TPH and PAHs in an oil-rich metropolis in SW Iran: implication for source apportionment and human health

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Negar Ashjar[a], Behnam Keshavarzi[a*], Farid Moore[a], Naghmeh Soltani[a], Peter S. Hooda[b], Mohammad Reza Mahmoudi[c]

[a] Department of Earth Sciences, College of Science, Shiraz University, 71454 Shiraz, Iran

[b] School of Geography, Geology and the Environment, Kingston University London, Kingston Upon Thames KT1 2EE, UK

[c] Department of Statistics, Faculty of Science, Fasa University, Fasa, Fars, Iran

*Corresponding author: Behnam Keshavarzi

Negar Ashjar: n.ashjar@shirazu.ac.ir

Behnam Keshavarzi: bkeshavarzi@shirazu.ac.ir

Farid Moore: Moore@shirazu.ac.ir

Naghmeh Soltani: Naghmeh.soltani@shirazu.ac.ir

Peter S. Hooda: p.hooda@kingston.ac.uk

Mohammad Reza Mahmoudi: Mahmoudi.m.r@fasau.ac.ir

ABSTRACT

Several priority environmental mutagens and carcinogenic compounds were investigated in Ahwaz metropolis soil to estimate the extent of contamination and the risk they pose to human health. This included determination of total petroleum hydrocarbons (TPHs) and polycyclic aromatic hydrocarbons (PAHs) in 58 and 92 industrial soil samples, respectively using gas chromatography/mass spectrometry (GC/MS). The results indicate that total TPHs range between 1.2 and 11000 mg kg^{-1}, with a mean of 999 mg kg^{-1}, while total PAHs concentration vary between 6 and 47103 µg kg^{-1}, with a mean of 1241 µg kg^{-1}. The mean value of total PAHs in Ahwaz soil is much higher than many industrial soils around the world. The PAHs abundance in the soil samples based on the number of hydrocarbon rings was found in the following order: 4, 3 2, 5 and 6 ring hydrocarbons. Also, diagnostic ratios indicate that both pyrogenic and petrogenic compounds constitute the sources of these organic pollutants. The incremental lifetime cancer risk resulting from contact with soil PAHs for children and adults is extreme at the industrial sites, however the risk via inhalation is lower compared with other pathways. The findings of this study provide valuable information about the distribution of harmful organic pollutants in the soil environment.

Keywords: Ahwaz metropolis, industrial activities, soil pollution, TPHs and PAHs, source apportionment

INTRODUCTION

Increased urbanisation and industrialisation, particularly in developing countries with industrial manufacturing are connected with multiple problems such as waste-disposal, high energy consumption, increasing road traffic and demand for land which have imposed immense pressure on urban areas (Han et al. 2021). So, deterioration in urban environment is an expected consequence (Ashraf et al. 2014; Xie et al. 2018) which causes many environmental issues including soil, water and air pollution (Yang et al. 2010). The contaminants of greatest concern in these environments are TPHs and PAHs due to their negative effects on flora and fauna (Kim et al. 2018; Lors et al. 2018). These pollutants comprise a cluster of chemical compounds which during the process of manufacturing and/or their use are released into the environment. Industrial discharges, some agricultural practices along with commercial and domestic activities, and improper waste disposal are commonly recognized as major pathways through which organic pollutants are introduced in the natural environment (Vane et al. 2019). TPH is a term used to describe any mixture of hydrocarbons, which is commonly used petroleum contamination assessments (Gielnik et al. 2020). TPHs are priority pollutants, because of their persistence and toxicity, and they are an important source of environmental pollution on a global scale which enter the environment by accidents, leaks, spills, or by-products of domestic, commercial, and industrial activities (Patowary et al. 2017). Polycyclic aromatic hydrocarbons have also caught much attention in recent years due to their persistence in the environment and bioaccumulation through the food-chain (Kim et al. 2013). Human exposure to PAHs may occur through inhalation of dust in the air, dermal contact and ingestion pathways (Peng et al. 2011; Juhasz et al. 2016; Tong et al. 2018). Among the hundreds of PAHs, United States Environmental Protection Agency (US EPA) has promulgated sixteen PAHs as significant contaminants, due to their mutagenic and toxic effects. These have been extensively studied in numerous environments such as soil, dust, natural waters and living organisms (e.g., Sarigiannis et al. 2015; Sun et al. 2016; Zheng et al. 2016; Idowu et al. 2020; Nováková et al. 2020; Peng et al. 2020).

Soil is an important and valuable natural resource (Cachada et al. 2018) which acts as the ultimate sink for many deleterious compounds discharged into the environment by human activities. It is estimated that 90% of the released TPHs and PAHs to the environment end up in soils (Wild and Jones, 1995). The persistence of organic pollutants i.e., TPHs and PAHs in soil due to their high hydrophobicity, low vapour pressure and poisonousness, threatens public and environment health (Fitzgerald and Wikoff 2014; Liu et al. 2020). It is thus important that their soil concentration, particularly in urban environments is assessed and monitored for risk assessment and remediation strategies.

Ahwaz metropolis is a flourishing city in southwest of Iran which has some significant industrial complexes particularly those related to oil and gas exploration, steel industry and petrochemicals (Mohit et al. 2019). These industrial complexes are often scattered and located in urban communities. Thus, flourishing industrial activities, construction works, population and transportation growth in the absence of emission control measures and improper treatment of wastes originating from the various processes can have harmful consequences for the local environment and surrounding areas, with potential risk to human health (Rastegari Mehr et al. 2016).

The health risks to the local population from industrial contamination are a serious concern for Ahwaz metropolis as a major industrial area with a high population density, but there is no information available on concentration and distribution of TPHs and PAHs in the soil environment of the region. Thus, the main aims of this investigation were: (i) to determine the concentration, composition and spatial distribution of TPHs and PAHs in Ahwaz industrial soil; (ii) to uncover probable sources of PAHs; and (iii) to assess cancer risk of PAHs arising from industrial soil of Ahwaz metropolis.

MATERIALS AND METHODS

Study Area

Ahwaz metropolis (31°19′45″ N, 48°41′28″ E) as the centre of Khuzestan province is a semi-arid area, placed on the Karoon riverbanks in southwestern Iran. According to USDA (United States Department of Agriculture) soil taxonomy Aridisols and Entisols are the most common soil classes in the area. Ahwaz area covers 140 square kilometres with its current population of around 1.2 million (Statistical Center of Iran 2019). The long-term annual mean temperature and precipitation are 32°C and 209.2 mm, respectively. Ahwaz metropolis is an industrialized hub in Iran as it hosts many crucial industries including steel, oil and petrochemical industries with many industrial townships, power plants and agro-industries.

Soil Sampling and Sample Preparation

Using a pre-cleaned stainless-steel scoop, topsoil samples (0-10 cm) were collected from diverse locations within the industrial areas of Ahwaz metropolis. (Fig. 1). The sampling locations were chosen considering the type of industries and their activities, apparently ‘affected’ and ‘not affected’ areas of each targeted industrial complexes. In other words, multiple samples were taken from individual units so as be able to better understand the distribution of the targeted chemicals at each industrial unit – see Table S1in the Supplementary Information (SI).

In total, 92 representative industrial soil samples were collected, of which 58 and 92 samples were analysed for the determination of TPHs and PAHs concentration, respectively. Soil samples were collected from various districts of Ahwaz metropolis comprising steel factories, oil companies, power plants, industrial townships, agro-industries, bricks making factories, pipe mills and industrial carbon units– see Table S1, Supplementary Information. The sampling sites were so chosen to reveal soil exposure to various pollution sources, as given in Fig. 1 including people working in these industrial units and those live in their vicinity. Among 92 sampling sites, 58 sites were selected for TPHs analysis; Table S1 (Supplementary Information) provides detailed information of sampling locations, industrial activity, and samples selected for TPHs (T) and PAHs (P) analysis. Each sample is comprised of a composite of four subsamples taken from a rectangular-shaped area of 10 m^2 (Carter and Gregorich 2007). Non soil materials in the samples, e.g., roots, leaves, and gravels, were removed during sample collecting process and consequently passed through a 2-mm sieve. The samples were instantly put into amber glass bottles prewashed with foamy water and n-hexane then heated in oven at 180 °C for 3 h. The collected samples were kept in icebox containing dry ice packs at 4°C to reduce microbial degradation. The samples were sent to the research Institute of Isfahan University for TPHs and PAHs analyses using gas chromatography/mass spectrometry (GC/MS) methods, with appropriate quality assurance protocols.

Analytical Method and Quality Control

Following the procedures described in EPA 3550B (extraction) (EPA 2007), EPA 3630C (clean up) (EPA 1996), EPA 8310 (determination) (EPA 1986), EPA Methods 8270 (EPA 2014) for PAHs and EPA 418 for TPH, the samples were analyzed. In the laboratory, the samples were air-dried for 7 days and after homogenizing, 2-g of each sample was mixed with 100 ml dichloromethane (CH_2Cl_2) for 8 h, the extracts were concentrated to 1 ml using a rotary vacuum evaporator and 20 µl of the extract was analysed for TPHs and 16 PAHs, using a gas chromatography–mass spectrometry (GC-MS) instrument (Agilent 6890N GC, 5975C mass selective detector, MSD USA). A silica gel column was used to "clean up" the sample extract before analysis.

Naphthalene (Nap), Acenaphthene (Ace), Fluorene (Fl), Phenanthrene (Phe), Anthracene (Ant), Fuoranthene (Flu), Pyrene (Pyr), Benzo[a]anthracene (B[a]A), Chrysene (Chr), Benzo[e]Pyrene (B[e]P), Benzo[b]Fluoranthene (B[b]F), Benzo[k]Fluoranthene (B[k]F), Benzo[a]Pyrene (B[a]P), Benzo[g.h.i]Perylene (B[ghi]P), Dibenz[a,h]Anthracene (D[ah]A) and Indeno[1,2,3 cd]Pyrene (Ind) are the 16 assessed PAHs .Furthermore, TPHs ranging from C7 to C40 are considered in this research.

