----------------|
| (Intercept)        | 837,151.658 | 526,288.152 | −1,942,654.165 – 1,868,657.482 | 2.530           |
| Naphthalene (Nap)  | −380,037.727 | 12,787.998  | −632,664.162 – −127,832.292   | 8.718           |
| Acenaphthene (Ace) | 61,220.822  | 35,232.369  | −7833.353 – 130,274.997       | 3.019           |
| Fluorine (Fl)      | −1,974,272.125 | 155,008.5368 | −3,012,987.257 – 1,063,848.024 | 1.622           |
| Phenanthrene (Phe) | −1,276,403.75 | 105,257.327 | −3,339,460.75 – 786,654.75   | 1.471           |
| Anthracene (Ant)   | 309,992.807  | 17,3687.2365 | −304,271.921 – 650,413.535    | 3.218           |
| Fluoranthene (Flu) | −1,791,407.92 | 5,4214.9736 | −1,241,812.97 – 8,383,579.94  | .109            |
| Pyrene (Pyr)       | −3,507,572.9 | 39,777.8450 | −1,136,668.872 – 4,225,745.15 | .806            |
| Benzo[a]anthracene (BaA) | 42,355.509 | 31,406.2369 | −1,919,584 – 103,910.602     | 1.819           |
| Chrysene (Chr)     | 142,193.976  | 580,296.6385 | 2,8457.975 – 25,929.978      | 6.004           |
| Benzo[ghi]pyrene (BghiP) | 239,388.030 | 25,3861.0317 | −25,821.333 – 73,689.594    | .899            |
| Indene (Ind)       | 277,878.724  | 14,0731.9145 | 2,048,770 – 55,370.737      | 3.899           |

Dependent Variable: TPH.  
Model: (Intercept), Naphthalene (Nap), Acenaphthene (Ace), Fluorine (Fl), Phenanthrene (Phe), Anthracene (Ant), Fluoranthene (Flu), Pyrene (Pyr), Benzo[a]anthracene (BaA), Chrysene (Chr), Benzo[ghi]pyrene (BghiP), Indene (Ind).  
Bold value signifies: P value < 0.05.

### Table 5
Backward GEE matrix indicating Nap, Chr, BbF and Ind effect on TPH concentration.

| Parameter          | Parameter B | Std. Error | 95% Wald Confidence Interval | Hypothesis Test |
|--------------------|-------------|------------|------------------------------|-----------------|
| (Intercept)        | 922,624.707 | 378,399.452 | 1,809,754.409 – 166,427.044  | 5.945           |
| Naphthalene (Nap)  | −1,130,549  | 18,294.082 | −4,716,123 – 2,455,025       | .382            |
| Chrysene (Chr)     | 17,765.174  | 15,210.922 | −120,526.866 – 475,733.033   | 1.363           |
| Benzo[b]fluoranthene (BbF) | −63,061.083 | 57,783.486 | −176,314.609 – 50,192.435   | 1.191           |
| Indene (Ind)       | 147,724.195 | 68,310.2945 | 138,384.478 – 281,609.912   | 4.677           |

Dependent Variable: TPH.  
Model: (Intercept), Naphthalene (Nap), Chrysene (Chr), Benzo[b]fluoranthene (BbF), Indene (Ind).  
Bold value signifies: P value < 0.05.

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**Fig. 5.** Source profiles of the street dust and air dust samples from PMF model analysis.
and air dust. Results indicate that the decreasing trend of transmission values of PAHs is as follows: LMW > MMW > HMW. Naphthalene has the highest transmission value from street dust to air dust. If it is assumed that all air dust PAHs originate from resuspended street dust (third scenario), the partitioning of PAHs must be almost similar to that of street dust.

3.5. PAHs ratio analysis

Diagnostic ratios of PAH species are commonly used to distinguish pyrogenic and petrogenic sources of PAH compounds. These ratios can explain potential PAHs emission sources. Generally, LMW/HMW, Phe/Ant, Ant/(Ant + Phe), Flu/(Flu + Pyr), BaA/(BaA + Chr) and Ind/(Ind + BghiP) ratios are used for this purpose (Table S4). LMW/HMW ratio < 1 indicates pyrogenic and > 1 shows a petrogenic source (Zhang, Dou et al., 2008). Phe/Ant ratio > 15 and < 10 reveals petrogenic and pyrogenic sources, respectively (Takada, Onda, Harada, & Ogura, 1991). Furthermore, Ant/(Ant + Phe) > 0.1 and < 0.1 are indicative of pyrogenic and petrogenic sources (Pies et al., 2008). Similarly Flu/(Flu + Pyr) < 0.4 ratio indicate a petroleum source, while ratios between 0.4 and 0.6 indicate gasoline emissions, while ratios between 0.6 and 0.7 indicate diesel emissions sources (Yunkera et al., 2002). If BaA/(BaA + Chr) is lower than < 0.2, it reveals petrogenic PAHs, and ranges from 0.22 to 0.55, 0.38 to 0.64 and 0.35 to 0.50 show gasoline emissions, diesel emissions and petrogenic origin, respectively (Simcik, Eisenreich, & Liow, 1999; Sicre et al., 1987; Wang, Tian, Yang, Liu, & Yi-Fan, 2009; Yunkera et al., 2002). Also, ratio of Ind/(Ind + BghiP) < 0.2; 0.2 to 0.5; and > 0.5 indicate petroleum and petrogenic; petroleum combustion; and coal, grass, and wood sources, respectively (Zhang, Luo, Wong, Zhao, & Zhang, 2006). Table S4 presents the calculated ratios in this study. As it can be seen, PAHs in Asaluyeh street dust, generally originate from pyrogenic sources, but a closer look at each sampling site (Fig. S3), reveals that PAHs sources (in both summer and winter) are mostly petrogenic in the industrial area and pyrogenic in urban areas, and probably originate from diesel and fossil fuel combustion and also automobiles, gasoline (Table S4 and Fig. S3). About (re-)suspended dust, all samples illustrated diesel emissions (except N2 sample that showed a mixed source). In the industrial areas, in addition to petrochemical units, the movement of vehicles is effective and the air pollution can move a long distance (Fig. S3).

