



Research article

Asphalt dust influence on the distribution of polycyclic aromatic hydrocarbon in crankcase oil stains of a concrete, covered parking structure

Muna Zabarmawi ^{a,b,*}, Fabien Kenig ^b^a Department of Environment and Agricultural Natural Resources, King Faisal University, Hofuf, Saudi Arabia^b Earth and Environmental Sciences, University of Illinois Chicago, Chicago, IL, USA

ARTICLE INFO

Keywords:

Crankcase oil
PAHs
Oil stains
Parking dust
Street dust
Biodegradation

ABSTRACT

Used crankcase oil is an important source of environmental polycyclic aromatic hydrocarbons (PAHs). Here, we use gas chromatography-mass spectrometry (GC-MS) to measure and compare the concentration of PAHs, including alkylated PAHs, in used oil against new and old oil stains and parking dust collected from a concrete, covered, open parking structure to understand the distribution of PAH in crankcase oil stains. PAH concentration in used oils ranges from 606 ng/mg to 1,592 ng/mg. The PAH distribution in used oil does not match that observed in parking oils stains, parking background, or parking dust. A comparison with PAH distributions in traffic related dusts extracted from the literature and dust collected from a neighboring open asphalt-paved parking suggests that covered parking dust includes substantial contributions from asphalt-paved parking dust, road dust, and/or coal tar dust. The parking dust is the most concentrated source of PAHs in the covered parking structure (PAHs up to 4,371 ng/mg), a small contribution of which can alter the distribution of PAHs in oil stains. Even with this contribution, we were able to observe a significant decrease of the ratio of low molecular weight PAHs to high molecular weight PAHs, and a significant increase in values of the phenanthrene/anthracene and fluoranthene/(fluoranthene + pyrene) ratios when oil stains age, suggesting biodegradation is an active attenuation process in covered, open parking structures.

1. Introduction

The adverse effects exerted by polycyclic aromatic hydrocarbons (PAHs) in used crankcase oil on the environment have been known for nearly four decades [1]. Engine oil comprises 80 %–90 % base oil [2,3] and up to 20 % oil additives that enhance performance [1,4]. When engines run, PAHs are transferred to crankcase oil as fuel-incomplete combustion byproducts and form in the oil at high temperatures [1,5–7]. The presence of PAHs in used crankcase oil is significant, even at low vehicle mileage [5,8]. When an engine leaks oil, PAHs are directly introduced into the environment as crankcase oil, which is then deposited on parking and roadway surfaces.

Although there are two main types of commonly used paving surfaces, Portland cement and asphalt, the latter is primarily used because it is cheap, easy to use, and easy to maintain [9,10]. For example, in the U.S. in 2019, 2.9 million miles of roads were paved,

* Corresponding author. King Faisal University, Unit 1, Hofuf, 36362, Saudi Arabia.

E-mail address: mzabarmawi@kfu.edu.sa (M. Zabarmawi).

<https://doi.org/10.1016/j.heliyon.2024.e35881>

Received 18 March 2024; Received in revised form 4 August 2024; Accepted 5 August 2024

Available online 8 August 2024

2405-8440/© 2024 Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

and approximately 92 % were paved with asphalt [11]. Over time, weather-related conditions such as changes in temperature, solar radiation, rainfall, and wind cause asphalt pavement to deteriorate. Thus, sealcoating is applied to protect the pavement [12]. The most common sealants used are asphalt- and coal-tar-based [13,14]. The PAH concentration in coal-tar sealant (50,000 ng/mg) is 1000 times higher than that in asphalt sealant (50 ng/mg) [15]. Among transportation-related PAH sources, used crankcase oil is the second highest contributor, only preceded by coal-tar sealant [16].

The amount of oil leaked on roadways and parking floors is directly dependent on the average age of light vehicles. Cars that have been driven for >80,000 to 100,000 miles generally leak crankcase oil as the engine seals and gaskets age [17,18]. Leaked engine oil is a worldwide issue, and its environmental and health consequences are particularly acute in developing countries where used cars with high mileage are imported in larger numbers than new cars. More than 60 % of annually registered vehicles in Africa are imported used vehicles [19,20]. Ayetor et al. [21] indicated that >85 % of the imported vehicle fleet in Africa was used, and Mbandi et al. [22] suggested that mileage of >300,000 miles is typical of cars in Africa. Many countries in Africa do not enforce limitations on the age and mileage of imported cars, and some countries, such as Nigeria, allow the import of vehicles up to 15 years of age [21].

Many PAHs are toxic or possibly carcinogenic to humans [23]. PAHs are hydrophobic, and high-molecular-weight (HMW) PAHs have low vapor pressure and low water solubility [24–26]. Thus, when released into the environment, PAHs tend to accumulate in soils and sediments [8,27,28]. The physicochemical properties of PAHs determine their natural attenuation processes and environmental fate [25,29,30]. Dissolution enhances PAHs bioavailability and subsequently facilitates their biodegradability [31–33], with biodegradation being the primary PAH attenuation mechanism [34,35].

Due to the negative impact of PAHs on human health and the environment, multiple studies have been conducted to investigate PAH distributions in urban runoff, waterbodies, dust, soils and sediments to identify PAH sources [15,36–44]. Latimer et al. [45] suggested that leaked oil on parking lots and roadways is a significant source of PAHs in urban runoff and that the degradation rate of leaked oil deposited on parking and road surfaces must be determined to understand its impact on the environment. To date, studies on PAH distribution in urban runoff have not distinguished between PAHs derived from asphalt and those derived from leaking crankcase oil, and these two sources of PAHs are considered one group [36,46,47]. Other studies have discussed the contribution of leaked crankcase oil to PAH particulates in road dust, urban runoff [39,48] and aerosols [49]. In addition, studies have evaluated the contribution of PAHs in parking sealcoats, pavements, and surface materials to pollution in urban streams [46,50]. To the best of our knowledge, the contribution of PAHs in leaked crankcase oil deposited on parking lot surfaces to the environment, independent of asphalt sources, where the composition of leaked oil may change owing to natural attenuation processes and where significant PAH accumulation may occur, has never been investigated.

In this study, we address this gap by characterizing the contribution of PAHs to urban environments via crankcase oil stains on parking surfaces separate from asphalt. We sampled oil stains from a concrete parking structure where leaking oil had accumulated for approximately 10 years. More specifically, we measured PAH concentration in used oil and in new and aging oil stains and reported the PAH profile of leaked crankcase oil of a covered concrete parking structure. The explanation provided for why the oil stains of the sampled concrete surfaces do not have the PAH composition of used crankcase oil, but have a composition similar to asphalt road dust, can be valuable for future studies designed to investigate the concentration of leaked crankcase oil PAHs in urban environments and runoff. Finally, we investigated natural attenuation mechanisms such as evaporation, water washing, and biodegradation, which determine the environmental fate of PAHs in accumulated oil stains.

2. Materials and methods

2.1. Samples

2.1.1. Sampling site

Samples were collected from a covered concrete parking structure located on 801 S Halsted Street in Chicago, IL, USA. This parking structure comprises three levels and a basement floor of over 7 ft. clearances for 310 parking spaces. This parking garage is covered; however, is considered open because it has uniformly distributed openings on two or more sides, and the minimum perimeter of these openings covers 20 % of wall area and 40 % of length [51]. The parking structure was built in 1979 and operated by the University of Illinois Chicago. The last major renovation occurred in 1998, when traffic membranes and waterproofing materials were added to protect concrete floors from deicer deterioration. The parking structure floor was swept as required and power-washed in 2009. The leaked crankcase oil had accumulated for approximately 10 years prior to sampling.

2.1.2. Parking samples collection

From April 22 until June 29, 2019, samples were collected from various parking spaces in covered parking structures. Samples were collected during daytime hours on days when temperatures were between 11 °C and 23 °C. Samples were not collected during precipitation events. In this study, we categorized leaked crankcase oil into two groups based on the age of the oil stain. The age of individual stains was estimated by their appearance based on daily monitoring of oil stains in the parking structure: new oil stains are shiny for 48–72 h, whereas old oil stains appear dry (Supplemental Fig. 1). Parking background samples were collected from areas within the parking structure that were free of obvious crankcase oil stains (Supplemental Fig. 1c), and their PAH content was likely derived from dry and wet deposition and exhaust. A total of 36 samples (17 new oil stains, 14 old oil stains, and 5 background locations) were collected from different parking spaces at different levels of the covered parking structure (Supplemental Fig. 2). Two dust samples were collected from the first and second parking floors. For comparison, 10 samples (8 background and 2 dust samples) were collected from an uncovered coal-tar sealed asphalt pavement parking lot located at 1135 S Morgan St, Chicago, IL, USA.