To monitor the analytical precision and accuracy of the methods for TPHs and PAHs a number of protocols such as procedural blanks (solvent), sample duplicates and standard mixtures were performed in every 10 samples. Furthermore, samples spiked with surrogate standards were included in the analysis (Pyrene-D10, lot: 10510 semi-volatile internal standards) for all species of PAHs, in other words PAHs compounds were calibrated by Pyr-D10 as internal standard and squalene was used as an internal standard for TPHs. Also, an ultrasonic bath (KUDOS, SK3210LHC model) was used during the extraction. The individual compounds recoveries ranged between 78% -106% with a mean of 87.8%. The analytical precision between the sample replicates ranged between 5 to 15%.

Physicochemical Properties of Soils

The soil pH was determined in 1:2 (w/v) soil-water suspensions, using a pre-calibrated pH meter. The soil organic matter was determined using the Walkley-Black procedure as outlined in Jha et al. (2014) and the hydrometer method was used to determine soil texture (Beretta et al. 2014).

PAHs' Source Identification

To assess the emission sources of PAHs in the industrial soil samples, diagnostic ratios and UNMIX model were applied (Finardi et al. 2017; Davis et al. 2019). Uncovering the source of the primary PAHs is essential to control their emissions in the field. Also, diagnostic ratios of PAHs are widely used to apportion these sources (Biache et al. 2014; Clément et al. 2015). So, these ratios (Table S2) were employed to distinguish between petrogenic (crude and fuel oils) and pyrogenic (petroleum, coal, and biomass combustion) sources (Yuan et al. 2014; Vaezzadeh et al. 2015). However, the distinction among particular pyrogenic or petrogenic sources, is limited due to the overlap between diagnostic ratios (Galarneau 2008; Stout and Emsbo-Mattingly 2008).

The Unmix mathematical receptor model based on factor analysis established by the U.S. Environmental Protection Agency (Morrison and Murphy 2015) is a common method to assign involvement from all main contaminant sources centred on measured profiles detected at sampling sites (Vega et al. 2000; Guo et al. 2004). A valuable method for estimating source contributions of PAHs in soil, sediment and other environmental matrices is Unmix model (EPA 2007; Norris and Henry 2019; Zhang et al. 2019), which assesses the number of sources relied on factor analysis (Lang et al. 2015). This model does not need prior information about emission sources (EPA 2007) and evaluates the number and composition of sources, and their contribution to each sample. Apportioning potential sources of PAHs in industrial soil of Ahwaz was done by applying the EPA Unmix 6.0 software.

Cancer Risk Assessment

The dominant pathways of lifetime exposure to the PAHs considered in this study for human are ingestion, inhalation and dermal contact. Amongst all recognized potentially carcinogenic PAHs, Benzo[a]pyrene is the only PAH for which toxicological data are adequate to prove its carcinogenic potency (Petry et al., 1996). Therefore, B[a]P (Benzo[a]Pyrene) toxic equivalent factors (TEFs) for each individual PAH (CCME 2010; Amjadian et al. 2016) and the concentration of individual PAHs (C) (µg kg^{-1}) given in Table 1, were used to calculate B[a]P toxicity equivalent (TEQ) concentration.

The (B[a]P) TEQ was determined using the following equation:

$$(B[a]P)TEQ = C \times TEF$$

Moreover, assessment of the exposure risk from environmental PAHs based on standard models was calculated using incremental lifetime cancer risk (ILCR) (USEPA 1991).

The following equations as per the USEPA standard models were used to calculate the ILCRs exposure via ingestion, dermal contact and inhalation (Gope et al. 2018). The exposure factors for ILCRs evaluation are given in the Supplementary Information (Table S3).

$$ILCRs_{\,Ingestion} = \frac{CS \times (CSF\ Ingestion \times \sqrt[3]{(BW/70))} \times IRSoil \times EF \times ED}{BW \times AT \times 10^{6}}$$

$$ILCRs_{\,Dermal} = \frac{CS \times (CSF\ Dermal \times \sqrt[3]{(BW/70))} \times SA \times AF \times ABS \times EF \times ED}{BW \times AT \times 10^{6}}$$

$$ILCRs_{\,Inhalation} = \frac{CS \times (CSF\ Inhalation \times \sqrt[3]{(BW/70))} \times IRair \times EF \times ED}{BW \times AT \times PEF}$$

Accordingly, negligible risk, potential risk and high cancer risk are associated with $\leq 10^{-6}$, 10^{-6} to 10^{-4}, and $>10^{-4}$, respectively (Chen and Liao 2006; Wei et al. 2015).

Geographical Information System (GIS) and Statistical Analysis

The inverse distance weighted technique (IDW) is a deterministic spatial interpolation procedure in geo-statistical information system. In this study IDW technique was applied to illustrate the path of spatial distribution of TPHs and ∑16PAHs concentration. Furthermore, to recognize correlation and probable sources of PAHs in the industrial soil samples of Ahwaz, principal component analysis (PCA) was applied using SPSS software version 24.0.

RESULTS AND DISCUSSION

TPH Concentrations

The concentrations of total petroleum hydrocarbons were determined in 58 industrial soil samples (Supplementary Information, Table S4). The results indicated that TPHs concentration range from 1.2 to 11000 mg kg^{-1}, with a mean of 999 mg kg^{-1} (Table 1). The highest TPHs concentration was measured at site T25 which is the waste storage site of Iran steel factory; and the lowest TPHs value was detected at site T37 (desalination unit of Karoon oil company). The mean TPHs concentration in industrial soil followed the following decreasing order: power plants (3134 mg kg^{-1}) > steel factories (1496 mg kg^{-1}) > pipe mills companies (1470 mg kg^{-1}) > industrial townships (1182 mg kg^{-1}) > bricks making factories (1053 mg kg^{-1}) > agro-industries (589.1 mg kg^{-1}) > oil companies (407.4 mg kg^{-1}) > industrial carbon units (21.5 mg kg^{-1}).

The highest limit of TPHs concentration in industrial soil according to the Mexican standard is 2000 mg kg^{-1} (ICRS, 2000). The concentration of TPHs in some stations including T25 (waste storage of Iran steel factory), T8 (Ramin power plant), T13 (Khuzestan steel factory), T5 (Zarghan power plant), T3 (industrial townships number 4), T58 (unit 3 of Karoon oil company), T22 (waste storage of pipe mills company) and T32 (unit 6 of Maroon oil company) exceeds the Mexican threshold value, while TPHs concentration in other sampled locations were below the threshold. In The Netherlands the intervention value (IV) for TPHs is 5000 mg kg^{-1} (VROM 2012; Pinedo et al. 2013). Accordingly, T3, T5, T13, T8 and T25 had TPHs concentrations are above the intervention value of 5000 mg kg^{-1}.

Furthermore, TPHs concentration in measured this study are lower than those detected in soil of a coastal Mexican refinery (non-detected (ND)-130000 mg kg^{-1}; Iturbe et al. 2004), subsoil of north-central Mexico (47-21093 mg kg^{-1}; Iturbe et al. 2005) and higher than the topsoil TPHs concentration in the proximity of a petrochemical complex in Guangzhou, China (1179-6354 mg kg^{-1}; Li et al. 2012).

The spatial distribution of total TPHs concentration in industrial soil of Ahwaz metropolis is presented in Fig. 2a. Heavily contaminated stations are situated close to industrial premises especially the steel factories, power plants and oil companies. While the stations located far from industrial premises with less anthropogenic activities are grouped as slightly contaminated. Elevated TPHs concentration in soil surrounding a petrochemical complex and oil field were also reported by Li et al. (2012) and Wu et al. (2021). Oil leakage during exploitation, transportation and temporary storage in various industrial areas/activities are the most important sources of TPHs (Teng et al. 2013).

PAHs Concentration

The PAHs concentration (Σ16PAHs) results in industrial soil of Ahwaz are presented in Table 1. The Σ16PAHs concentration range from 6 to 47103 μg kg^{-1} (mean 1241 μg kg^{-1}) – see Table S5, SI. P58 and P4 are the sites with the highest Σ16PAHs concentration, probably due to the presence of several petroleum units adjacent to these sites (Fig. 1). P77 is the site with the lowest Σ16PAHs concentration, as it is farthest from intense industrial activities (Fig. 1). The mean PAHs concentration (Supplementary Information, Table S5) in Ahwaz industrial soil were found to follow the following decreasing order: power plants (3893 μg kg^{-1}), industrial townships (2369 μg kg^{-1}), oil companies (1728 μg kg^{-1}), industrial carbon units (1234 μg kg^{-1}), steel factories (556.4 μg kg^{-1}), bricks making factories (490.8 μg kg^{-1}), pipe mills companies (309 μg kg^{-1}), agro-industries (133.1 μg kg^{-1}). The spatial distribution of total PAHs concentration is shown in Fig. 2b. Maliszewska- Kordybach (1996) presented a classification for soil contamination by PAHs, as summarized in Table 2. According to their classification,11 of our 92 sites (P58, P4, P11, P39,P7, P89,P6 , P15, P61, P47, P16) should be considered as “heavily contaminated”; 8 sites (P31, P25, P28, P88, P26, P42, P8, P56) as “contaminated”; 13 sites (P82, P40, P18, P55, P9, P41, P30, P49, P84, P78, P37,P29, P48) as “weakly contaminated” and the rest must be categorized as “uncontaminated”.

