Ecological Risk Assessment and Source identification of PAHs by PMF model in petroleum contaminated soils; West of Kermanshah province

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Abstract

Soils around the petroleum industry sites in the west of Kermanshah province are susceptible to contamination by anthropogenic activities. The risk assessment of polycyclic aromatic hydrocarbons (PAHs) in west of Kermanshah, was evaluated by collecting 23 soil samples from the petroleum contaminated sites (PC). Source apportionment was carried out by using Positive Matrix Factorization (PMF) technique. Level of risk attributed to PAHs was evaluated using ecological and carcinogenic risks. Total PAHs concentration, show a mean value of 92.79 mg/kg, ranging from 7.37 to 609.67 mg/kg in PC soil samples. The average abundance order of different PAH ring compounds are 3 rings > 5+6 rings > 4 rings> 2 rings. Ecological risk assessment of PAHs revealed that all of the PAHs levels are higher than the effects range low (ERL) value and show higher concentrations than the effect range median (ERM) values, except for Pyr, Chr, BaA, BbF, BkF and BaP in the soil samples. Result of benzo (a) pyrene equation (BaP_{eq}) indicates that

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the carcinogenic potency of PAHs demands more attention due to the impending environmental risk in the study areas. Based on the PMF analysis, four sources of PAHs identified, including biomass/wood burning (21.48%), vehicular source (13.74%), unburned petroleum (20.84%) and creosote (43. 92%). Obtained result indicates that petroleum activities are the major source of PAHs contamination in the west of Kermanshah province.

Keywords: PAHs, PMF model, Ecological risk, Soil, Kermanshah, Iran

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are one of the most important classes of environmental pollutants [1] and their presence in soil has been one of the greatest concerns due to their health implications [2 and 3]. PAHs are a large group of organic pollutants that consist of two or more fused aromatic rings [4]. The US Environmental Protection Agency has listed 16 PAHs as priority pollutants and considered seven of them as carcinogenic chemicals [5]. Because of their toxicity, mutagenicity and carcinogenicity, PAHs have received considerable attention [6]. PAHs generally have high chemical stability and hydrophobic properties, which result in enhanced accumulation and high distribution capacity in the environment [4, 7 and 8]. PAHs are abundant environmental pollutants that once released may persist in the environment for a long time and undergo long-range transportation [9]. PAHs are generated during the combustion processes and its emitted primarily by anthropogenic sources, such as vehicle emissions, coal and fossil fuel power generation, petroleum refining, straw and firewood burning, industrial processing, chemical

manufacturing, oil spills and coal tars [10]. Soil is a reservoir for PAHs and they enter into soil by dry and wet deposition once released into the atmosphere [11 and 12]. Soil is a good indicator of long-term environmental pollution because PAHs are strongly associated with soil organic matter [12 and 13]. Therefore, PAHs contaminated soils should be carefully examined for decreasing the risk of human exposure and environmental pollution [14].

In recent years, many reports published about the concentrations, sources and risk assessment of PAHs in soils from different regions and countries [12, 15, and 16]. Kermanshah province located in the west of Iran and is one of the most important oil fields in the country. Soils from the petroleum industry areas in the west of Kermanshah province (Figure 1) are susceptible to contamination by anthropogenic activities. Oil exploration and field development, oil pumping station, pipeline and transport are the main contributors to the discharge of ∑16-PAHs to the soil of west areas of Kermanshah province in the form of industrial wastewater, solid waste, runoff and atmospheric deposition. There have been limited studies on the soil quality and environmental assessment in this area and all published environmental data are restricted to local scale. Average annual rainfall in the study area is about 550 mm, which mainly takes place between September and May. The average annual temperature in the northern and eastern part of study area is about 14 $^{\circ}$C while in the western regions of the province is about 20 $^{\circ}$C.