Table 6
Logistic regression analysis comparing petrogenic and pyrogenic sources of PAHs in industrial and urban areas, Asaluyeh County.

| Variables in the Equation | 95% C.I. for EXP (B) |
|---------------------------|----------------------|
|                          | B        | S.E.  | Wald | df | Sig. | Exp (B) | Lower | Upper |
| Step 1 a                |          |       |      |    |      |         |       |       |
| Industrial (1)          | 2.416    | 1.177 | 4.212| 1  | 0.04 | 11.2    | 1.115 | 112.518 |
| Constant                | −3.332   | 1.018 | 10.721 | 1 | 0.001 | 0.036   |       |       |

Bold value signifies: P value < 0.05.
* Variable(s) entered on step 1: Industrial.
For more certainty, logistic regression analysis was used in the current study. A benefit of logistic regression analysis compared with other statistical methods (such as t-test) is that it takes into account the number of polluted stations, while other statistical methods are based on the concentration of pollutants. In the current study, logistic regression analysis was used to compare pyrogenic and petrogenic sources of PAHs between industrial and urban areas (Table 6). It can be seen that there is a significant difference between industrial and urban areas in terms of PAHs origin (Sig = 0.04). Accordingly, Exp (B) indicated that petrogenic PAHs in industrial areas are 11.2 times more abundant than in urban areas. The reason is that in industrial areas, petrochemical and refining processes and consequently petrogenic sources for PAHs are more common. Also, combustion of fossil fuels by motor vehicles in urban areas produces pyrogenic PAHs.

### 3.6. Health risk assessment

Human health risk assessment was carried out assuming that adults and children are exposed to PAHs (based on residential/commercial and industrial scenarios) (Table S2). Table 1 shows calculated toxic equivalency concentration (TEQ) for Asaluyeh street dust along with toxic equivalency factors (TEF) of PAH species. TEQ is used in the incremental lifetime cancer risk (ILCR) formula. Generally, the acceptable value for ILCR is equal to or lower than $10^{-6}$ while ILCR between $10^{-8}$ and $10^{-6}$ indicates potential risk, and above $10^{-4}$, represents high health risk potential (US EPA, 2008).

The results revealed that TEQ in summer is higher than winter (Fig. 2d) obviously as already mentioned PAHs concentration in summer is higher. Based on residential/commercial and industrial scenarios for dermal contact and ingestion exposure pathways, the average estimated ILCRs for both adults and children is more than $10^{-4}$ and for inhalation pathway, lower than $10^{-6}$ (Table 7). Therefore, dermal and ingestion pathways are the main routes of exposure to PAHs and pose a high potential health risk, while exposure through inhalation pathway is acceptable (Table 7). The results also indicated that mean cancer risk is higher than $10^{-4}$ and carcinogenic risk is high and worrying. Also, the results revealed that estimated ILCR for residential/commercial areas is higher than in industrial areas and that in the industrial areas dermal and inhalation pathways for indoor workers are more hazardous. Finally, according to different groups and scenarios, children are exposed to higher health risk (Table 7).

### 4. Conclusion

TPH and PAHs distribution in Asaluyeh County revealed that the reason for pollutants accumulation in the street dust is not confined to human activity. The streets enriched with dust are a dynamic environment and can change easily. For instance, human activity, precipitation, wind blow, street wash out and management plans all affect street dust. On the other hand, pollutants are affected by temperature, sunlight, human activity, technology level, remediation operation and several other factors. Therefore, all above-mentioned factors should be considered in environmental monitoring. However, in the current study in order to obtain more precise results, strong statistical methods such as GEE, backward GEE, logistic regression, PCA-MLR and PMF were used. Logistic regression demonstrated petrogenic sources for PAHs in the industrial and pyrogenic sources in the urban areas. Since TPH is used as an organic pollutants indicator including PAHs, backward GEE model was used and demonstrated that TPH is more influenced by HMW PAHs, especially Indene. Also, decreasing trend of LMW PAHs concentrations is: air dust > winter street dust > summer street dust. This clearly shows that two major factors affecting LMWPAHs concentration include (i) temperature (ii) volatility. Eventually, this study will help to design effective control and mitigation strategies to improve ambient air quality by providing information about source pollutants and create engineering mechanisms for air ventilation. Finally, the proposed statistical methods provide a valuable and reliable means of environmental evaluation.

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### Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.scs.2018.11.015.

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