Samples were collected by swabbing oil stains with ~ 0.2 g of extracted cotton (Soxhlet extracted for 24 h in dichloromethane:methanol [DCM:MeOH, 7.5:1, v:v]). Dichloromethane and methanol were purchased from Thermo Fisher Scientific (Waltham, MA, USA), checked for contaminants, and, if necessary, glass distilled in the laboratory. Sample swabbing was performed using clean, solvent-rinsed (DCM:MeOH; 1:1, v/v) circular stainless steel rings with a total open surface area of 6.60 cm^2 . The ring was swabbed until the floor of the parking lot was visually clear of oil stains. Dust samples were collected by swabbing the dust with ~ 0.2 g of

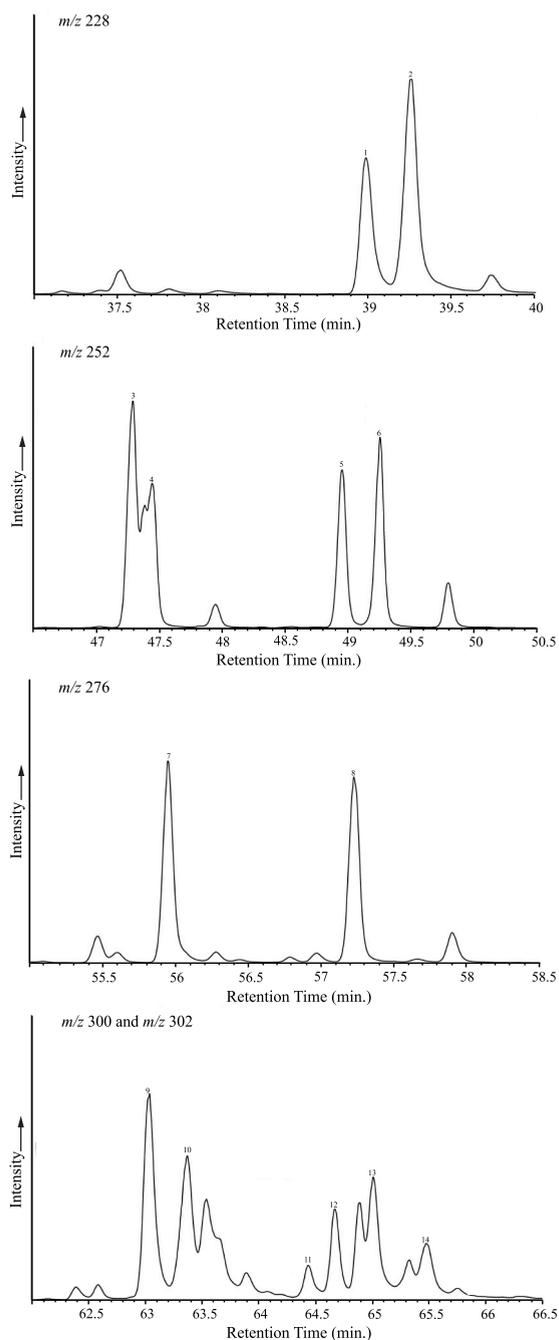


Fig. 1. Selected ion monitoring (SIM) trace of a dust sample collected in a covered concrete parking structure located at 801 S Halsted Street in Chicago, IL. (1) benzo(a)anthracene; (2) chrysene; (3) benzo(b)fluoranthene; (4) benzo(j)fluoranthene; (5) benzo(e)pyrene; (6) benzo(a)pyrene; (7) indeno(1,2,3-cd)pyrene; (8) benzo(ghi)perylene; (9) naphtho(1,2-k)fluoranthene; (10) dibenzo(b,k)fluoranthene; (11) naphtho(2,3-e)pyrene; (12) coronene; (13) dibenzo(a,l)pyrene; (14) dibenzo(a,i)pyrene.

extracted cotton (without using a stainless-steel ring) until the cotton could not hold more dust. The surface area sampled for dust was not measured exactly but was estimated to be 40 cm². All collected samples were placed in baked (overnight at 500 °C) 50 mL glass vials with a solvent rinsed Teflon cap liner, wrapped with aluminum foil, and stored in the dark to prevent photo degradation. Collected samples were sorted at 20 °C and prepared for analysis within 10 days.

2.1.3. Used oil sample collection

Five used oils were obtained from the Audi branch of Fletcher Jones automotive (Chicago, IL, USA). Oil samples were collected from automobiles with a known number of miles driven since the last oil change at the same dealership. Samples were collected from the following car models: Audi-A5 (2013), Audi-A8 (2002), Audi-A4 (2006), Audi-A4 (2010), and Audi-S8 (2010). All tested oils were fully synthetic (Mobil 10 W-30) that did not contain PAHs.

2.2. Extraction and analytical methods

The sample preparation and instrumental analysis procedures were developed based on the USEPA Compendium Method TO-13A [52,53]. Cotton swabs used to collect samples were spiked with 1 µg of each deuterated analytical surrogate (acenaphthene-d10, fluoranthene-d10 and chrysene-d12) prior to Soxhlet extraction. Acenaphthene-d10 and chrysene-d12 were obtained from Sigma-Aldrich (St. Louis, MO, USA). Fluoranthene-d10 was obtained from SPEX CertiPrep (Metuchen, NJ, USA). Acenaphthene-d10 was used for low-molecular-weight (LMW) PAHs, composed of three-ringed PAHs, whereas fluoranthene-d10 and chrysene-d12 were used for HMW PAHs, composed of four- or more ringed PAHs (Supplemental Table 1). The collected samples were Soxhlet extracted for 24 h with approximately 200 mL of DCM:MeOH (7.5:1, v:v). The excess solvent from the extraction was evaporated with a Buchi rotavapor R-114 and concentrated to approximately 2 mL. Concentrated extracts were transferred using a Pasteur pipette into glass vials, evaporated to dryness under a flux of nitrogen (PRAXAIR, 5.0, ultra-high purity, 99.999 %), and weighed. The extracts were then dissolved in cyclohexane (100 µL per mg). Unused and used oils were weighed and dissolved in cyclohexane (100 µL per mg). Cyclohexane, Suprasolv, and Omnisolv were purchased from Thermo Fisher Scientific.

PAHs were identified and quantified using gas chromatography-mass spectrometry (GC-MS) operated in scan mode and selected ion monitoring mode (SIM), respectively. GC-MS was performed on a Hewlett-Packard (HP) 6890 GC coupled to an HP 5973 mass-selective detector operated in the electron ionization (EI) mode at 70 eV and scanning a mass range (scan mode) of m/z 40 to m/z 650 at 2.44 scans/s. Temperatures of the ion source and transfer line were set at 230 °C and 290 °C, respectively. The capillary column used was a HP-5MS (30 m × 0.25 mm × 0.25 µm) with helium as a carrier gas (PRAXAIR, 5.0 Ultra High Purity, 99.999 %). The temperature of the GC oven was maintained at 60 °C for 1.50 min and programmed to increase to 140 °C at 10 °C/min, then increase to 320 °C at 3 °C/min. The injector temperature was set at 300 °C and operated in pulsed splitless mode (40 PSI for 1.5 min).

Targeted compounds were identified based on their mass spectral fragmentation with the help of the Wiley and NIST EI mass spectral databases, in-house, literature-based mass spectral databases, and relative retention times of parent PAHs and methyl PAHs (MPAHs) reported in previous studies (Supplemental Table 2). Fig. 1 shows the isomeric distribution of selected PAHs (m/z 228, m/z 252, m/z 276, m/z 300 and m/z 302) of a dust sample collected of a covered concrete parking structure. All used oil, covered parking structure and uncovered parking lot samples had the same isomeric distributions of PAHs. Quantitation was based on the primary ions of the selected parent PAHs and MPAHs operated in the SIM. Methyl PAHs were quantified by using the relative response factor (RRF) of their respective parent PAHs.

2.3. Quality assurance/quality control (QA/QC)

Blank samples, solvents, analytical surrogates, and standard solutions were regularly analyzed to monitor contaminants. Method blanks were used to detect carryover contamination between samples. All glassware was washed, double rinsed with distilled water, and heated in a muffle furnace at 500 °C for at least 12 h before use.