Phe, Nap, Pyr (non-carcinogenic PAHs) and BaA (carcinogenic PAHs) are the major compounds measured which accounted for about 23.1%, 20.2%, 13.7% and 10.9% of the total concentration of Σ16PAHs, respectively. Total concentrations of potentially carcinogenic PAHs including B[a]A, Chr, B[b]F, B[k]F, B[a]P, Ind and D[ah]A (Σ7CarPAHs) (USEPA 1993) range between 1.2 and 9215 µg kg^{-1} with the mean being 347.1 µg kg^{-1}. The Σ7CarPAHs make up about 26% of Σ16PAHs. Hence, carcinogenic compounds are less than non-carcinogenic compounds in most samples. The mean concentration of high molecular weight (HMW) PAHs (4-6 rings) is 589.9 µg kg^{-1} and the mean concentration of low molecular weight (LMW) PAHs (2 - 3 ring PAHs) is 651.4 µg kg^{-1} which means LMW PAHs are more abundant than HMW PAHs. Considering the number of aromatic rings, the 16 PAHs compounds can be separated into 5 categories comprising 2, 3, 4, 5, and 6-rings PAHs. Profiles of PAHs according to the number of aromatic rings in industrial soil of Ahwaz are plotted in Fig.3. 4 and 3-rings PAHs are more abundant and account for 38% and 32% of the total PAHs, respectively.

Numerous investigations on PAHs concentration in industrial soil have been undertaken around the world. The PAHs concentration in this study are considerably lower than those found in Loess Plateau, China (1010 -18068 µg kg^{-1}; Wang et al. 2018). However, the concentration range of Σ16PAHs in this study is still higher than several studies carried out around the world including Dalian in China (8738-13068 µg kg^{-1}; Wang et al. 2008), Tianjin in China (796.2-818.2 µg kg^{-1};

Wang et al. 2003), Benxi in China (729-783 µg kg^{-1}; Li et al. 2011), Terragona in Spain (34.4-6051 µg kg^{-1}; Nadal et al. 2007), Ulsan in Korea (65-12000 µg kg^{-1}; Kwon and Choi 2014).

Soil characteristics

Organic compounds fate in soil is influenced by soil characteristics (Maliszewska-Kordybach et al. 2009; Wang et al. 2018). Physicochemical characteristics of the soils determined in this study are summarized in Table 1. Soil pH is an important parameter in sorption and desorption of pollutants in soil (An et al. 2010; Olu-Owolabi et al. 2015). The industrial soil samples were generally alkaline with a mean pH of 8, ranging from 6.9 to 9.9, with no association of ∑PAHs and TPHs concentration with soil pH ($r < 0.01$), which indicate that the influence of pH was insignificant (Maliszewska-Kordybach et al. 2009).

The proportion of fine-grained particles (silt and clay) is higher than coarse grained particles (sand) in all analysed samples (Table 1). PAHs behaviour in soils is influenced by particle size i.e., soil mineralogy. It is well known that particle size plays an important role in the stabilization of PAHs, especially in regions with high PAHs pollution (Fang et al. 2007). Correlation analysis between clay content and ∑PAHs and TPHs concentration revealed a poor correlation ($r < 0.03$), which conflicts with the findings of Muller et al. (2000) and Krauss and Wilcke (2002).

A principal factor that affects PAHs' fate in the soil environment, is soil organic matter (SOM) as soils with greater amounts of SOM are known to adsorb greater amounts of PAHs (Cornelissen et al. 2005; Ukalska-Jaruga and Smreczak 2020). The highest SOM content was determined in Samadian brick – making factory while the minimum content was found in the vicinity of Karoon oil company soil. However, both areas are recognized as non-contaminated sites considering Maliszewska- Kordybach (1996) classification (Table 2). In addition, the poor association of PAHs and TPHs with SOM content ($r < 0.06$) may suggest that SOM may not play a significant role in

TPHs or PAHs content in soil which conflicts with the discoveries of Nam et al. (2008). Since no significant association was detected among the physicochemical variables (pH, clay content and SOM) with the PAHs concentration as found by Nadal et al. (2004) and TPHs concentration, hence, the accumulation or adsorption of contaminants in the soil were more affected by sources adjacent the sampling sites rather than the soil properties (Cetin 2016).

PAHs sources in soil

Chemical structures, emission sources, and combustion temperature commonly affect the distribution of PAHs in the environment (Kuppusamy et al. 2016). Isomer ratios are claimed to recognize PAHs sources (Finardi et al. 2017; Kim et al. 2017; Ozaki et al. 2020). Since both natural and anthropogenic emissions are major sources of PAHs that may affect the composition of PAH compounds in soil. Discriminating between pyrogenic and petrogenic PAHs was achieved by employing four PAHs diagnostic ratios (Fig. 4). Based on the $\sum$LMW/$\sum$HMW ratios, between the 92 sampling sites, 14 sites (P4, P46, P53, P57, P58, P60, P70, P71, P73, P76, P87, P88, P90, P91) were found to be influenced by petrogenic sources and 78 sites by pyrogenic sources (Fig. 4a). Within the affected sites by petrogenic sources, 9 sites were close to oil companies, 4 sites were located in agro-industries and 1 site was in the vicinity of an industrial township. Therefore, petrogenic origin of PAHs in these sites obviously has resulted from oil installations and oil leakage/spillage (Soclo et al. 2000; Kwon and Choi 2014; Sojinu et al. 2010).

The results indicate that at most sampling locations the An/ (An + Phe) ratio is < 0.1 and Flu / (Flu + Pyr) ratio is < 0.4, suggesting petrogenic sources for most contaminated industrial soil (Fig. 4b).

BaA/(BaA + Chr) ratio is 0.41 signifying the pyrogenic source of PAHs, while the ratio of Flu/(Flu+Pyr) (< 0.4) which indicates petrogenic, biomass and coal combustion and mixed sources

(Fig. 4c). The ratio of Flu/ (Flu+Pyr) (< 0.4) indicates all the sites except P4 site are influenced by petrogenic sources (Fig. 4d). Thus, PAHs diagnostic ratios illustrated different PAHs sources, indicative of biomass and coal combustion, petrogenic and pyrogenic sources in the sampling sites as reported by others (e.g., Yang et al. 2013; Chen et al. 2018; Yurdakul et al. 2019; Minkina et al. 2020).

In this study PCA was applied to assess the degree of involvement of diverse PAHs sources. Based on PCA, two factors related to industrial soil PAHs sources were extracted. The results indicated that 80% of the total variance is described by two major components constituting 48.7% and 31.3% for PC1 and PC2, respectively (Table 3). PC1 is dominated by Flu, Pyr, B[a]A, Chr, B[e]P, B[b]F, B[k]F, B[a]P, D[ah]A, B[ghi[P, and Ind while PC2 included Nap, Ace, Fl, Phe and Ant.PC1 and PC2 correlate with HMW (high molecular weight) PAHs and LMW (low molecular weight) PAHs, respectively (Table 3). Based on the number of aromatic rings, the principal components revealed two distinctive PAH clusters. Component 1 strongly correlates with 4-6 ring PAHs linked to industrial activities. Flu, Pyr and BaP suggest that PAHs may be associated with coal combustion (Simcik et al. 1999; Larsen and Baker 2003). BbF is usually a constituent of fossil fuel combustion (Rogge et al. 1993; Kavouras et al. 2001). Flu and BbF compounds with high loading coefficients are also indicative of coal combustion (Zeng et al. 2019). IcdP, BaP and BghiP often originate from traffic emissions (Liu et al. 2010); while BaA and Chr are associated with incineration of both diesel and natural gas (Khalili et al. 1995). Thus, PC1 indicates that a large portion of PAHs in Ahwaz industrial soil samples results from pyrogenic sources. All PAHs in PC2 belong to low molecular weight PAHs, revealing that they originate from highly volatile petroleum sources (Pampanin and Sydnes 2013) and non-combusted petroleum products (Feng et al. 2020). Additionally, high loadings of most low-ring-number PAHs, such as Nap, Ace and Fl, are considered as products of wood- and coal-burning emissions (Dong and Lee 2009). Therefore, PC2 was considered a combination of wood, coal and petroleum sources.

A valuable tool in understanding and depicting PAHs emission sources is the Unmix model (Norris and Henry 2019). The model determined three categories of PAHs with the percentages of factors 1, 2 and 3 being 62.7 %, 20.9% and 9.8%, respectively (Fig. 5).

Naphthalene and low loading of Chr, BkF, BbF, B (ghi)P and Ind comprise factor 1(or source 1) (Fig. 5). The maximum burden of Nap reflects that an important part of the crude oil and petroleum products is the lighter portion (Mai et al. 2003; Saha et al. 2009). Ind and Chr are frequently measured as indicators of diesel engine emission, whereas B[b]F, B[k]F and B[ghi]P are vital constituents of fossil fuels (Li and Kamens 1993; Harrison et al. 1996). Therefore, factor 1 is probably a mixed source of petrogenic and pyrogenic origins.

High values of Fl and Nap were identified in factor 2 (or source 2) (Fig. 5). Compounds resulting from coking emissions are consistent with Fl (Khalili et al. 1995; Simcik et al. 1999). B[ghi]P and Ind are usual indicators of gasoline combustion emission (Khalili et al. 1995; Larsen and Baker 2003; Jo and Lee 2009) and heavy oil combustion (Harrison et al. 1996; Lee et al. 2004). As reported in the literature high factor loadings for B[b]F and B[k]F are most probably connected to diesel motor vehicle emissions (Harrison et al. 1996; Lee et al. 2004). Hence, factor 2 is connected to vehicular emissions.