The main objectives of this paper are: (1) evaluating distributions and concentrations of 16 priority PAHs from the petroleum contaminated soils

in the west of Kermanshah province, (2) assess the environmental risk by ERL/ERM and toxic equivalency factors (TEF); and (3) identify the potential sources of PAHs by positive matrix factorization model (PMF).

Material and methods

1. Soil sampling and preparation

Soil samples were collected from the petroleum-contaminated areas of Kermanshah province (PC soils). For sampling, the oil production industries, oil transport lines, oil well installations, and the pumping stations were of particular importance for selecting sampling points. 23 top soil samples were collected from 0-30 cm depth (Table 1). In order to take a representative sample, composite samples were prepared by mixing the four samples taken at the corners of a 2 m square. The samples were thoroughly mixed and a final sample of 1 kg was obtained by repeated coning and quartering. Sampling sites were selected in a way to cover an impacted area based on known anthropogenic sources. The samples were stored in an ice chest at 4 °C and conveyed to the laboratory, where they were stored at −20 $^{\circ}$C prior to analysis. The sample locations are shown in Figure 1 and Table 1.

2. Analytical methods

In the laboratory, samples were freed from foreign materials, air-dried to a constant weight and then sieved through a 200 μm mesh. Particles <63 μm were prepared for PAH analyses using gas chromatography (GC) with flame ionization detector (FID) in the Iranian Celco lab. Organic carbon content was determined using Gaudette et al. (1974) [17] titration method. Soil pH was measured in a suspension of 1:2 soil to water ratio using a calibrated ELE pH meter.

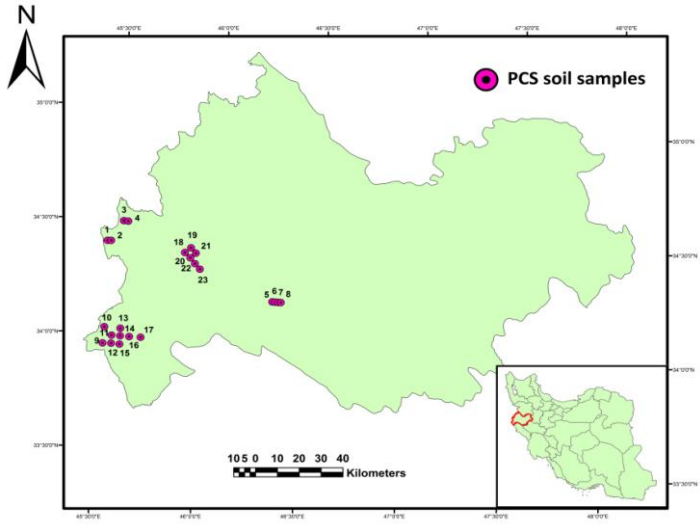

Figure 1. Locations of the PC sampling site

Table 1. Coordination of petroleum contaminated soil samples in west of Kermanshah province

Sampling code	Longitude	Latitude	Sampling site
PC1	544097.00	3807835.00	Oil pipeline, Khosravi area
PC2	545805.00	3807972.00	Oil pipeline, Khosravi area
PC3	550772.00	3818025.00	Oil pipeline, Khosravi area
PC4	552822.00	3817957.00	Oil pipeline, Khosravi area
PC5	621772.00	3784421.00	Oil pipeline, Kerend- Islamabad gharb
PC6	623106.00	3784421.00	Oil pipeline, Kerend- Islamabad gharb
PC7	624392.00	3784421.00	Oil pipeline, Kerend- Islamabad gharb
PC8	625726.00	3784469.00	Oil pipeline, Kerend- Islamabad gharb
PC9	546146.00	3757890.00	Oil well, Naft Shahr Area
PC10	546241.00	3765834.00	Oil well, Naft Shahr Area
PC11	549891.00	3762029.00	Oil well, Naft Shahr Area
PC12	550013.00	3758097.00	Oil well, Naft Shahr Area
PC13	553603.00	3765693.00	Oil well, Naft Shahr Area
PC14	553832.00	3762010.00	Oil well, Naft Shahr Area
PC15	553879.00	3757974.00	Oil well, Naft Shahr Area
PC16	558000.00	3762015.00	Oil well, Naft Shahr Area
PC17	563232.00	3762129.00	Oil well, Naft Shahr Area
PC18	579920.00	3804972.00	Oil pumping station, Shaheen Ghaleh Village
PC19	582540.00	3807491.00	Oil pumping station, Shaheen Ghaleh Village
PC20	582611.00	3802613.00	Oil pumping station, Shaheen Ghaleh Village
PC21	584947.00	3805084.00	Oil pumping station, Shaheen Ghaleh Village
PC22	584959.00	3799959.00	Oil pumping station, Shaheen Ghaleh Village
PC23	587446.00	3797471.00	Oil pumping station, Shaheen Ghaleh Village