To assess the validity of the method, three replicates, ~0.2 g of clean unused cotton, were spiked with phenanthrene, anthracene, pyrene, fluoranthene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, benzo(g,h,i)perylene, and dibenzo(a,h)anthracene, all purchased from Sigma-Aldrich, and coronene, purchased from SPEX CertiPrep, reaching a final concentration of 0.035 ng/µL for each PAH and 0.35 ng/µL for coronene. These triplicates were processed in all the steps of the method. The relative standard deviation (RSD) of method validation replicates was ≤34 % for all PAHs except analytical surrogate acenaphthene-d10 (RSD = 132 %). Average recoveries for PAHs were 44 % for phenanthrene, 39 % for anthracene, 67 % for pyrene, 65 % for fluoranthene, 97 % for benzo(a)anthracene, 96 % for chrysene, 78 % for benzo(b)fluoranthene, 83 % for benzo(k)fluoranthene, 79 % for benzo(a)pyrene, 91 % for indeno(1,2,3-cd)pyrene, 98 % for benzo(g,h,i)perylene, 85 % for dibenzo(a,h)anthracene, and 84 % for coronene. However, the average recovery of acenaphthene-d10 was not determined. Acenaphthene-d10 was not detected, below the acceptance limit and above the acceptance limit for the three replicates. Among the tested PAHs, phenanthrene and anthracene were less accurate than other PAHs, with average recoveries of 44 % and 39 %, respectively. The results obtained for acenaphthene-d10 were neither precise nor accurate.

To assess the validity of the used oils method, unused oil samples containing no PAHs were weighted and spiked with 2.5 ng/µL of PAHs to yield final concentrations of 0.25 ng/µL for all PAHs and 0.125 ng/µL for coronene. The RSDs for PAHs ranged from 5 % to 20 %, whereas average recoveries ranged from 61 % to 99 %.

The instrument detection limits (IDL) of the PAHs were determined based on five calibration standards for 16 PAHs, including analytical surrogates. The concentrations of the calibration series are (in pg/µL): 0.50, 0.65, 1.50, 2.00, and 10.00. The instrument

response to the PAHs in each calibration solution was recorded as the peak height. The linearity of the instrument response was evaluated by plotting the amount of PAHs injected against the peak height [54]. The coefficients of determination values were $R^2 = 0.94$ and $R^2 \geq 0.97$ for acenaphthene-d10 and tested PAHs, respectively. The calculated IDL and instrument quantitation limit were used to estimate the initial method detection limit (MDL_i). The MDL_i was used to calculate the method detection limit (MDL) and method quantification limit (MQL) for the PAHs [54]. Recoveries of analytical surrogates for analyzed samples (53 % of acenaphthene-d10, 70 % of fluoranthene-d10, and 82 % of chrysene-d12) were within the acceptable range of 40–140 % [53]. The PAH concentration between MDL and MQL was replaced by $\frac{1}{2}$ MQL [54]. We reported PAHs as not detected (n.d.) when no signal was generated or when the concentrations were below the MDLs. For the calculations, n.d. = 0. When performing statistical analysis, we only used compounds for which we had a value above the MDL. Minitab statistical software was used for data analysis.

3. Results and discussion

3.1. Parking oil stains, background, and dust

The mean of the sum of PAH concentrations for each sample was higher for new oil stain samples (531 ± 285 ng/mg; $n = 17$) than for old oil stain samples (200 ± 112 ng/mg; $n = 14$), whereas the mean concentrations of PAHs for used oil and parking background were 947 ± 404 ng/mg ($n = 5$) and 30 ± 15 ng/mg ($n = 5$), respectively. The Kruskal–Wallis statistical test for comparison (reject null hypothesis if $p < 0.05$) indicated that the total PAH concentrations in the old oil stains were significantly lower than those in the new oil stains ($p = 0.000$; Fig. 2). The mean concentration for each category decreased from used oil to new and old oil stains and to parking background (Fig. 2). The two parking dust samples collected had markedly higher PAHs concentrations (1, 254 ng/mg and 4, 371 ng/mg). Only one of the tested oil samples had a total PAH concentration within this range (1,592 ng/mg; Fig. 2). The PAH distribution of the full synthetic oil samples we tested was similar to that observed in other synthetic used oils [5,55] and in samples collected from service stations from mixed synthetic and conventionally used oils [48], with pyrene being more abundant than fluoranthene. In four of our five used oil samples, benzo(a)anthracene was more abundant than chrysene, suggesting that the PAH distribution observed in our used full synthetic oils is representative of modern used oil in general.

The mean percentage of each parent PAH relative to the total PAHs within each sample population is shown in Fig. 3 for the used oil, oil stain, parking background, and parking dust samples. The PAH distribution of the used oil was different than that of parking oil stains (new and old), parking backgrounds, and parking dust. Phe and Pyr were the predominant parent PAHs in used oil. LMW PAHs were not predominant in parking oil stains or covered parking dust, and were only present in one of the five covered parking background samples. Pyr was more abundant than Flu in used oil, whereas the reverse was true for all collected parking samples, all with p -values < 0.05 . In used oil, BaAn had a higher relative abundance than Chry and Bbflu; however, the reverse was observed in all samples of oil stains, parking backgrounds, and parking dust (covered concrete and open asphalt-paved). BaAn was significantly higher in relative abundance than Chry, with p -values ≤ 0.003 in all oil stain samples. The relative abundance of IP in the used oil was significantly lower than that of BghiP, whereas the relative abundances of these compounds were not significantly different in any of the parking samples. HMW PAHs comprising five or six rings (m/z 278 and m/z 302) were either not detectable in used oil or were present in small amounts compared to covered parking stains (new and old), covered parking dust, and open parking dust (Fig. 3;

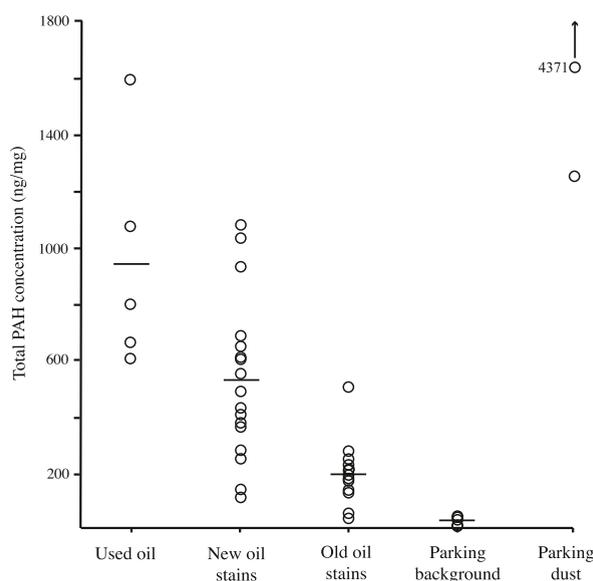


Fig. 2. Total PAH concentration in used oil samples collected from an Audi dealership ($n = 5$), parking oil stains (new $n = 17$ and old $n = 14$), parking background ($n = 5$) and parking dust ($n = 2$). Solid lines represent PAH concentration means.

years. Such an approach must have favored a convergence of the distribution of PAHs in all parking stains (Fig. 3) and perhaps helped explain the large variability in the total PAH concentration data within the new oil stain samples (Fig. 2). The direct link between the stains formed under the engines of cars on parking floors cannot be doubted; however, we must review the processes that may be at the origin of this difference in PAH distribution. In the following sections, we first consider the potential contribution of other sources of PAHs to used oil and then discuss the processes of natural attenuation that may affect the PAH distribution of oil stains.

3.1.1. Transportation-related PAH sources

Leaked crankcase oil does not appear to be the main source of accumulated PAHs in parking oil stains, and the contribution of PAHs to crankcase oil stains from other traffic-related PAH sources, such as automobile exhaust, atmospheric fallout (dry or wet deposition), tire particles, asphalt pavements, and street dust [33,59–61] must be considered.

Chi-square (X^2) was used to evaluate the similarities between profiles based on 13 PAHs (PAH₁₃; Phe, An, Flu, Pyr, BaAn, Chry, Bbflu, Bkflu, Bepyr, Bapyr, IP, BghiP, and D(a,h)an) among the used crankcase oils, oil stains, covered parking background and covered parking dust, asphalt parking background and asphalt parking dust, and the PAH₁₃ profiles of transportation-related PAH sources analyzed by Van Meter et al. [62] (Fig. 4). X^2 is the sum of the squared difference in the PAHs proportional values (in % of a defined group of PAHs) between two samples divided by the mean of these two proportional values [15,63]. Low values of X^2 (close to 0) indicated similarities in distribution, whereas high values indicated large differences in distribution. Using the raw data of Van Meter et al. [62], we calculated the proportional PAHs abundance using PAH₁₃ for street dust, coal-tar sealant dust, and asphalt-paved parking dust (unsealed).