High ratios of HMW PAHs, comprising Chr, B[k]F, B[b]F, B[ghi]P and Ind occur in factor 3 (or source 3) (Fig. 5). HMW PAHs, comprise the principal PAHs in the vehicular emissions as reported in previous research (Amador-Muñoz et al. 2010). Lee et al. (2004) attributed the occurrence of HMW PAHs to heavy oil combustion. Consequently, factor 3 is thought to result from pyrogenic sources.

Cancer risk assessment

The carcinogenic toxic equivalents (TEQ) of PAHs for industrial soil of Ahwaz metropolis were calculated. The results indicate that TEQ concentration for PAHs in Ahwaz soil samples ranged from 0.3 to 1332.3 µg kg^{-1}. The highest TEQ concentration occurred at site P58 (unit 6 Maroon oil company); while the lowest TEQ concentration occurred at site P72 (unit1 of Karoon oil company). According to the risk-based soil criterion for human health protection from Canada, the TEQs levels of PAHs in all sampling sites except P58, P4, P11 and P39 sites were below the safe level of 600 µg kg^{-1} (CCME 2010). TEQ of PAHs in the industrial soil of Ahwaz metropolis (81.8 µg kg^{-1}) is much lower than that reported from China (Liu et al. 2010) and Turkey (Yurdakul et al. 2019).

The results of ILCRs exposure assessment are presented in Table 4. Probably due to low body weight of the children and higher volumes of unintentional soil ingestion, the cancer risk for children is much higher than for adults. Furthermore, children often explore their environments with bare feet and hands, increasing the surface area of exposure. Thus, children are faced with greater health hazards than adults, which is consistent with other findings (Cao et al. 2019). In this study the major ILCRs pathway of exposure to soil is through dermal absorption which many studies have shown that dermal absorption is a significant pathway for chemical exposure (Schachter et al. 2020). In fact, passive diffusion of chemicals from the skin surface to its inner layers controls the absorption of chemical into the human body (US-EPA 1992). The skin condition and chemical concentration gradient such as higher PAH concentrations, drier skin, and skin occlusions due to layers of clothing (Semple, 2004) play an important role in the uptake of chemicals through contact with human skin and can result in greater chemical absorption.

The total assessed ILCR, exceed the standard limit of USEPA (ranging between 10^{-6} and 10^{-4}), and indicates that urban inhabitants living in the vicinity of industrial townships are exposed to adverse health effects (Table 4).

4. CONCLUSION

Distribution of TPHs and PAHs in the industrial soil samples of Ahwaz metropolis were studied in this research. The ILCR model for PAHs revealed that cancer risk for children is much higher than for adults, mainly because of their investigative behaviours. Various PAHs sources including wood and coal combustion, petroleum and industrial sources, pyrogenic and vehicular emission are distinguished. Local contamination originating from industrial activities, particularly oil industry contributes to PAHs accumulation in the soils. Moreover, local industries play a significant role in increasing traffic and the resultant pollution. The results also indicated that 67.4% of the samples with TPHs values higher than Dutch intervention value, apparently come from petroleum and its products. Thus, it is necessary to control contamination sources and current level of pollution to protect the health quality of a large number of Ahwaz metropolis residents.

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- Competing interests

The authors declare that they have no competing interests

- Availability of data and materials

All data generated or analysed during this study are included in this published article [and its Supplementary Information files].

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Table 1. Descriptive statistics of TPHs (mg kg $^{-1}$) and PAHs (µg kg^{-1}) in industrial soil of Ahwaz

Compound	TEF	Aromatic ring	N	DL	Minimum	Maximum	Mean
TPH			58		1.2	11000	999
Nap	0.001	2	92	0.2	BDL	18000	250
Ace	0.001	3	92	0.2	BDL	820	23.3
Fl	0.001	3	92	0.3	BDL	5800	78.8
Phe	0.001	3	92	0.1	0.3	13000	287
Ant	0.01	3	92	0.1	BDL	340	11.1
Flu	0.001	4	92	0.4	BDL	820	43.6
Pyr	0.001	4	92	0.1	BDL	5100	170
B[a]a	0.1	4	92	0.1	BDL	4700	136
Chr	0.01	4	92	0.1	0.3	3900	119
B[e]p	0.01	5	92	0.3	BDL	610	36.6
B[b]f	0.1	5	92	0.1	BDL	300	15.5
B[k]f	0.1	5	92	0.3	BDL	510	22.2
B[a]p	1	5	92	0.3	BDL	330	7.8
Db[ah]a	1	5	92	0.2	BDL	280	17.1
B[ghi]p	0.01	6	92	0.2	BDL	200	14.2
Indene	0.1	6	92	0.2	BDL	85	6.6
∑PAH					6	47103	1241
LMW					0.8	32270	651
HMW					4.9	14833	589
% 2 rings					0.1	64.9	14.3
% 3 rings					1.8	65.3	13.1
% 4 rings					18.2	82.2	49.9
% 5 rings					1.9	44.6	17.2
% 6 rings					0.001	23.4	5.3
SOM (%)					0.1	15.1	5.1
pH					6.9	9.9	8
Clay (%)					2.3	47.6	17.9
Silt (%)					6.6	74.6	37.5
Sand (%)					7.7	83.7	44.7

DL: detection limit

BDL: below detection limit

ΣPAHs: total 16PAHs concentration

LMW: low molecular weight (2–3 ring PAHs) (Mai et al. 2003)

HMW: high molecular weight (4–6 ring PAHs) (Essumang et al. 2011)

TEF: PAHs toxic equivalency factor with respect to Bap (Nisbet and LaGoy 1992)

Table 2. Classification of soil contamination by PAHs (Maliszewska- Kordybach 1996)

Class of soil contamination	$\sum$P16 PAH (μg kg^{-1})
Not contaminated	<200
Weakly contaminated	200–600
Contaminated	600–1000
Heavily contaminated	>1000

Table 3. PCA analysis of PAHs in Ahwaz industrial soil

	Component	
Compound	PC1	PC2
Nap	0.1	**0.8**
Ace	0.5	**0.8**
Fl	0.5	**0.8**
Phe	0.6	**0.7**
Ant	0.5	**0.7**
Flu	**0.8**	0.4
Pyr	**0.7**	0.6
B[a]A	**0.7**	0.6
Chr	**0.7**	0.6
B[e]P	**0.9**	0.3
B[b]F	**0.9**	0.2
B[k]F	**0.9**	0.3
B[a]P	**0.5**	0.4
Db[ah]A	**0.8**	0.4
B[ghi]P	**0.8**	0.4
Indene	**0.9**	0.3
% of Variance	48.7	31.3
Cumulative %	80.00	

Table 4. R values of three exposure routes and total cancer risk of PAHs in Ahwaz industrial soil

	ILCR ingestion		ILCR dermal		ILCR inhalation		Cancer risk	
	Children	**Adult**	**Children**	**Adult**	**Children**	**Adult**	**Children**	**Adult**
Maximum	7.76E-01	5.65E-01	4.78E+00	1.93E+00	7.75E-06	4.51E-05	5.56E+00	2.50E+00
Minimum	2.15E-04	1.57E-04	1.33E-03	5.36E-04	2.15E-09	1.25E-08	1.54E-03	6.93E-04
Mean	4.77E-02	3.47E-02	2.94E-01	1.19E-01	4.76E-07	2.77E-06	3.42E-01	1.54E-01