Sixteen USEPA priority listed PAHs were targeted for analysis including naphthalene (NaP), acnaphthene (Ace), acenapthylene (Acy), fluorene (Flu), phenanthrene (Phe), anthracen(Ant), fluoranthene(Flt), pyrene (Pyr), benzo(a)anthracene (BaA), chrysene (Chr), benzo(k)fluoranthene (BkF), benzo (b) fluoranthene (BbF), benzo(a) pyrene (BaP), indeno (1,2,3-cd) pyrene (Ind), benzo(g,h,i) perylene(Bpe), and dibenzo(a,h)anthracene (DBA).

Sample extraction and cleanup was performed using the USEPA Method 3550B [18]. In brief, ten grams of soil samples were extracted using a Dionex ASE 300 accelerated solvent extractor equipped with 34 mL stainless-steel cells (Dionex, Sunnyvale, CA, USA). Two solvents of DCM and acetone (1:1, v/v) were utilized as extraction solvents. Selected operating conditions were as follows: the cell was preheated for 7 min to reach the set temperature of 140˚C, pressure of 1500 psi followed by a static extraction step of 5 min, and the extraction processes were performed twice. Before extraction, a range of surrogate PAHs (NaP-d8, Ace-d10, Ant-d10, Chr-d12 and Perelyne-d12) was spiked into soil samples (approximate twenty percent) for monitoring the efficiency of the extraction and cleanup procedures. The extracts were purified by loading on a silica gel column and finally adjusted to 1 mL under a gentle stream of N_2 prior to gas chromatograph analysis.

The individual PAH was quantified by gas chromatography (SHIMADZU 2010, Japan) using FID detector. An appropriate mass of 2-Fluoro-1,1'-biphenyl and pterphenyl-d_{14} was spiked into the vial as internal standards prior to each analysis. An HP-5 capillary column (length 30 m,

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internal diameter 0.25 mm, thickness 0.5µm, Agilent Technology) was used with five percent methyl phenyl silicon resin as stationary phase. The oven temperature was programmed as follows: 60˚C for 3 min., ramped at 10˚C per min to 120˚C and held for 3 min, ramped at 3˚C per min. to 300˚C and held for 23 min., with a total run of 95 min. The carrier gas was high-purity nitrogen (99.999 percent) with 2 mL per min flow rate and injection volume was 1µL. Injector and FID temperatures were kept at 280 and 320˚C, respectively.

3. Quality control and quality assurance

All data were subjected to strict quality assurance and control procedures. For every five samples, a method blank (solvent and glassware) and a matrix spike (working standards spiked into pre-extracted soil) together with the soil samples, and two duplicates were processed during the entire extraction, cleanup, and analysis. Detection limits (DL) of 16 individual PAHs were 0.02 (5- ring PAHs) and 1.17 (Phe) mg/kg.

4. PMF modeling

Several methods such as isomer ratios, principal components analysis (PCA) and positive matrix factorization (PMF) have been employed to identify PAHs sources in the environmental matrices [15, 19, 20, 21]. In this research, PMF model is used to determine PAHs sources.