The heat map of X^2 values (Fig. 4) illustrates the difference between the used oil and the new and old parking stains with values of 0.53 and 0.76, respectively. In contrast, the heat map illustrates the similarity between the PAH₁₃ profiles of the new and old oil stains, with a X^2 of 0.06. The PAH₁₃ profiles of new and old oil stains were also related to those of the covered parking dust, all with X^2 values of 0.17 and 0.20, respectively. Parking dust was enriched in PAHs (1,254 and 4,371 ng/mg) relative to new oil stains (531 ± 285 ng/mg; $n = 17$), old oil stains (200 ± 112 , $n = 14$), and parking background (30 ± 15 ng/mg; $n = 5$), and it is unlikely that the parking dust derived from dry and wet deposition and/or drying oil stain residue as the total PAH concentration decreased with aging of the stains. A second similarity cluster was visible in the heat map of X^2 values, reflecting the similarity of PAH₁₃ distribution among the dust samples. The covered parking dust was similar to the asphalt parking dust ($X^2 = 0.06$). In particular, the covered parking dust most resembled the asphalt-paved parking background, and the asphalt-paved parking dust ($X^2 = 0.05$) and coal-tar sealant dust ($X^2 = 0.05$) of Van Meter et al. [62]. The similarities between PAH profiles of the covered parking dust and the asphalt-paved parking and coal-tar sealant dusts of Van Meter et al. [62] were unexpected. In Van Meter et al.'s [62] study, samples were collected from various parking lot locations with environmental conditions (i.e., traffic volume, industrial pollution, and urban sprawl) that differed from those surrounding the covered parking structure where dust samples were collected for this study. The similarities between PAH profiles of covered parking dust, asphalt-paved parking dust, and coal-tar sealant dust suggest that asphalt pavement and coal-tar sealant were

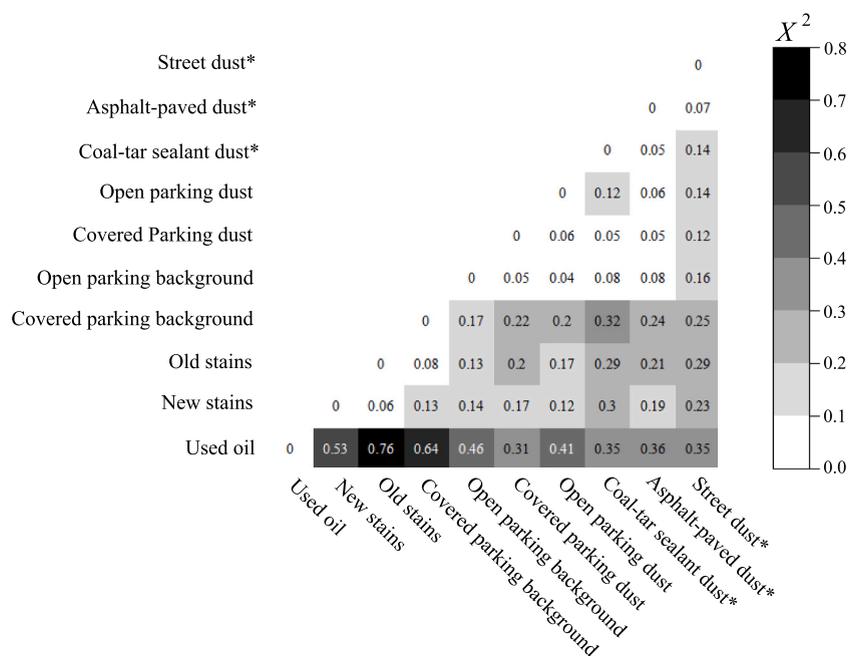


Fig. 4. Chi square heat map for the mean distribution of 13 PAHs (see text for list) in all sample groups from the covered parking (new oil stains, old oil stains, parking background and parking dust), open parking (parking background and parking dust) and three transportation-related dusts derived from Van Meter et al. [62] (marked by an asterisk). Chi square values are shown.

the major contributor to PAHs in covered parking dust. The covered parking dust may thus have been greatly derived from sources outside the parking structure. In our case, the dust may have originated from a contiguous asphalt-paved and coal-tar-sealed open parking lot located north of the concrete structure or from two adjacent asphalt-paved streets and a highway (HW 90) located west, south, and east of the concrete structure, respectively. For accuracy, note that HW 90 was positioned ~12 m below the first floor of the concrete parking structure. The difference between the distribution of PAHs in oil stains and used oil could be explained by the contribution of parking dust to the stains.

Soon after the deposition of used oil on the parking floor, we observed that dust was trapped by new oil stains that spread on the parking floor. The PAH concentrations in the covered parking dust (1,254 and 4,371 ng/mg) were sufficiently high to modify the distribution of PAHs in the oil stains. The lowest and highest PAH contents measured in asphalt-paved open parking dust were 21,746 ng/mg and 136,091 ng/mg, respectively. Coal-tar sealant is a well-known source of PAHs in traffic-related source materials (70,000 ng/mg) [16], and is at least two orders of magnitude more concentrated than used motor oil. Consequently, a small contribution of coal-tar sealant dust or asphalt-paved parking dust can alter the distribution and concentration of PAHs in the covered parking dust and oil stains. Transportation-related PAH sources, such as street dust, road asphalt-paved dust, and coal-tar sealant dust, likely contributed to the covered parking oil stain PAHs and masked the original used crankcase oil signal. These results reinforce the concept that if you have nearby sealant-coated asphalt surfaces and/or asphalt surfaces, the dust derived from these surfaces will prevent the characterization of other sources of PAHs [64].

We also calculated X^2 using vehicle exhaust data from Hu et al. [65] Supplemental Table 4. Because Hu et al. [65] did not report the concentration of Bepyr, we used 12 compounds (PAH₁₃ – Bepyr). The X^2 values for oil stains and covered parking dust versus vehicle exhaust were between 0.91 and 1.61, demonstrating that vehicle exhaust was not a significant contributor to our parking stains and parking dust. Wakeham et al. [66] dismissed automobile engine exhaust as a major contributor to street dust PAHs; instead, they suggested that asphalt particles might be a major contributor to PAHs in street dust. We expected the contribution of vehicle exhaust emission PAHs to parking dust to be small; exhaust-related emission particles have significantly decreased in recent years owing to advances in technology and regulation requirements (i.e., the use of catalytic convertors) [67].

To investigate tires fragments as a possible source of HMW PAHs in our samples, we calculated X^2 values based on a group of 14 PAHs (PAH₁₄; Bbflu, Bkflu, Bepyr, Bapyr, Perylene [Per], D(a,h)an, Picene [Pic], IP, BghiP, Cor, Dibenzo(a,l)pyrene (D(a,l)pyr), Dibenzo(a,e)pyrene (D(a,e)pyr), Dibenzo(a,i)pyrene (D(a,i)pyr) and Dibenzo(a,h)pyrene (D(a,h)pyr)) reported for tires by Sadiktsis et al. [67]. The X^2 values were >1.4 for all oil stains, parking background, and parking dust samples (Supplemental Table 4), demonstrating the absence of similarity between the HMW PAHs distribution of these samples and that of tire particles. X^2 was not calculated for used oil because many of the 14 HMW PAHs were not detected.

3.1.2. Natural attenuation

The processes of natural attenuation, evaporation, water washing, and biodegradation are possible factors contributing to

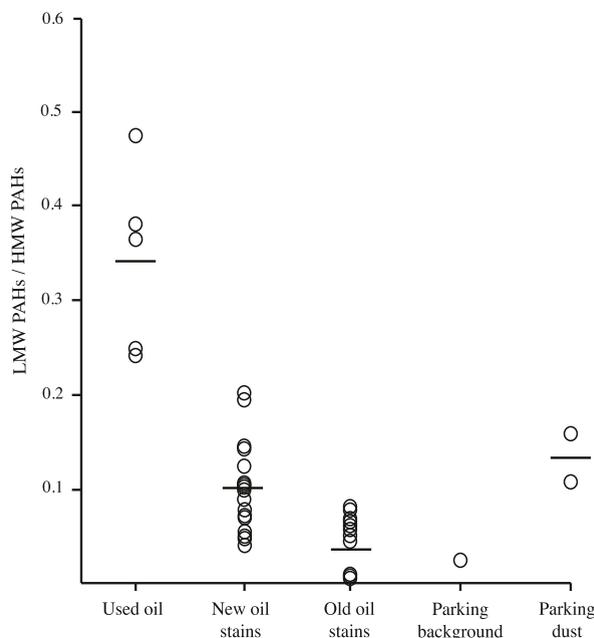


Fig. 5. Ratio of sum of LMW PAHs (phenanthrene and anthracene) to the sum of HMW PAHs (fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, benzo(ghi)perylene and dibenzo(a,h)anthracene) in used oils (n = 5), new oil stains (n = 17), old oil stains (n = 14), parking background (n = 1) and parking dust (n = 2). Mean values of these ratios are indicated by solid lines.

differences in PAH signatures between used oil and parking oil stains and to variability in the abundance of PAHs in parking oil stains. In the studied covered parking lot, water availability was limited to water dripping from cars entering the parking structure during precipitation events and to the condensation of moisture on the ground when the parking concrete was colder than the dew point. The loss of LMW aromatic compounds, including PAHs smaller than phenanthrene and anthracene, from used oil to recent stains indicated that evaporation played a role in the attenuation of these compounds.