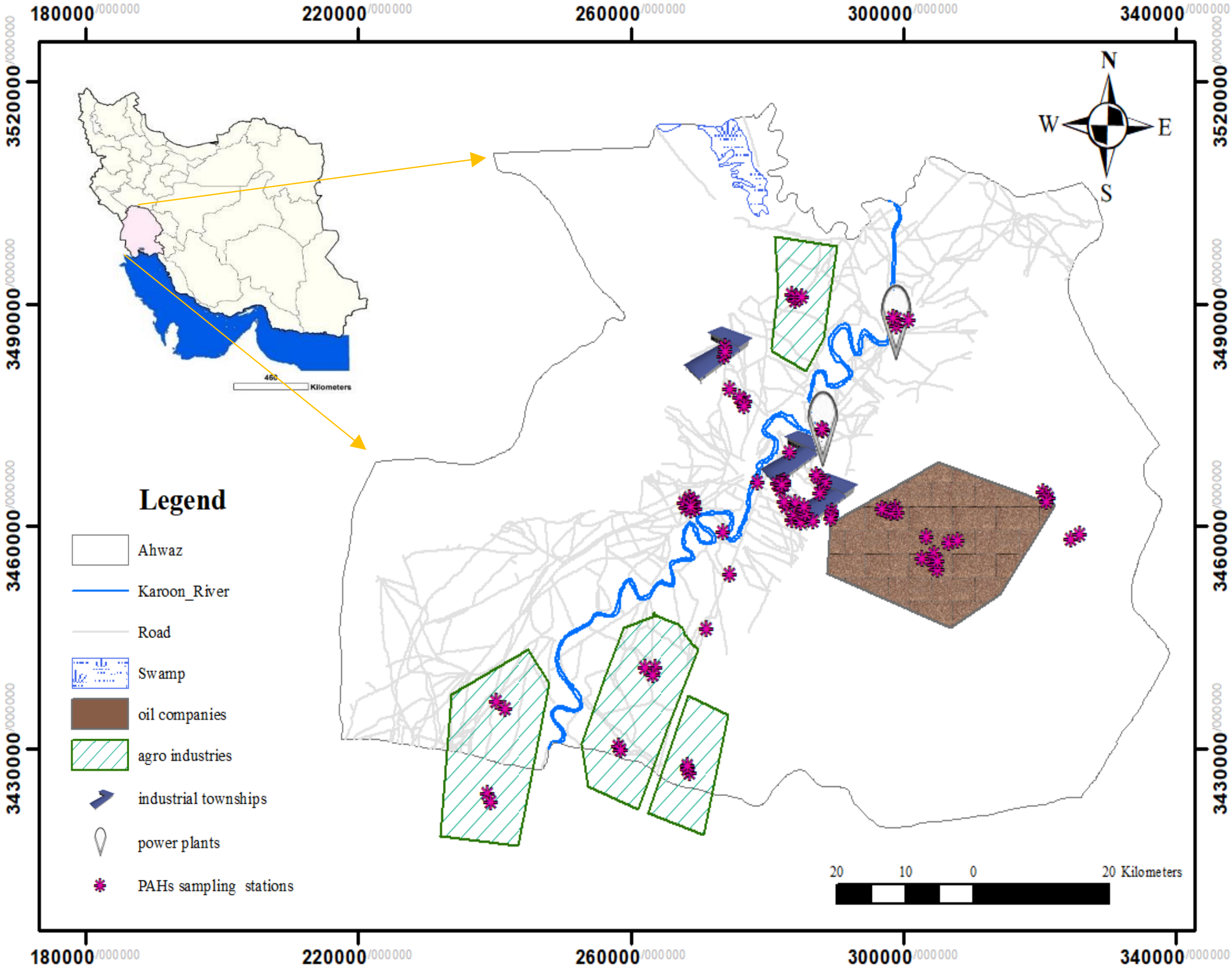

Fig. 1. Sampling sites of Ahwaz industrial soil

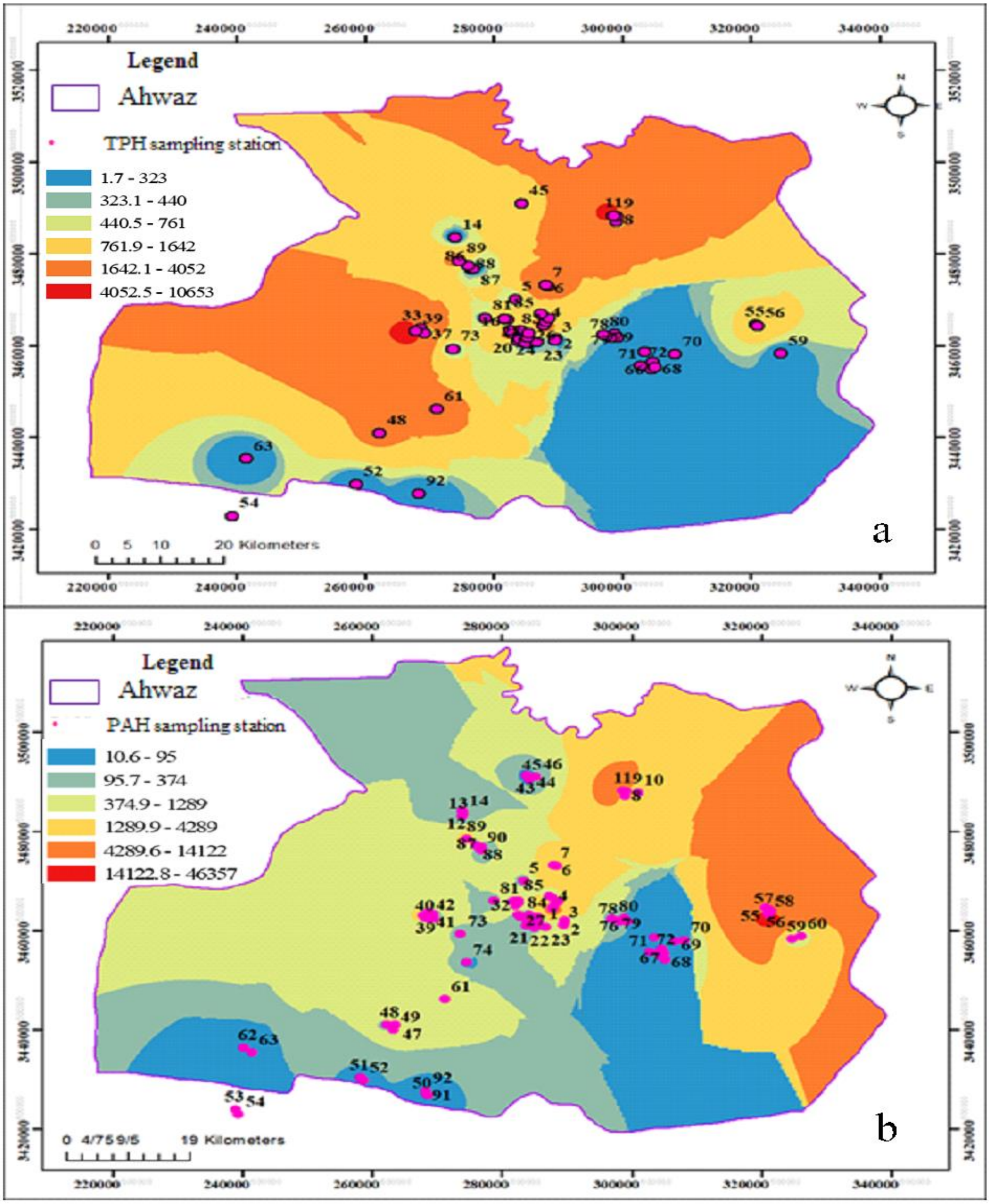

Fig. 2. Distribution map (a) TPHs concentration (mg kg $^{-1}$) (b) PAHs concentration (µg kg^{-1}) in industrial soil of Ahwaz

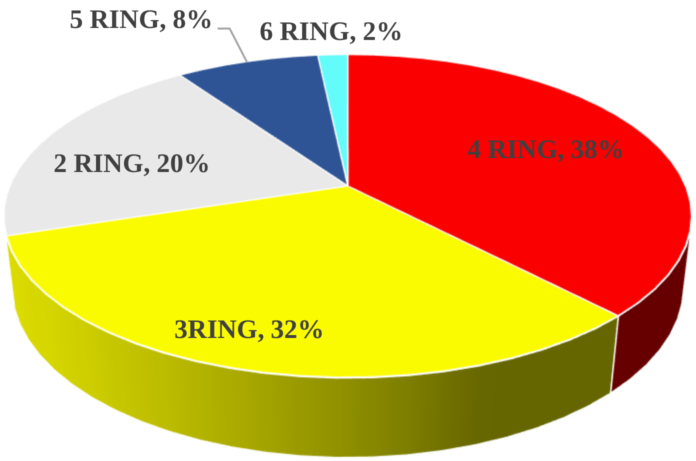

Fig. 3. Distribution of PAHs in Ahwaz industrial soil samples according to the number of aromatic rings

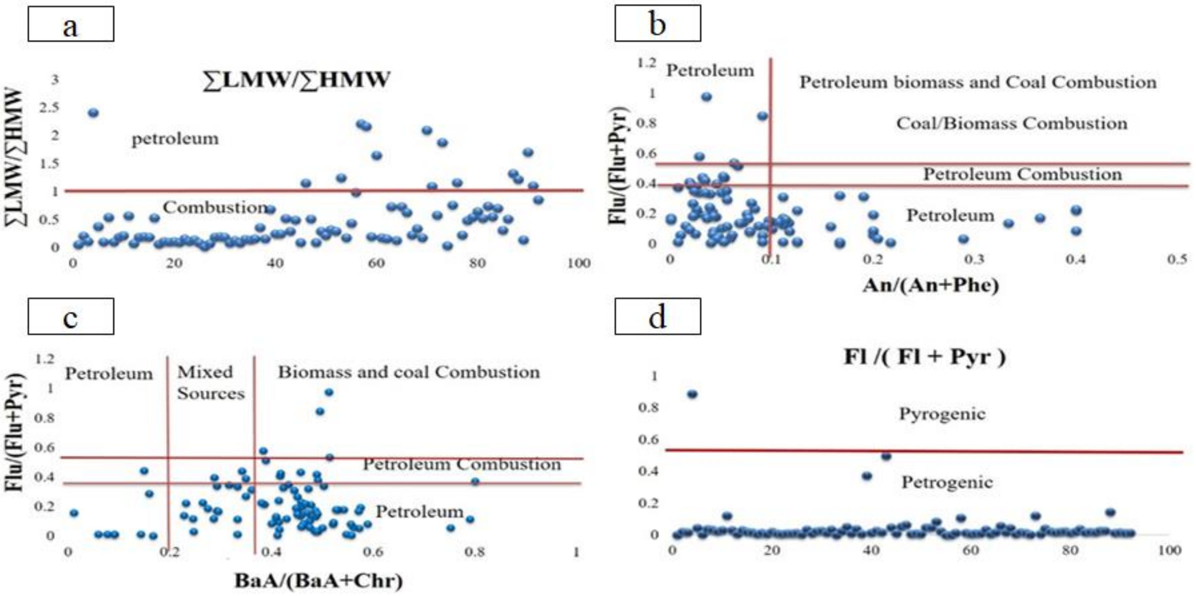

Fig. 4. Diagnostic ratio charts for (a) ∑LMW/∑HMW, (b) Ant/ (Ant +Phe) and Flu/ (Flu + Pyr), (c) BaA/ (BaA + Chr) and Flu/ (Flu + Pyr) and (d) Fl/ (Fl+Pyr) in Ahwaz industrial soil