PMF is a receptor modeling tool developed in the early 1990s by Paatero and Tapper [22], and utilized non-negativity constraints for finding physically realistic meanings. Detailed concept and application of PMF source apportionment were described in EPA PMF 5.0 Fundamentals &

User Guide (www.epa.gov/heasd/products/pmf)[23 and 24]. In brief, the PMF model is based on the following equation:

$$x_{ij} = \sum_{k=1}^{P} g_{ik} \mathcal{F}_{kj} + e_{ij}$$

Where x_{ij} is the j_{th} species concentration, measured in the i_{th} sample, g_{ik} is the k_{th} source's contribution to sample i, and $\mathcal{F}_{kj}$ is the j_{th} element's concentration in source k. e_{ij} is the residual associated with the j_{th} species concentration measured in the i_{th} sample. The objective function (Q) related to the residual and uncertainty is minimized using weighted least-squares by PMF, which is defined as:

$$Q(E) = \sum_{i=1}^{n} \sum (e_{ij}/u_{ij})^2$$

Where n and m are the number of samples and species, respectively; p represents the number of factors extracted; i=1, 2, ⋯⋯, n samples; j=1, 2, ⋯⋯, m species; k=1, 2, ⋯⋯, p sources, e_{ij} is the difference between the observations and the model; u_{ij} is the uncertainty for each observation.

The PMF solution minimizes the object function Q based upon the given uncertainty u [25 and 26]. The uncertainties for each sample were calculated using measurement uncertainties (MU %) and method detection limits (MDL). If the concentration ≤ MDL, the uncertainty u is calculated as:

$$u = \frac{5}{6} \times MDL$$

If the concentration > MDL, u is calculated as:

$$u = \sqrt{(\text{Error Fraction} \times \text{concentration})^2 + (0.5 \times MDL)^2}$$

PMF analysis was carried out using the US EPA PMF 5.0 model [24].

Results and discussion

1. Descriptive statistics and PAH distribution

Descriptive statistics of PAHs, pH and OC in petroleum-contaminated soils (PC) is summarized in Table 2. Average, max. and min. of organic carbon (OC) content are 1.12%, 0.06 and3.92% respectively. Soil pH varies between 7.04 and 7.92 with an average of 7.57 in PC soils. The lower OC content may be related to the alkaline nature of soils in the study area. pH shows negative correlation with PAHs, while OC reveals meaningfully positive correlation with total PAHs.

In PC soil samples, PAHs have a mean value of 92.82, ranging from 7.37 to 678.49 mg/kg. The average abundance order of different PAH ring compounds are 3 rings > 5+6 rings > 4 rings> 2 rings (Table 2 and Fig 2). Oil pipe lines (samples 6 and 8) indicate highest concentration of 5+6 rings (Figure 2).

Concentration of the 2-ring PAHs is in range of 0.06 to 13.47 dry weights (dw), while those of the 3-ring PAHs is in range of 0.07 to 361.15 mg/kg dw in PC soils. The dry weights (dw) of 0.02-15.13 mg/kg were recorded for the 4-ring PAHs. In addition, the concentration of the 5- and 6-ring PAHs ranged from 0.02 to 37.83 mg/kg in PC soils. The average abundance of carcinogenic PAHs is presented in Figure 3. P22, P21, P8, and P6 stations reveal higher concentration of carcinogenic PAHs, respectively.