The ratios of the sum of LMW parent PAHs (Phe and An) to the sum of HMW parent PAHs (Flu, Pyr, BaAn, Chry, Bbflu, Bkflu, Bapyr, IP, BghiP, and D(a,h)An) in used oils, parking oil stains (new and old), and parking backgrounds were compared. The LMW/HMW PAHs values were higher for the used oil than for the parking stains and parking backgrounds (Fig. 5). Statistical analysis indicated that the decreasing trend in the LMW/HMW PAHs ratios observed with oil aging (from new to old oil stains) was significant ($p = 0.001$). Parking background and parking dust were not included in the statistical analyses of the LMW/HMW PAHs and Phe/An ratios because of the small sample size.

The persistence of PAHs in the environment increases with the number of PAH rings [68,69]. HMW PAHs are more stable and less water-soluble than LMW PAHs [70–72]. Consequently, LMW PAHs were more easily attenuated than HMW PAHs. The significant decrease in the ratio of LMW PAHs to HMW PAHs from new oil stains to old oil stains indicates the loss of LMW PAHs as the oil stains age, possibly because of the conjugated action of attenuation processes, although none of these processes can be considered dominant. During wet events, LMW PAHs can be washed off into parking drains. Biodegradation can also be activated if some water remains on

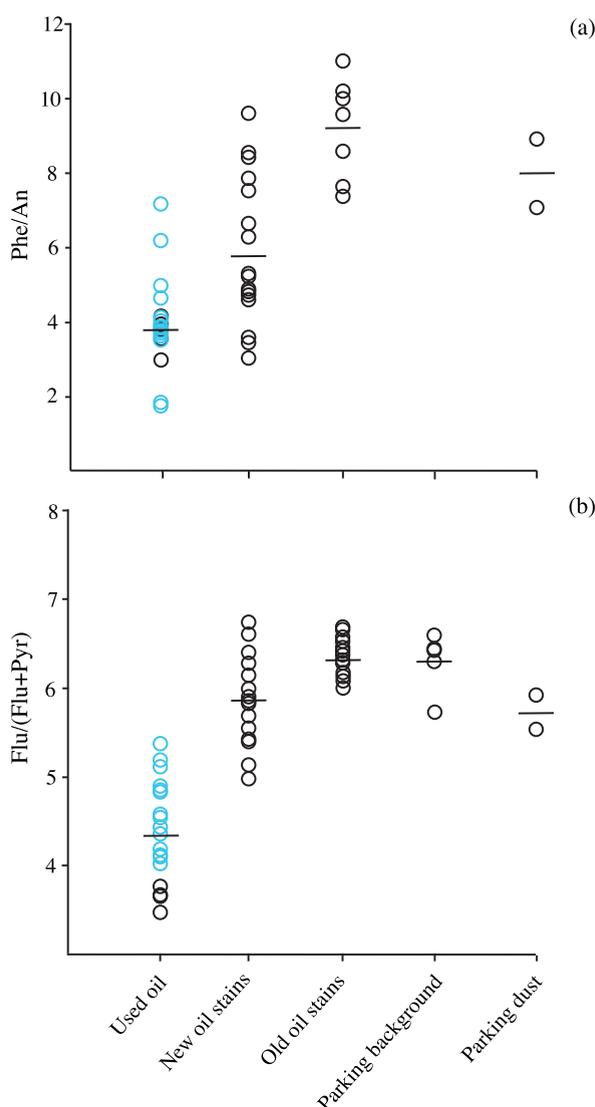


Fig. 6. (a) Phe/An and (b) Flu/(Flu + Pyr) ratios in the five tested used oils (black circles), used oils measured by Wang et al. [5], Wong and Wang [55] and Purell and Quinn [73] blue circles, samples collected from the stains of the covered parking, parking background and parking dust. Mean values of these ratios are indicated by solid lines.

the stains. We used the Phe/An and Flu/(Flu + Pyr) ratios to differentiate the influence of biodegradation from that of water washing (Fig. 6).

The values of the Phe/An and Flu/(Flu + Pyr) ratios were significantly lower in used oils compared to those obtained for covered parking stains and parking backgrounds ($p < 0.05$; Fig. 6), and parking dust (p was not calculated due to dust sample size, $n = 2$). The Phe/An ratio increased significantly for the old oil stains compared to that for the new oil stains ($p = 0.002$; Fig. 6a). Both the old oil stains and parking background exhibited Flu/(Flu + Pyr) values that were significantly higher than those calculated for the new oil stains (Fig. 6b). The mean Phe/An and Flu/(Flu + Pyr) values for the parking dust were lower than those for the parking background and old oil stains.

Each pair of PAHs in these ratios has the same molar mass and physicochemical properties; thus, their predicted environmental fate processes should be similar [29]. However, phenanthrene is more soluble than its structural isomer, anthracene [25], and anthracene is

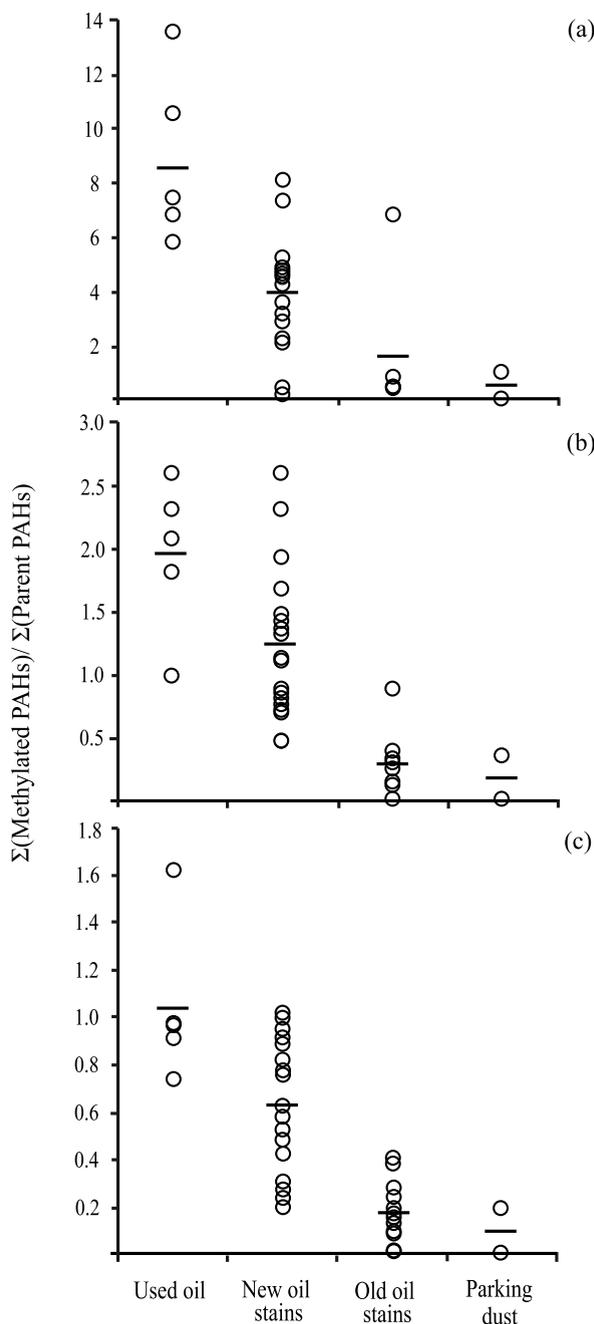


Fig. 7. Ratios of the sum of methylated PAH concentrations to the sum of their corresponding parent PAHs (a) phenanthrene and anthracene, (b) pyrene and fluoranthene, and (c) benzo(a)anthracene, triphenylene and chrysene. Solid lines represent PAH concentration means.

more biodegradable than phenanthrene [74]. The Phe/An ratio decreases when washing with water, which is the major process for the natural attenuation of PAHs in the environment. In contrast, the Phe/An ratio increases when biodegradation is the dominant process during natural attenuation [74]. Additionally, fluoranthene is more volatile and soluble than its isomer, pyrene [24], and is more resistant to biodegradation than pyrene [74]. Thus, biodegradation was indicated by an increase in the Flu/(Flu + Pyr) ratio [75]. Here, the Phe/An and Flu/(Flu + Pyr) ratios increased significantly between the new and old oil stains (Fig. 6), suggesting that biodegradation is an active process of PAH attenuation in the oil stains of the covered parking structure.