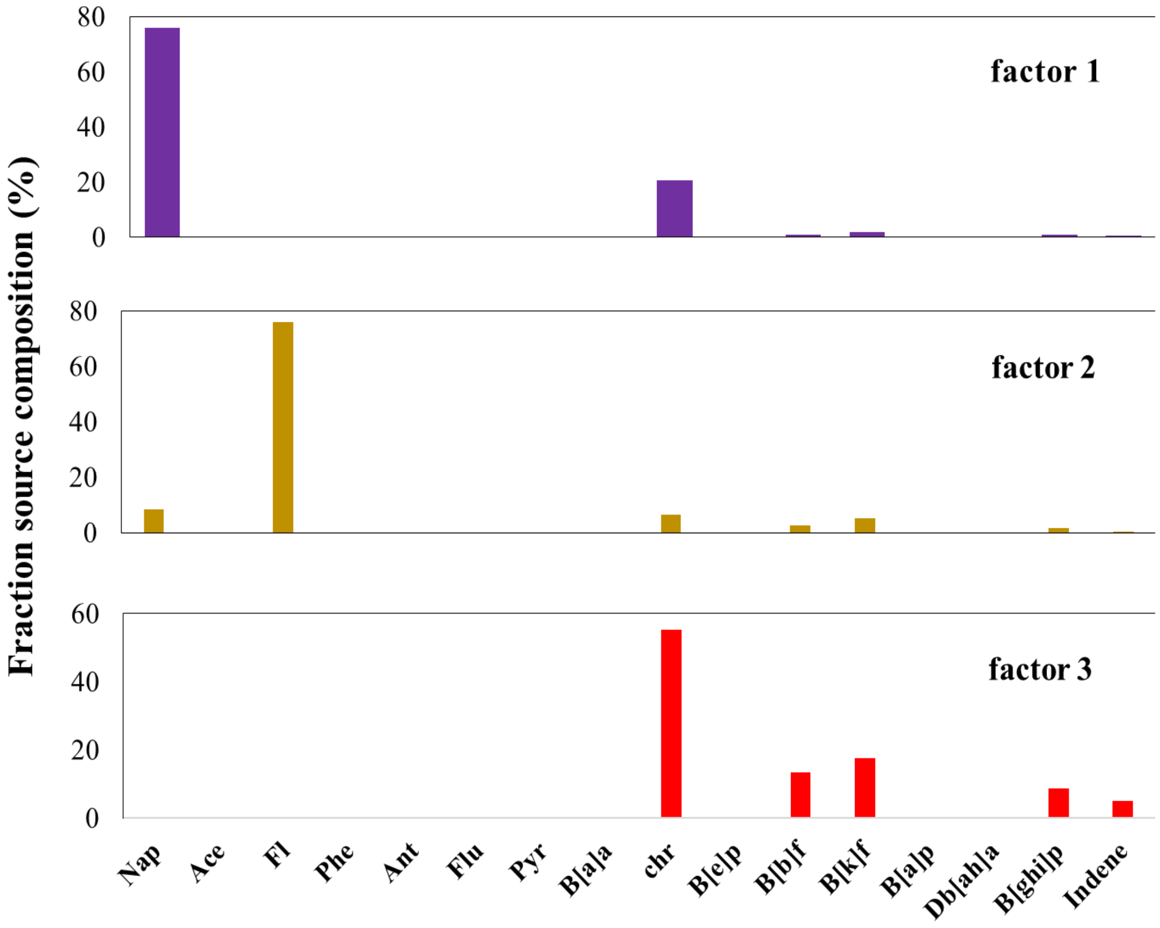

Fig. 5. Unmix model analysis of PAHs in Ahwaz industrial soil

SUPPLEMENTARY INFORMATION

Table S1. Sampling sites of Ahwaz industrial soil.

Description of the industrial soil sampling sites at Ahwaz metropolis	**UTM zone 39 N**		**Sample ID**	
	X	**Y**	**PAH**	**TPH**
Industrial town number 3 (in front of Padideh Oxin company, Sanat Street 4)	289717	3462004	P1	
Industrial town number 3 (in front of Paya steel company and Parsumash casting)	289726	3461578	P2	T1
Industrial town number 3 (Andisheh street 3)	289532	3461109	P3	T2
Industrial town number 4	287838	3464387	P4	T3
Industrial town number 1 (mostly turnery)	283380	3470015	P5	T30
Zargan power plant (end of power plant, near waste storage)	288413	3472933	P6	T4
Zargan power plant (adjacent to cooling unit 1)	288099	3473125	P7	T5
Ramin Power Plant (south part, adjacent to chimneys)	299130	3487036	P8	T6
Ramin power plant (north part, between mazut reservoirs)	299202	3488058	P9	T7
Ramin power plant (outpart power plant, in wind direction)	300968	3487760	P10	
Near Ramin power plant (fuel trucks)	298592	3488218	P11	T8
Industrial town number 2 (north part)	273887	3484169	P12	
Industrial town number 2 (southern part)	273867	3482986	P13	
Industrial town number 2 (central part)	274011	3483522	P14	T9
Carbon company (adjacent to unit 2 "in operation")	282056	3465601	P15	T10
Carbon company (adjacent to unit 1 "in operation")	282248	3465592	P16	T11
Khuzestan steel complex (waste storage)	284240	3463234	P17	T12
Khuzestan steel complex (north-west waste storage oil waste)	282889	3462706	P18	T13
Khuzestan steel complex (waste storage, southwest)	283798	3460888	P19	T14
Khuzestan steel complex (between steel making and pelletizing unit)	284052	3461480	P20	T15
Khuzestan steel complex (southeast part in wind direction)	284976	3461073	P21	T16
Out part the area of Khuzestan steel complex (in wind direction, Khit village)	285049	3460486	P22	T17
Southeast of Khuzestan steel (in wind direction)	286793	3460731	P23	T18
Oxin steel (adjacent to Khuzestan steel)	285373	3461772	P24	T19
Oxin steel (south part)	285722	3461670	P25	
The north part of the Oxin steel plant	285561	3462736	P26	T20
Upstream of Khuzestan steel factory (against wind direction)	282657	3463252	P27	T21
Oil company piping (Jahad waste storage)	281705	3465836	P28	T22

Continue Table S1. Sampling sites of Ahwaz industrial soil.

Description of the industrial soil sampling sites at Ahwaz metropolis	**UTM zone 39 N**		**Sample ID**	
	X	**Y**	**PAH**	**TPH**
Oil company pipeline (first yard, uncovered pipe storage)	282215	3465933	P29	
Oil company piping (pipe covering workshops)	282592	3466042	P30	
The second area of the oil company's pipeline	282544	3465585	P31	
The second area of the oil company’s pipeline (southeast part)	282204	3464981	P32	
Kavian steel plant (waste storage)	268708	3463733	P33	T23
Kavian steel factory	268916	3463303	P34	
Rolling and pipe factory (with metal chips, between Kavian and Ahwaz rolling)	269000	3463185	P35	
Rolling factory and pipelines (east part of the factory)	269457	3463270	P36	
Ahwaz rolling and piping factory (in front of the rolling unit)	269303	3462713	P37	T24
Ahwaz rolling and piping (waste collection site, factory border and Khoramshahr road)	269610	3462384	P38	
factory of national Iranian steel industrial group (waste storage)	267899	3463078	P39	T25
National Iranian steel industrial group (transportation of waste collection and dust filters)	268306	3462501	P40	
National Iranian steel industrial group (next to Kowsar complex)	268895	3462219	P41	
National Iranian steel industrial group (adjacent to the melting plant)	268826	3462676	P42	
Dehkhoda agro-industry (behind the factory, there is a lot of metal and wood waste)	283829	3491335	P43	
Dehkhoda agro-industry (south part of the factory)	284298	3490424	P44	
Dehkhoda agro-industry (adjacent to the main factory)	284423	3490905	P45	T26
Dehkhoda sugarcane (north part)	285308	3490982	P46	
Dabal khazaei agro-industry (east part)	263637	3440981	P47	
Dabal khazaei agro-industry (end of factory)	262262	3440969	P48	T27
Dabal khazaei agro-industry	263337	3440006	P49	
Farabi agro-industry (against wind direction)	268659	3426661	P50	
Salman farsi agro-industry (administrative department)	258213	3430369	P51	
Salman farsi agro-industry (adjacent to the main factory)	258686	3429780	P52	T29
Agro-industry of Mirza kuchak khan	239014	3423972	P53	
Agro-industry of Mirza kuchak khan (in the direction of the factory wind)	239454	3422890	P54	T28
Unit 6 of Maroon operating company (adjacent to the desalination pool)	320694	3464567	P55	T31
Unit 6 of Maroon exploitation company (between well 258 and exploitation torch)	321144	3464282	P56	T32

Continue Table S1. Sampling sites of Ahwaz industrial soil.

Description of the industrial soil sampling sites at Ahwaz metropolis	**UTM zone 39 N**		**Sample ID**	
	X	**Y**	**PAH**	**TPH**
Unit 6 of Maroon exploitation company with a distance from the burners	321537	3463880	P57	
Unit 6 of Maroon operating company (Chah 302)	321130	3463310	P58	
Unit 1 of Maroon oil company (adjacent to salt desalination pool)	324748	3458233	P59	T33
Unit 1 of Maroon oil (adjacent to the torches)	326121	3458829	P60	T34
Pottery factory (Sweet pottery)	271245	3446183	P61	T35
Agro-industry of Amir kabir	240270	3436347	P62	
Agro-industry of Amir kabir (east part)	241549	3435354	P63	T36
Karoon oil company (desalination unit)	304404	3455579	P64	T37
Unit 1 of Karoon (adjacent to the salt desalination pool)	304700	3456343	P65	T38
Unit 1 Karoon (southern long torches)	304597	3454831	P66	T39
Unit 1 of Karoon (south of the area of pressure booster burners)	305181	3454161	P67	
Unit 1 of Karoon (fingerprint burners that are off)	305151	3455368	P68	T40
Unit 1 of Karoon (Maroon petrochemical)	306729	3457847	P69	
Unit 1 of Karoon (adjacent to 4 long torch of the refinery)	308182	3458063	P70	T41
Unit 1 Karoon (channel adjacent to well 408)	303525	3458581	P71	T42
Unit 1 of Karoon (western part of unit 1)	302869	3455617	P72	T43
Jangieh and Jill brickwork range	273690	3459218	P73	T44
Samadian brick making factory	274573	3453503	P74	
Unit 4 Karoon oil (in wind direction, Karoon burners)	298573	3462035	P75	T45
Unit 4 Karoon oil	298885	3462450	P76	T46
Unit 4 of Karoon (at a greater distance from the torches)	299302	3461812	P77	T47
Unit 4 of Karoon (oil effluent exits at this point)	298252	3461781	P78	T48
Karoon 4 (beginning of the small torch)	297558	3462108	P79	T49
Karoon 4 (west side, the last torch)	297020	3462410	P80	T50
Karoon 2 complex (Aghajari town)	278783	3465938	P81	T51
Karoon 2 complex (east and southeast of the torches)	288200	3465199	P82	T52
Karoon 2 (east of the region)	288676	3465907	P83	T53
Karoon 2 (next to the desalination pool)	287754	3466660	P84	

Continue Table S1. Sampling sites of Ahwaz industrial soil.