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Table 2. Descriptive statistics of PC soils

Petroleum contaminated soils							
PAH compounds(ppm)	Ring	Minimum	Maximum	Mean	S. Deviation	Median	TEF**
Nap	2	0.06	13.47	23.14	3.85	0.52	0.001
Acy	3	0.14	118.10	12.86	32.12	1.2	0.001
Ace	3	0.07	361.15	43.90	95.47	3.27	0.001
Flu	3	0.82	35.93	7.75	11.22	2.37	0.001
Phe	3	1.17	33.82	9.09	7.72	6.62	0.001
Ant	4	0.03	10.69	3.93	2.88	3.55	0.01
Flt	4	0.11	15.13	2.30	4.33	0.63	0.001
Pyr	4	0.02	12.67	1.72	3.46	0.32	0.001
*Chr	4	0.06	2.64	0.65	0.68	0.36	0.01
*BaA	5	0.02	1.88	0.41	0.41	0.3	0.1
*BbF	5	0.02	12.29	1.31	3.44	0.19	0.1
*BkF	5	0.02	6.75	0.77	1.86	0.06	0.1
*BaP	5	0.02	8.60	1.23	2.29	0.63	1
Bp	5	0.02	37.83	2.30	2.51	0.33	1
*Ind	5	0.02	33.32	3.51	10.62	0.13	0.1
*DBA	6	0.07	12.05	1.02	9.42	0.14	0.01
pH		7.04	7.92	7.57	0.20	*	*
OC(%)		0.06	3.92	1.12	1.37	*	*
Sum PAHs		7.37	678.49	92.82	163.02	*	*
Sum PAHcarc		0.78	82.33	12.30	23.07	*	*

*Carcinogenic PAHs

** Toxic equivalancy factor

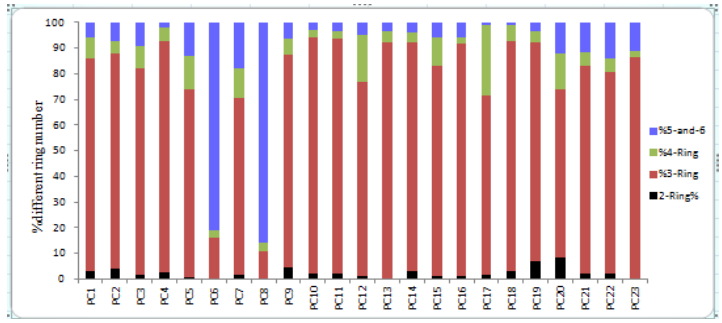

Figure 2. Percentage of aromatic rings in the soil samples

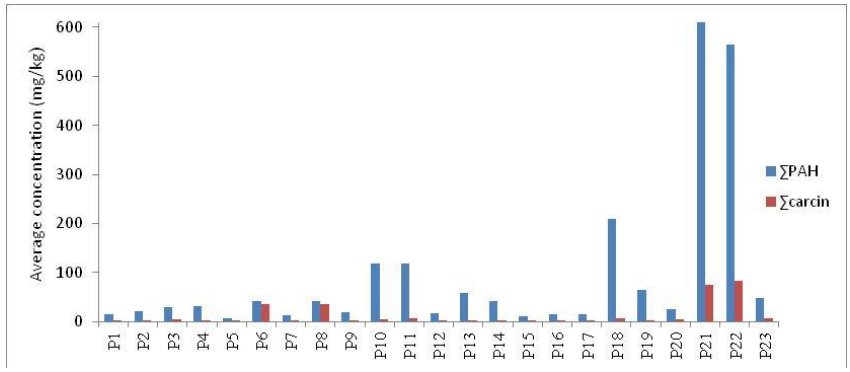

Figure 3. The average abundance of carcinogenic PAHs in PC soil samples

2. Risk assessment

Based on a large number of experimental studies, Long et al [27] and Jon et al [28] suggested the effects range low (ERL) and effect range median (ERM) criteria for determining the potential biologic effects of organic pollutants in soil, which is reflecting soil quality in marker levels of biologic effects. The ERL and ERM criteria were established using the 10^{th} and 50^{th} percentile of data sort in increasing concentrations order, related with adverse biological effects, in which ERL (4,022 μg/kg) stands for the potential eco-risk probability and ERM (44,792 μg/kg) is the transition point. Both of ERL and ERM are considered as the Eco-risk guidelines delineating three relative safety ranges. Concentrations below the ERL value represent a "Minimal-effects" range, a range intended to estimate conditions in which effects would be rarely observed. Concentrations equal to and above the ERL and below the ERM represent a "Possible-effects" range, showing occasionally occurring effects and finally, concentrations equal to and above the ERM value represent a "Probable-effects" indicating