The methylated Phe and An (m/z 192, m/z 206, m/z 220, and m/z 234), methylated Pyr and Flu (m/z 216, m/z 230, m/z 244, and m/z 258), and methylated Chry, BaAn, and triphenylene (Trph; m/z 242, m/z 256, and m/z 270) concentrations were measured in the used oils and samples collected from the covered parking lot (Fig. 7). In used oil, the mean ratio of the sum of methylated Phe and An to the sum of Phe and An was 8.5 ± 2.7 ($n = 5$; Fig. 7a). In covered parking oil stains, this mean ratio decreased from 3.9 ± 2.1 ($n = 16$) to 1.6 ± 2.6 ($n = 6$) in new and old oil stains, respectively. Similarly, the mean ratio of methylated Pyr and Flu to the sum of Pyr and Flu (m/z 202) decreased with age, showing the same trend as that of the mean ratio of methylated Chry, BaAn, and Trph to the sum of Chry, BaAn, and Trph (m/z 228) (Fig. 7b and c).

Some studies have indicated that the rate of PAH biodegradation decreases with increasing levels of alkylation [76–78]. However, methylated PAHs are less water-soluble than their corresponding parent PAHs [79] and are expected to be less biodegradable [77]. Our results (Fig. 7) indicated that the mean ratio of MPAH/PAH for parking oil stains decreased with age. This decreasing trend is not concordant with biodegradation or water-washing mechanisms. The MPAH/PAH ratios were expected to increase with biodegradation or water-washing processes. Inconsistencies between the MPAH/PAH ratio and other biodegradation proxies have been observed in previous studies. Lee and Kwon [79] stated that the biodegradation rate of 1-methylpyrene by *Sphingobium quisquiliarum* EPA505 was higher than that of pyrene, whereas no difference in the degradation rate was observed between pyrene and 1-methylpyrene by *S. paucimobilis* EPA505, as reported by Dimitriou-Christids et al. [80]. Siddiqui et al. [81] noted that *S. paucimobilis*, when using fluoranthene as a source of carbon and energy, degrades 5-methylchrysene, 7-methylbenzo(a)anthracene and 3-methylfluoranthene nearly twice as fast as their unsubstituted parents. Huang et al. [77] reported that the biodegradation of dimethylphenanthrene is faster than that of methylphenanthrene. Thus, the decreasing trend in MPAH/PAH ratios with increasing stain age, showing fast attenuation of MPAH relative to their parents, may be the result of biodegradation.

4. Conclusions

In this study, we investigated the distribution of PAHs in crankcase oil stains of a covered concrete parking structure. The results revealed the PAHs profile of crankcase oil stains in a parking facility that had none previously known. While the distribution of PAHs in used oil differs from that in samples of oil stains (new and old) collected in the parking spaces, a clear direct link exists between leaking crankcase oil and the stains. Unlike used oil, low molecular weight PAHs were not predominant in covered parking oil stains or dust samples. The total PAH concentration decreased from used oil (947 ± 404 ng/mg) to new oil stains (531 ± 285 ng/mg) to old oil stains (200 ± 112 ng/mg); however, dust samples had a higher concentration of PAHs than oil stains (up to 4,371 ng/mg). In a covered, open, concrete parking structure, parking dust receives a significant contribution of PAHs from dust derived from adjacent asphalt surfaces, parking, and roadways. This process may be exacerbated by the contribution of the coal-tar-sealed asphalt surfaces. Relative to oil stains, parking dust is rich in PAHs, and salting of new oil stains by parking dust has been observed. The PAH₁₃ profiles of new and old oil stains were related to that of the covered parking dust where the latter resembles not only the asphalt-paved parking background, but also the asphalt-paved parking dust and coal-tar sealant dust ($X^2 = 0.05$). Based on these findings, we suggest the contribution of parking dust to oil stains is sufficient to alter the PAH profile of oil stains because it masks the original crankcase oil profile. This study confirms that the use of asphalt surfaces in urban environments leads to the spread of PAHs [64,82,83] and that sealed asphalt dust contributes to the spread of large quantities of carcinogenic PAHs across urban environments [47,84–86].

The significant decrease in the concentration of PAHs from new oil stains to old oil stains ($p = 0.001$) suggests that natural attenuation processes occur in covered parking structures. In addition, increases in the PAH ratios Phe/An and Flu/(Flu + Pyr) suggest that biodegradation is active in the covered parking structures. This study has limitations in terms of sample collection, which separated oil stains into only two categories. The findings of this study will help inform the design of studies that investigate the distribution of PAHs in the oil stains of parking facilities, where oil is the only source of PAHs, in different regions globally. This study will also help future efforts to develop management practices that include source and treatment controls to reduce PAH concentrations on parking surfaces.

Data availability statement

The data are included in article and supplementary materials in this article.

CRedit authorship contribution statement

Muna Zabarmawi: Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Conceptualization.
Fabien Kenig: Writing – review & editing, Visualization, Validation, Supervision, Methodology, Investigation, Formal analysis, Conceptualization.

Declaration of competing interest

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

Acknowledgments

We thank the Saudi Ministry of Education for support to M.Z. We thank Professor An Li for her advice and useful discussions. This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.heliyon.2024.e35881>.