Description of the industrial soil sampling sites at Ahwaz metropolis	**UTM zone 39 N**		**Sample ID**	
	X	**Y**	**PAH**	**TPH**
Karoon 2 (west side, near the city)	287304	3466950	P85	T54
Unit 3 of Karoon (east of the exploitation unit, in wind direction)	276595	3476693	P86	T55
Unit 3 of Karoon (east of the Torches)	276898	3476839	P87	T56
Unit 3 of Karoon (between salt basin and torches)	276072	3477348	P88	T57
Unit 3 of Karoon (the western point of the region)	274651	3478434	P89	T58
Unit 3 Karoon (short torch, company entrance)	276823	3476171	P90	
Farabi agro-industry (in the middle of the factory)	268344	3427231	P91	
Farabi agro-industry (beginning of the company, accumulation of plastic waste)	268380	3427730	P92	T59

Table S2. Diagnostic ratios used in identifying PAHs pollution sources in Ahwaz industrial soil.

PAH ratio	Value range	Source	refrence
∑LMW/∑HMW	<1	Pyrogenic	Magi et al., 2002; Soclo et al., 2000
	>1	Petrogenic	
Fl/(Fl + Pyr)	<0.4	Petrogenic	Xiao et al., 2014
	>0.4	Pyrogenic	
Ant/(Ant+Phe)	<0.1	Petrogenic	Budzinski et al., 1997; Yunke et al., 2002
	>0.1	Pyrogenic	
Ind/Ind+BghiP	<0.2	Petrogenic	Ye et al., 2004
	0.2-0.5	Liquid fossil fuel combustion	
	>0.5	Pyrogenic	
BaA/(BaA+Chr)	<0.2	Petrogenic	Zhang et al., 2006; Pies et al., 2008; Kuppusamy et al., 2016
	0.2-0.35	Pyrogenic	
	>0.35	Combustion of coal, grass and wood	
Flu/(Flu+Pyr)	<0.4	Petrogenic	Yunker et al., 2002
	0.4-0.5	Fossil fuel combustion	
	>0.5	Grass, wood, coal combustion	

Table S3. Parameters used in the incremental lifetime cancer risk assessment.

Exposure variable	**Unit**	**Children**	**Adult**	**Reference**
BW (body weight)	kg	13.9	58.7	MHC (2007)
EF (exposure frequency)	day $year^{-1}$	350	350	USDOE (2011)
ED (exposure duration)	year	6	24	Hu et al. (2017)
$IR_{inhalation}$ (inhalation rate)	m3 day^{-1}	10	17	Hu et al. (2017)
$IR_{ingestion}$ (soil ingestion rate)	mg/day	200	100	USDOE (2011)
SA (dermal exposure area)	cm^2	2800	5700	US EPA (2001)
AF (dermal adherence factor)	mg cm^{-2}	0.2	0.07	US EPA (2001)
ABS (dermal adsorption fraction)	Unitless	0.13	0.13	US EPA (2001)
AT (average lifespan)	day	70 × 365 = 25550	70 × 365 = 25550	Ferreira-Baptista and De Miguel (2005)
PEF (particle emission factor)	m3 kg^{-1}	1.36×10^9	1.36×10^9	US EPA (2001)

Table S4. TPHs concentrations (mg kg^{-1}) in Ahwaz industrial soil.

Sample	TPHs	Sample	TPHs	Sample	TPHs
T1	33	T21	22	T42	1.4
T2	21	T22	2900	T43	3.2
T3	5800	T23	43	T44	7.6
T4	33	T24	41	T45	14
T5	6000	T25	11000	T46	14
T6	29	T26	1200	T47	4.7
T7	10	T27	1900	T48	480
T8	9600	T28	410	T49	16
T9	40	T29	10	T50	1000
T10	22	T30	20	T51	13
T11	21	T31	4.4	T52	1700
T12	11	T32	2400	T53	4.2
T13	6700	T33	4.2	T54	510
T14	38	T35	2100	T55	160
T15	36	T36	6.2	T56	3.7
T16	19	T37	1.2	T57	2
T17	32	T38	12	T58	3200
T18	18	T39	220	T59	8.8
T19	21	T40	3.6		
T20	14	T41	7.1		

Table S5. PAHs concentrations (μg kg^{-1}) in Ahwaz industrial soil

sample/Compound	**Nap**	**Ace**	**Fl**	**Phe**	**Ant**	**Flu**	**Pyr**	**B[a]a**	**Chr**	**B[e]p**	**B[b]f**	**B[k]f**	**B[a]p**	**Db[ah]a**	**B[ghi]p**	**Indene**
P1	0.3	0.2	0.3	5.6	0.3	5.1	42	7.6	8.4	9.3	5.7	6.7	4.7	4.8	4.3	1.8
P2	3.9	1	0.5	5.2	0.4	3.5	21	4.8	5.7	4.8	2.7	3	0.3	2.5	1.7	1
P3	4.5	0.6	0.4	0.3	0.2	2.2	22	4.4	5.1	4.6	2.9	1.7	2.1	2.8	1.4	0.8
P4	1000	820	5800	5100	340	820	700	950	900	610	300	510	78	280	200	50
P5	2.8	0.8	0.7	15	0.4	4.2	15	5.2	5.7	4.5	2	2.4	0.3	6.3	4	1.8
P6	17	2.5	2	140	7.9	290	370	160	190	170	88	130	20	63	34	19
P7	94	12	20	990	26	300	480	530	550	91	39	27	8.9	18	20	18
P8	37	6	8	6.1	3.5	47	220	42	51	52	33	44	25	22	23	16
P9	8.5	1.8	1.5	46	0.9	43	61	25	35	40	21	33	4.6	20	16	8
P10	3.5	0.5	0.6	3.2	0.2	0.8	19	2.7	2.8	2.3	1.9	1.8	2	1.2	1.1	0.8
P11	1500	530	610	3400	290	420	4400	3000	2100	390	260	490	0.3	0.2	0.2	0.2
P12	0.3	1	1.3	3	0.3	2.5	40	7.1	5.3	6.5	4.1	3.9	0.3	2.6	2.1	1.1
P13	2.4	0.5	0.4	9.3	0.6	3.1	47	7.9	2.6	1.5	0.7	0.7	0.8	0.7	0.9	0.4
P14	2.5	0.6	0.4	3.8	0.1	3.1	12	3.4	4	3.3	1.5	1.9	1.2	2.4	1.7	1
P15	15	11	7	190	7.8	160	320	110	150	140	49	50	10	77	95	42
P16	230	4.3	4.2	120	3.4	120	230	35	85	87	27	21	3.7	35	20	9.2
P17	0.3	0.2	0.3	1.2	0.3	1.7	7	2.6	3.2	3.7	1.9	1.8	0.8	1.8	1.3	0.8
P18	11	2.9	2	33	2.7	35	140	120	89	19	7.5	6.5	0.3	6.6	4	1.8
P19	0.3	0.2	0.3	2.8	0.1	1.6	6.7	1.7	4.5	8.1	2.4	0.8	0.7	1.6	1.2	0.8
P20	0.3	1.2	1	9.1	1.2	7.8	47	11	12	8.5	5.1	5.8	0.3	3.8	4.5	2
P21	1.2	0.4	0.5	8.3	0.7	4.2	46	8.4	9.8	9.3	5.4	6.7	1.2	7.5	8	3.8
P22	1.2	0.2	0.3	2.8	0.1	3.9	7.5	1.9	3.8	3.1	1.4	0.5	0.6	1.2	1.4	0.5
P23	0.3	0.2	0.3	1.3	0.1	0.8	5.7	0.8	2	1.9	0.9	0.3	0.3	0.8	0.6	0.15
P24	1.6	0.2	0.3	2.8	0.2	5.4	5	2.6	4.1	4.8	2.1	2.2	0.7	2.8	2.1	0.6
P25	18	2.2	1.8	45	1.7	27	130	320	240	37	12	8.5	9.1	11	6.2	2.6
P26	3	0.5	0.3	11	0.6	73	89	21	120	160	44	9.2	9.7	62	48	21
P27	0.3	0.2	0.3	2.1	0.1	5.6	8.3	2.1	5.2	3.5	1.2	0.8	0.7	2	2.5	1.1
P28	33	2.5	2.7	100	5.3	120	230	91	90	65	33	39	0.3	31	17	8