a range in which effects would frequently occur [27 and 29]. In addition, Long et al [27] proposed that there was no safe minimum value for BbF, BkF, IcP, and DaA.

In the PC soil samples, individual concentrations of 16 PAHs ranged from 20 to 361150 ng/g dw. The measured concentrations of PAHs compared with the ERL and ERM values is presented in Table 3. All of the PAHs levels are higher than the ERL value, in the studied soil samples. In addition, all PAHs samples reveal higher concentrations than the ERM values, except Pyr, Chr, BaA, BbF, BkF and BaP in the PC soil samples. These results show that the PAHs levels in the soil samples would stand-in possible and Probable-effects to environment and organisms.

Benzo[a]pyrene (BaP) is used for a carcinogenic potency factor among all of the known potentially carcinogenic PAHs [30 and 31]. The toxic equivalency factors (TEFs) are available to quantify the carcinogenicity of other PAHs relative to BaP. According to USEPA, the TEFs values used in this study indicate carcinogenic potencies of PAHs in the PC soils (Table 2). These values are used to estimate benzo[a]pyrene equivalent doses (BaP_{eq} dose) by using the following equation:

$$\text{Total } BaP_{eq} \text{ dose} = \sum \text{dose}_i \times \text{TEF}$$

Where; dose_i is the concentration of special PAH and TEF_i is the corresponding toxic equivalency factor.

The total BaP_{eq} dose calculated for soil samples varied from 37.90 to 24010.70 μg/kg with a mean value of 2617.32 μg/kg in the soil samples. In comparison with other studies, the mean value in all of the PC soil samples is higher than those of surface soils of Agra, India (650 μg/kg-BaP_{eq}) [32], soil around airport in India (1021 μg/kg-BaP_{eq}) [33], soil from Tarragona

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County of Spain (124 μg/kg-BaP_{eq}) [34] and roadside soil of Shanghai, China (892 μg/kg-BaP_{eq}) [35]. The toxicity and carcinogenetic potency of the investigated site in PC soil samples was estimated by comparing the total carcinogenic potency with reference once (Dutch target). In PC soil samples of the study area, the values are higher than the Dutch target content (32.96 μg/kg), indicating the increased carcinogenic burden of these sites' soils. The value of BaP_{eq} for PC soil samples is shown on the Fig.4. PC21 and PC22 stations, due to higher concentrations of BbF, BaP, DBA and Ind, indicate considerable values of BaP_{eq} among petroleum soil samples.

Table 3. Standard pollution criteria of PAH components for soil (ppb)

Petroleum contaminated soils				
PAH compounds	ERL (ppb)	ERM (ppb)	average (ppb)	Maximum
Nap	160	2100	2314.5	13470
Acy	44	640	12866.8	118100
Ace	16	500	43908.6	361150
Flu	600	5100	7757.3	35930
Phe	240	1500	9095.0	33820
Ant	853	1100	3931.4	10690
Flt	19	540	2304.5	15130
Pyr	665	2600	1721.8	12670
Chr	384	2800	651.8	2640
BaA	261	1600	407.7	1880
BbF	320	1880	1317.3	12290
BkF	280	1620	769.8	6750
BaP	430	1600	1234.8	8600
DBA	63.4	260	1021.1	12050
Ind	Nd	Nd	3519.3	33320
Bpe	430	1600	2295.0	37830
Total	4022	44792	92821.8	678490