References

- [1] R. Vazquez-Duhalt, Environmental impact of used motor oil, *Sci. Total Environ.* 79 (1989) 1–23, [https://doi.org/10.1016/0048-9697\(89\)90049-1](https://doi.org/10.1016/0048-9697(89)90049-1).
- [2] X. Maleville, D. Faure, A. Legros, J. Hipeaux, Oxidation of mineral base oils of petroleum origin: the relationship between chemical composition, thickening, and composition of degradation products, *Lubric. Sci.* 9 (1996) 1–60, <https://doi.org/10.1002/ls.3010090102>.
- [3] S. Srivastava, *Developments in Lubricant Technology*, first ed., John Wiley & Sons, Inc., 2014 <https://doi.org/10.1002/9781118907948>.
- [4] I. Minami, Molecular science of lubricant additives, *Appl. Sci.* 7 (2017) 445, <https://doi.org/10.3390/app7050445>.
- [5] J. Wang, C. Jia, C. Wong, K. Wong, Characterization of polycyclic aromatic hydrocarbons created in lubricating oils, *Water, Air, Soil Pollut.* 120 (2000) 381–396, <https://doi.org/10.1023/A:1005251618062>.
- [6] P.D. Boehm, in: R.D. Morrison, B.L. Murphy (Eds.), *Polycyclic Aromatic Hydrocarbons, Environmental Forensics: Contaminant Specific Guide*, Elsevier Academic Press, 2006, pp. 316–337, <https://doi.org/10.1016/B978-012507751-4/50037-9>.
- [7] L. Xu, J. Yu, G. Wan, L. Sun, Emission characteristics and source identification of polycyclic aromatic hydrocarbons (PAHs) from used mineral oil combustion, *Fuel* 304 (2021) 121–357, <https://doi.org/10.1016/j.fuel.2021.121357>.
- [8] P. Paneque, P. Caballero, J. Parrado, I. Gómez, M. Tejada, Use of a biostimulant obtained from okara in the bioremediation of a soil polluted by used motor car oil, *J. Hazard Mater.* 389 (2020) 121820, <https://doi.org/10.1016/j.jhazmat.2019.121820>.
- [9] M. Santamouris, Using cool pavements as a mitigation strategy to fight urban heat island - a review of the actual developments, *Renew. Sustain. Energy Rev.* 26 (2013) 224–240, <https://doi.org/10.1016/j.rser.2013.05.047>.
- [10] K. Hossain, L. Fu, F. Hosseini, M. Muresan, T. Donnelly, S. Kabir, Optimum winter road maintenance: effect of pavement types on snow melting performance of road salts, *Can. J. Civ. Eng.* 43 (9) (2016) 802–811, <https://doi.org/10.1139/cjce-2016-0010>.
- [11] U.S. Department of Transportation, Federal Highway Administration, 2020. Author, <http://www.fhwa.dot.gov/policyinformation/statistics/2019/hm12.cfm>.
- [12] M. Scoggins, N.L. McClintock, L. Gosselink, P. Bryer, Occurrence of polycyclic aromatic hydrocarbons below coal-tar sealed parking lots and effects on stream benthic macroinvertebrate communities, *J. North Am. Benthol. Soc.* 26 (4) (2007) 694–707, <https://doi.org/10.1899/06-109.1>.
- [13] I. Titaley, A. Chlebowski, L. Truong, R. Tanguay, S. Massey Simonich, Identification and toxicological evaluation of unsubstituted PAHs and novel PAH derivatives in pavement sealcoat products, *Environ. Sci. Technol. Lett.* 3 (6) (2016) 234–242, <https://doi.org/10.1021/acs.estlett.6b00116>.
- [14] S. Kane Driscoll, K. Kulacki, S. Marzooghi, A Review of the literature on potential effects of runoff from refined coal-tar based sealant coating on aquatic organisms, *Integrated Environ. Assess. Manag.* 16 (1) (2020) 17–27, <https://doi.org/10.1002/ieam.4210>.
- [15] P.C. Van Metre, B.J. Mahler, Contribution of PAHs from coal-tar pavement sealcoat and other sources to 40 U.S. lakes, *Sci. Total Environ.* 409 (2010) 334–344, <https://doi.org/10.1016/j.scitotenv.2010.08.014>.
- [16] B. Mahler, P. Van Metre, Coal tar based pavement sealants: a potent source of PAHs, *North American Lake Management Society* (37) (2017) 13–18.
- [17] C. Hadfield, *Today's Technician Classroom Manual for Automotive Engine Repair and Rebuilding*, Cengage Learning, 2014. Clifton Park, NY: Delmar.
- [18] A. Young, *The Cadillac Northstar V-8: A History*, McFarland & Company, Incorporated Publishers, Jefferson, NC, 2017.
- [19] J.C. Ssempebwa, D.O. Carpenter, The generation use and disposal of waste crankcase oil in developing countries: a case for kampala district, Uganda, *J. Hazard Mater.* 161 (2) (2009) 835–841, <https://doi.org/10.1016/j.jhazmat.2008.04.028>.
- [20] United Nations Environment Programme (UNEP), Used vehicles and the environment. <https://www.unep.org/resources/report/global-trade-used-vehicles-report>, 2020.
- [21] G. Ayetor, I. Mbonigaba, M. Sackey, P. Andoh, Vehicle regulations in Africa: impact on used vehicle import and new vehicle sales, *Transp. Res. Interdiscip. Perspect.* 10 (2021) 100–384, <https://doi.org/10.1016/j.trip.2021.100384>.
- [22] A. Mbandi, J. Böhnke, D. Schwela, H. Vallack, M. Ashmore, L. Emberson, Estimating on road vehicle fuel economy in Africa: a case study based on an urban transport survey in Nairobi, Kenya, *Energies* 12 (6) (2019) 11–77, <https://doi.org/10.3390/en12061177>.
- [23] The International Agency for Research on Cancer (IARC), List of Classifications, 2022. Author, <https://monographs.iarc.who.int/listofclassification>.
- [24] M.D. La Grega, P.L. Buckingham, J.C. Evans, *Hazardous Waste Management*, McGraw-Hill, New York, NY, 1994.
- [25] S.W. Rogers, S.K. Ong, B.H. Kjarntanson, J. Golchin, G.A. Stenback, Natural attenuation of polycyclic aromatic hydrocarbon of contaminated sites: review, *Pract. Period. Hazard. Toxic Radioact. Waste Manage.* 6 (2002) 141–155, [https://doi.org/10.1061/\(ASCE\)1090-025X\(2002\)6:3\(141\)](https://doi.org/10.1061/(ASCE)1090-025X(2002)6:3(141)).
- [26] S. Lamichhane, K.C. Bal Krishna, R. Sarukkalgie, Surfactant-enhanced remediation of polycyclic aromatic hydrocarbons: a review, *J. Environ. Manag.* 199 (2017) 46–61, <https://doi.org/10.1016/j.jenvman.2017.05.037>.
- [27] S. Net, R. El-Osmani, E. Prygiel, S. Rabodonirina, D. Dumoulin, B. Ouddane, Overview of persistent organic pollution (PAHs, Me-PAHs and PCBs) in freshwater sediments from Northern France, *J. Geochem. Explor.* 148 (2015) 181–188, <https://doi.org/10.1016/j.gexplo.2014.09.008>.
- [28] T.R. Pretorius, C. Charest, L.E. Kimpe, J.M. Blais, The accumulation of metals, PAHs and alkyl PAHs in the roots of *Echinacea purpurea*, *PLoS One* 13 (12) (2018) 208–325, <https://doi.org/10.1371/journal.pone.0208325>.
- [29] M. Tobiszewski, J. Namieśnik, PAH diagnostic ratios for the identification of pollution emission sources, *Environ. Pollut.* 162 (2012) 110–119, <https://doi.org/10.1016/j.envpol.2011.10.025>.
- [30] O. Alegbeleye, B. Opeolu, V. Jackson, Bioremediation of polycyclic aromatic hydrocarbon (PAH) compounds: (acenaphthene and fluorene) in water using indigenous bacterial species isolated from the Diep and Plankenburg rivers, Western Cape, South Africa, *Braz. J. Microbiol.* 48 (2) (2017) 314–325, <https://doi.org/10.1016/j.bjm.2016.07.027>.
- [31] J.L. Li, B.H. Chen, Surfactant-mediated biodegradation of polycyclic aromatic hydrocarbons, *Materials* 2 (2009) 76–94, <https://doi.org/10.3390/ma2010076>.
- [32] N. Ismail, N. Kasmuri, N. Hamzah, Microbial bioremediation techniques for polycyclic aromatic hydrocarbon (PAHs)- A review, *Water, Air, and Soil Pollution* 233 (4) (2022), <https://doi.org/10.1007/s11270-022-05598-6>.