Continue Table S5. PAHs concentrations (μg kg^{-1}) in Ahwaz industrial soil

sample/Compound	Nap	Ace	Fl	Phe	Ant	Flu	Pyr	B[a]a	Chr	B[e]p	B[b]f	B[k]f	B[a]p	Db[ah]a	B[ghi]p	Indene
P29	12	1.2	1.6	21	0.9	18	64	17	27	18	6.9	4.8	0.3	14	7	2
P30	8.6	1.8	2.5	42	0.1	19	89	36	38	9.9	19	29	4	16	10	8
P31	14	1.6	2	56	1.5	36	120	18	50	170	44	11	14	180	140	80
P32	2.5	0.4	0.5	1.7	0.4	6.5	14	3.1	5.5	3.3	1.7	1.3	1.3	1.2	2	1.1
P33	0.3	0.2	0.3	6.8	0.3	3.9	41	8.9	8.2	6.9	4.2	0.3	0.3	4.2	3.4	1.8
P34	2.7	0.4	0.5	2.3	0.1	1.3	19	2.8	3.1	2.9	1.8	1.6	2.5	1.8	1.2	0.6
P35	5.2	1	1.2	1.6	0.3	3	22	17	4.5	4.9	2.6	2.4	0.3	3.2	2.6	1.2
P36	1.3	0.2	0.06	0.9	0.1	0.6	5.3	1.2	1.7	1.6	0.8	0.6	0.6	1	0.6	0.5
P37	15	1.8	2.2	40	0.9	12	53	26	22	14	7.7	8.7	4.8	7.2	4.3	2.6
P38	6.8	0.4	0.3	2	0.1	2.3	44	2.2	3.1	2.3	0.9	0.7	0.7	1.4	1	0.8
P39	580	95	84	1300	130	810	140	530	540	340	210	240	0.3	150	130	85
P40	2.1	1.5	1.1	96	2.8	110	79	28	45	44	16	16	3.4	32	23	15
P41	5.9	2.5	2	62	1.3	46	71	22	41	41	16	11	5.9	11	14	8
P42	100	3.3	2	110	6.4	55	100	52	68	51	19	17	6.5	19	18	10
P43	0.3	0.2	0.3	2.7	0.1	2.6	0.1	2	1.9	1.3	0.7	0.6	0.3	0.5	0.7	0.3
P44	2.5	0.4	0.3	3.3	0.3	1.8	5.9	1.1	1.3	0.9	0.6	0.6	0.3	0.4	0.5	0.4
P45	0.3	0.2	0.3	0.8	0.1	0.4	5.4	1.1	1.3	1.1	0.6	0.6	0.3	0.7	0.5	0.3
P46	45	1.9	1.5	38	1.3	19	25	6.3	8.8	4.9	2.2	2.2	1.3	2.1	2.3	1.8
P47	8.1	35	22	330	3.3	21	310	230	180	11	2.7	3.8	5.2	3.2	2.4	1.9
P48	0.3	0.9	0.5	17	0.8	15	67	35	31	12	7.4	5	0.3	8.5	5.1	2.5
P49	11	1	0.7	49	1.6	44	55	14	27	19	9.4	8.1	1.6	11	13	8
P50	1.7	0.2	0.3	0.8	0.2	0.4	6.1	1.2	1.2	0.8	0.6	0.7	0.3	0.6	0.7	0.3
P51	2.4	0.4	0.4	5.7	0.2	5.7	7.8	4.2	4.4	1.6	0.7	0.6	0.3	1.1	1	0.5
P52	2.5	0.4	0.5	2.1	0.1	0.4	10	1.6	1.7	1.4	1	0.9	0.3	0.8	0.7	0.3
P53	4.8	0.7	0.5	8.9	0.2	2	5.4	0.9	1.1	0.8	0.5	0.4	0.3	0.3	0.5	0.15
P54	4.4	0.5	0.4	2.4	0.3	7.3	16	4.4	5.5	2.8	1.6	1.4	1.4	1.8	1.5	0.5
P55	95	0.2	0.3	42	1	30	55	18	39	51	22	35	3.4	18.6	24.3	12.3
P56	220	0.3	0.3	80	5.8	10	62	90	95	15	2.5	1.5	9.3	8.6	7.2	6.3

Continue Table S5. PAHs concentrations (μg kg^{-1}) in Ahwaz industrial soil

sample/Compound	Nap	Ace	Fl	Phe	Ant	Flu	Pyr	B[a]a	Chr	B[e]p	B[b]f	B[k]f	B[a]p	Db[ah]a	B[ghi]p	Indene
P57	18	0.2	0.3	0.9	0.1	0.7	3.9	0.9	1.1	0.5	0.2	0.3	0.3	0.6	0.5	0.2
P58	18000	550	620	13000	100	91	5100	4700	3900	340	8.7	140	330	95	87	42
P59	2	0.2	0.3	0.8	0.1	0.9	4.2	0.7	1.7	1.4	0.6	1.1	0.3	1.9	1.2	0.8
P60	15	0.3	0.3	2.4	0.1	0.4	6.6	0.7	1	0.8	0.3	0.3	0.3	0.6	0.5	0.2
P61	130	4.2	3.8	64	8.5	30	310	150	120	53	11	20	12	178	169	54
P62	2.1	0.2	0.3	1.6	0.2	0.9	6	1.8	2.6	2.5	1.2	2.5	0.2	3.2	2.1	1
P63	4.5	0.3	0.3	15	0.6	2.8	8.5	2.4	3.4	2.3	0.8	1.4	0.3	3.1	2.3	0.8
P64	2.1	0.2	0.3	1.7	0.1	2.8	6.7	0.7	3.7	4.5	2.1	2.8	0.3	3.3	2.3	0.7
P65	5.1	0.2	0.3	0.8	0.1	0.4	3.5	0.1	0.8	0.4	0.1	0.3	0.3	1	1.3	1
P66	10	0.3	0.3	1.2	0.1	1	4.8	2.5	6	1.7	0.1	0.3	0.3	0.9	1.1	0.5
P67	0.3	0.2	0.3	0.9	0.1	0.4	3.5	0.1	0.5	0.6	0.2	0.4	0.3	0.2	0.2	0.2
P68	2.8	0.3	0.3	0.7	0.1	1.9	6.5	0.3	1	0.3	0.1	0.3	0.3	1	0.9	0.2
P69	0.3	0.2	0.3	2.1	0.2	1.1	7.9	1.8	2.4	0.3	0.5	0.3	0.4	0.2	0.2	0.2
P70	14	0.2	0.3	0.7	0.1	0.4	3.5	0.3	0.6	0.6	0.3	0.3	0.3	0.9	0.6	0.2
P71	8	0.2	0.3	1	0.1	0.4	3.6	0.1	0.6	0.6	0.2	0.3	0.3	1.4	1.6	0.2
P72	18	0.3	0.3	2.3	0.2	4.9	13	2.2	4.1	3.4	1.6	2.9	0.3	1.7	1.4	0.2
P73	45	0.9	1.1	39	0.3	4.7	7.8	20	5	2.1	0.4	0.3	0.3	1.8	2.3	1.2
P74	0.3	0.2	0.3	0.3	0.2	2	6.9	2.7	3.1	1.6	0.8	1.2	0.3	1.4	1.6	1
P75	38	0.3	0.3	13	1.4	1.3	7	25	26	5.4	0.5	2.3	1	0.4	0.3	0.2
P76	23	0.5	0.3	2.5	0.5	0.4	11	0.6	3	2.4	0.1	0.8	0.6	1.8	1.7	0.9
P77	0.3	0.2	0.3	0.7	0.1	0.4	3.3	0.1	0.5	0.3	0.1	0.3	0.3	0.4	0.3	0.2
P78	68	1.2	1	4.2	2.1	7.6	47	29	42	5.7	1.9	0.9	5.5	5.8	6.2	3.2
P79	36	0.9	1.1	3.2	1.3	1.7	45	5.9	18	0.3	2	0.3	0.6	1.8	1.5	0.9
P80	65	0.8	0.6	3.9	1	1.6	40	22	23	0.3	0.4	0.3	5.8	5.9	8.2	2.1
P81	16	0.5	0.4	5	0.6	2.9	17	2.3	7.8	3.4	0.1	0.4	0.5	5.2	3.1	0.2
P82	52	3	3.6	170	3.3	10	93	98	90	3.3	3	2	6	2.5	2.8	0.2
P83	23	0.3	0.3	2.5	0.5	7.7	16	4.2	4.7	4.6	2	3.6	0.3	3	1.6	0.2
P84	72	0.7	0.6	25	3.2	5.7	29	39	44	11	0.7	1.4	2.5	4.6	3.6	1.5

Continue Table S5. PAHs concentrations (µg kg^{-1}) in Ahwaz industrial soil

sample/Compound	Nap	Ace	Fl	Phe	Ant	Flu	Pyr	B[a]a	Chr	B[e]p	B[b]f	B[k]f	B[a]p	Db[ah]a	B[ghi]p	Indene
P85	28	1	0.4	0.9	0.6	6	20	9.2	15	17	1.3	2.4	3.9	9.8	7.6	4.3
P86	19	0.5	0.4	4.5	0.2	3.2	14	10	9	3.6	0.9	1.9	0.3	2	1.5	0.8
P87	32	0.6	0.4	1.9	0.2	1.8	13	1.2	3.7	2	0.7	0.9	0.3	1	1.2	0.9
P88	2.6	18	22	360	0.2	25	130	0.8	71	57	22	4.8	0.3	8.2	7.3	3
P89	140	6.5	6.9	130	36	5.7	490	740	590	67	7.1	40	100	52	48	22
P90	12	0.2	0.3	0.5	0.1	0.4	3.4	0.1	0.3	0.6	0.2	0.3	0.3	1	1.2	0.5
P91	8	0.2	0.3	0.8	0.2	0.4	4.1	0.8	1.2	0.3	0.2	0.3	0.3	0.5	0.5	0.2
P92	3.3	0.2	0.3	5.1	0.3	0.6	4.4	0.4	0.8	0.3	0.2	0.3	0.3	1.2	1.7	0.5