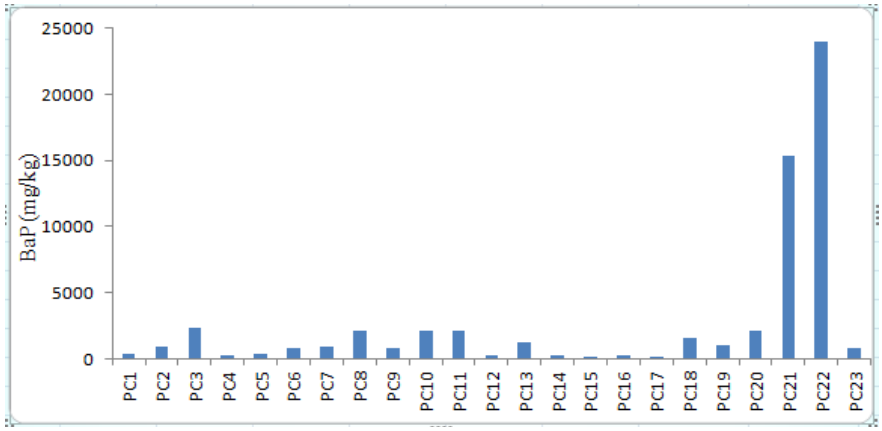

Figure 4. Concentration of BaP in sampling sites,

Source identification of PAHs using PMF

In order to evaluate the contribution of various sources affecting the PAHs contamination, PMF was adopted to model the data of PAHs associated with PC soil samples of Kermanshah province.

The PMF analysis used PAH concentrations as input data and was run in robust mode and three to seven factors were examined. As PMF is not an Eigen-based analysis, there is no apparent order in the factors arrangement.

Four factors identified by the PMF model for PAHs in PC soil samples are given in Figures 5a, b, c and d.

The first factor, accounting for 21.48% of the total variance, showing high concentrations of Phe and Ant that is indicator of biomass combustion [36]. It also has a moderate weighting of Acy applied as a trace of biomass combustion [37 and 38]. Phe is an important indicator of wood combustion [39]. Therefore, the source of this factor is identified as biomass/wood combustion (Figure 5a). Similarly, Liu et al, 2017[40] reported that the

wood/biomass burning is one of the main sources of PAHs in topsoil of the Issyk-Kul Lake Basin.

Factor 2, which accounted for 13.74 % of the sum of determined PAHs, was heavily weighted by Ace (Figure 5b). According to literature, its source is vehicular (gas and diesel) in nature [37 and 41].

Factor 3, explained 20.84% of the total variance (Figure 5c). Ace, Acy and Phe are dominated and typically emitted from coal or fossil fuel combustion [12, 39, 42 and 43]. High concentrations of Ace and Acy reveal oil contribution (unburned petroleum) [36]. This factor could be considered as a fossil fuel combustion/unburned petroleum (Fig 5c). Shakeri et al, 2016 [44] reported that the fossil fuel combustion is one of the main sources of PAHs in the industrial and bitumen contaminated soils of Kermanshah.

Factor 4 explained 43.92 % of the total variance. Ace, Flt and Pyr are predominant components of PAHs in creosote [45], identified as a creosote (Figure 5d).

Average mass contribution (percentage) obtained from PMF model for each factor is shown in Figure 6.

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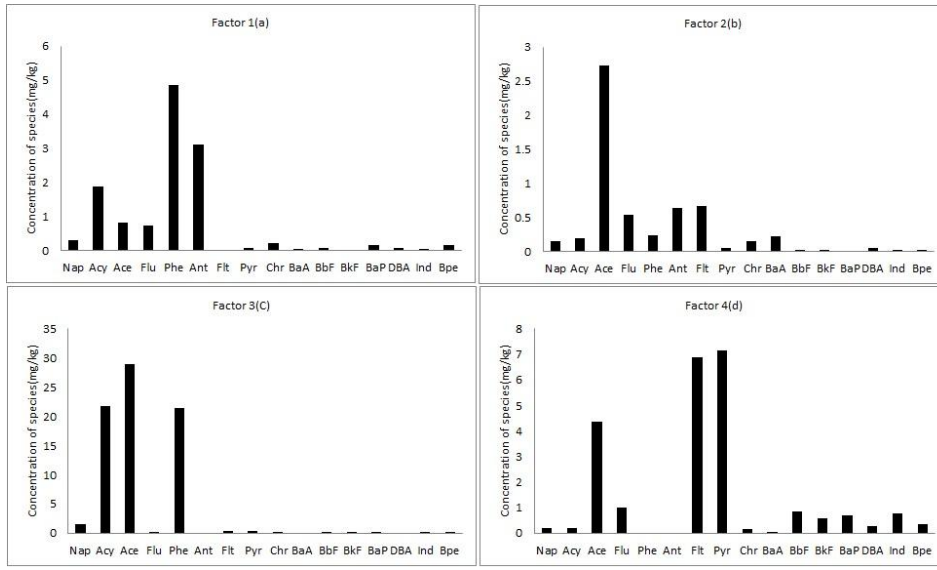

Figure 5. Source profiles of PC soils obtained from PMF model (a, b, c, d)

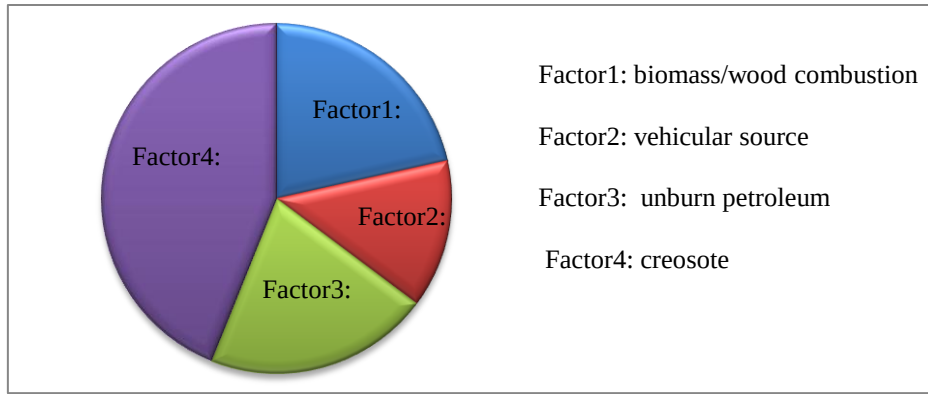

Figure 6. Source average mass contribution (%) of each factor for total PAH in PC soils

Conclusions

Soil samples were collected in petroleum contaminated soils of Kermanshah province to evaluate the health risk and investigate sources of polycyclic aromatic hydrocarbons (PAHs). The total PAHs concentration, have a mean value of 92.79 mg/kg, ranging from 7.37 to 609.67 mg/kg in PC soil samples. The average abundance order of different PAH ring compounds in PC soils are 3rings> 5+6 rings> 4 rings> 2rings. PMF model were used for sources identification of PAHs. PMF analysis identified four sources of PAHs including biomass/wood burning, vehicular source**,** unburned petroleum and creosote in soil samples. The PMF model provides a better result in comparison with other models, since it is based on point-by-point estimates of uncertainty errors in the dataset. The ecological risk assessment based on ERL and ERM showed that the PAHs levels in the soil samples stand-in possible and probable-effects to the environment and organisms. Result of the toxic equivalency factors based on benzo (a) pyrene equation (BaP_{eq}) values suggests that the carcinogenic potency of PAHs should be given more attention due to alarming potential of environmental risk in the west of Kermanshah province. Therefore, long-term monitoring of PAHs is essential to understand the fate of PAHs and their source-receptor relationship in the study area.

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