- [33] A. Rabieimesbah, S. Sobhanardakani, M. Cheraghi, B. Lorestani, Concentrations, source identification and potential ecological and human health risks assessment of polycyclic aromatic hydrocarbons (PAHs) in agricultural soils of hamedan county, west of Iran, *Soil Sediment Contam.* 33 (4) (2024), <https://doi.org/10.1080/15320383.2023.2215867>.
- [34] K.H. Wammer, C.A. Peters, Polycyclic aromatic hydrocarbon biodegradation rates: a structure-based study, *Environ. Sci. Technol.* 39 (2005) 2571–2578, <https://doi.org/10.1021/es048939y>.
- [35] F. Lang, J. Destain, F. Delvigne, P. Druart, M. Ongena, P. Thonart, Biodegradation of polycyclic aromatic hydrocarbons in mangrove sediments under different strategies: natural attenuation, biostimulation, and bioaugmentation with *Rhodococcus erythropolis* T902.1, *Water Air Soil Pollut.* 227 (9) (2016) 1–15, <https://doi.org/10.1007/s11270-016-2999-4>.
- [36] J. Brown, B. Peake, Sources of heavy metals and polycyclic aromatic hydrocarbons in urban stormwater runoff, *Sci. Total Environ.* 359 (1) (2006) 145–155, <https://doi.org/10.1016/j.scitotenv.2005.05.016>.
- [37] R. Boonyatumanond, M. Murakami, G. Wattayakorn, A. Togo, H. Takada, Sources of polycyclic aromatic hydrocarbons (PAHs) in street dust in a tropical Asian mega-city, Bangkok, Thailand, *Sci. Total Environ.* 384 (1) (2007) 420–432, <https://doi.org/10.1016/j.scitotenv.2007.06.046>.
- [38] M. Liu, S.B. Cheng, D.N. Ou, L.J. Hou, L. Gao, L.L. Wang, Y.S. Xie, Y. Yang, S.Y. Xu, Characterization, identification of road dust PAHs in central Shanghai areas, China, *Atmos. Environ.* 41 (38) (2007) 8785–8795, <https://doi.org/10.1016/j.atmosenv.2007.07.059>.
- [39] A.R. Mostafa, A.H. Hegazi, M.S. El-gayar, J.T. Andersson, Source characterization and the environmental impact of urban street dusts from Egypt based on hydrocarbon distributions, *Fuel* 88 (2009) 95–104, <https://doi.org/10.1016/j.fuel.2008.08.0>.
- [40] A.E. Witter, M.H. Nguyen, S. Baidar, P.B. Sak, Coal-tar-based sealcoated pavement: a major PAH source to urban stream sediments, *Environ. Pollut.* 185 (2014) 59, <https://doi.org/10.1016/j.envpol.2013.10.015>, 6.
- [41] E. Alsobou, M.A. Zaitoun, A.M. Alasoufi, A. Al Shra'ah, Concentration and source assessment of polycyclic aromatic hydrocarbons in the street soil of Ma'an city, Jordan, *Arch. Environ. Cont. Tox.* 77 (2019) 619–630, <https://doi.org/10.1007/s00244-019-00665-2>.
- [42] J. Hou, T.A. Li, A comparison of sources and risk assessment of polycyclic aromatic hydrocarbons in urban stormwater runoff from ground and highway roads in Shanghai China, *Polycycl. Aromat. Comp.* 40 (3) (2020) 670–680, <https://doi.org/10.1080/10406638.2018.1472110>.
- [43] O. Canlı, K. Çetintürk, B. Güzel, A comprehensive assessment, source input determination and distribution of persistent organic pollutants (POPs) along with heavy metals (HMs) in reservoir lake sediments from Çanakkale province, Türkiye, *Environ. Geochem. Health* 45 (6) (2023), <https://doi.org/10.1007/s10653-023-01480-4>.
- [44] B. Yüce, B. Güzel, O. Canlı, B. Onat, Characterization, source identification and risk assessment of POPs (PAHs, PCBs, and OCPs) in indoor dusts from two metropolitan cities (Istanbul and Kocaeli) of Türkiye with intensive industrial and human activities, *Stoch. Environ. Res. Risk Assess.* 38 (4) (2024), <https://doi.org/10.1007/s00477-023-02631-w>.
- [45] J. Latimer, E. Hoffman, G. Hoffman, J. Fasching, J. Quinn, Sources of petroleum hydrocarbons in urban runoff, *Water Air Soil Pollut.* 52 (1999) 1–21, <https://doi.org/10.1007/BF00283111>.
- [46] B.J. Mahler, P.C. Van Metre, T.J. Bashara, J.T. Wilson, D.A. Johns, Parking lot seal coat: an unrecognized source of urban polycyclic aromatic hydrocarbons, *Environ. Sci. Technol.* 39 (15) (2005) 5560–5566, <https://doi.org/10.1021/es0501565>.
- [47] U. Yim, S. Hong, S. Ha, G. Han, J. An, N. Kim, D. Lim, H. Choi, J. Shim, Source- and region-specific distribution of polycyclic aromatic hydrocarbons in sediments from Jinhai Bay, Korea, *Sci. Total Environ.* 470–471 (2014) 1485–1493, <https://doi.org/10.1016/j.scitotenv.2013.07.069>.
- [48] M.P. Zakaria, H. Takada, S. Tsutsumi, K. Ohno, J. Yamada, E. Kouno, H. Kumata, Distribution of polycyclic aromatic hydrocarbons (PAHs) in rivers and estuaries in Malaysia: a widespread input of petrogenic PAHs, *Environ. Sci. Technol.* 36 (2002) 1907–1918, <https://doi.org/10.1021/es011278>.
- [49] D.R. Worton, G. Isaacman, D.R. Gentner, T.R. Dallmann, A.W. Chan, C. Ruehl, T.W. kirchstetter, K.R. Wilson, R.A. Harley, A.H. Goldstein, Lubricating oil dominates primary organic aerosol emissions from motor vehicles, *Environ. Sci. Technol.* 48 (7) (2014) 3698–3706, <https://doi.org/10.1021/es405375j>.
- [50] R.T. Pavlowsky, Coal tar pavement sealant use and polycyclic aromatic hydrocarbon contamination in urban stream sediments, *Phys. Geogr.* 34 (2013) 392–415, <https://doi.org/10.1080/02723646.2013.848393>.
- [51] F. Ching, S. Winkel, *Building Codes Illustrated: A Guide to Understanding the 2012 International Building Code*, John Wiley & Sons, Hoboken, NJ, 2012.
- [52] USEPA, *Determination of Polycyclic Aromatic Hydrocarbons (PAHs) in Ambient Air Using Gas Chromatography/mass Spectrometry (GC/MS)*, Compendium Method TO-13A, US Environmental Protection Agency, Office of research and development, Cincinnati, OH, 1999.
- [53] A. Li, T.M. Schoonover, Q. Zou, F. Norlock, L.M. Conroy, P.A. Scheff, R.A. Wadden, Polycyclic aromatic hydrocarbons in residential air of ten Chicago area homes: concentrations and influencing factors, *Atmos. Environ.* 39 (19) (2005) 3491–3501, <https://doi.org/10.1016/j.atmosenv.2005.02.029>.
- [54] U.S. Environmental Protection Agency, Assigning Values to Non-detected/non-Quantified Pesticide Residues in Human Health Food Exposure Assessments, Office of Pesticide Programs, Washington, DC, 2000, <https://archive.epa.gov/pesticides/trac/web/pdf/trac3b012.pdf>.
- [55] P. Wong, J. Wang, The accumulation of polycyclic aromatic hydrocarbons in lubricating oil over time - a comparison of supercritical fluid and liquid-liquid extraction methods, *Environ. Pollut.* 112 (2001) 407–415, [https://doi.org/10.1016/S0269-7491\(00\)00142-1](https://doi.org/10.1016/S0269-7491(00)00142-1).
- [56] M. Saha, A. Togo, K. Mizukawa, M. Murakami, H. Takada, M. Zakaria, N. Chiem, B. Tuyen, M. Prudente, R. Boonyatumanond, S. Sarkar, B. Bhattacharya, P. Mishra, T. Tana, Sources of sedimentary PAHs in tropical Asian waters: differentiation between pyrogenic and petrogenic sources by alkyl homolog abundance, *Mar. Pollut. Bull.* 58 (2009) 189–200, <https://doi.org/10.1016/j.marpolbul.2008.04.049>.
- [57] J. Mandić, J. Tronczyński, G. Kuspilic, Polycyclic aromatic hydrocarbons in surface sediments of the mid-Adriatic and along the Croatian coast: levels, distributions and sources, *Environ. Pollut.* 242 (Pt A) (2018) 519–527, <https://doi.org/10.1016/j.envpol.2018.06.095>.
- [58] S.D. Emsbo-Mattingly, E. Litman, Polycyclic aromatic hydrocarbon homolog and isomer fingerprinting, in: S. Stout, Z. Wang (Eds.), *Standard Handbook Oil Spill Environmental Forensics* Second Edition, Elsevier Inc., 2016, pp. 255–312, <https://doi.org/10.1016/B978-0-12-803832-1.00005-2>.
- [59] W. Rogge, L. Hildemann, M. Mazurek, G. Cass, B. Simoneit, Sources of fine organic aerosol. 3. Road dust, tire debris, and organometallic brake lining dust: roads as sources and sinks, *Environ. Sci. Technol.* 27 (9) (1993) 1892–1904, <https://doi.org/10.1021/es00046a019>.
- [60] S. Lee, J. Kwak, H. Kim, J. Lee, Properties of roadway particles from interaction between the tire and road pavement, *Int. J. Automat. Technol.* 14 (1) (2013) 163–173, <https://doi.org/10.1007/s12239-013-0018-y>.
- [61] A. Nádudvari, M. Fabiańska, L. Marynowski, B. Kozielska, J. Koniecznyński, D. Smolka-Danielowska, S. Ćmiel, Distribution of coal and coal combustion related organic pollutants in the environment of the Upper Silesian Industrial Region, *Sci. Total Environ.* 628–629 (2018) 1462–1488, <https://doi.org/10.1016/j.scitotenv.2018.02.092>.
- [62] P.C. Van Metre, B.J. Mahler, J.T. Wilson, PAHs underfoot: contaminated dust from coal-tar sealcoated pavement is widespread in the United States, *Environ. Sci. Technol.* 43 (2009) 20–25, <https://doi.org/10.1021/es802119h>.
- [63] A.K. Baldwin, S.R. Corsi, M.A. Lutz, C.G. Ingersoll, R. Dorman, C. Magruder, M. Magruder, Primary sources and toxicity of PAHs in Milwaukee-area streambed sediment: sources of Toxicity of PAHs in Milwaukee-area sediment, *Environ. Toxicol. Chem.* 36 (2017) 1622–1635, <https://doi.org/10.1002/etc.3694>.
- [64] M. Ahrens, C.A. Depree, Source mixing model to apportion PAHs from coal tar and asphalt binders in street pavements and urban aquatic sediments, *Chemosphere* 81 (11) (2010) 1526–1535, <https://doi.org/10.1016/j.chemosphere.2010.08.030>.
- [65] W. Hu, L. Guangbin, T. Yong, Z. Qin, Emission of polycyclic aromatic hydrocarbons from different types of motor vehicles' exhaust, *Environ. Earth Sci.* 74 (7) (2015) 5557–5564, <https://doi.org/10.1007/s12665-015-4570-9>.
- [66] S. Wakeham, C. Schaffner, W. Giger, Polycyclic aromatic hydrocarbons in recent lake sediments-I. Compounds having anthropogenic origins, *Geochem. Cosmochim. Acta* 44 (3) (1980) 403–413, [https://doi.org/10.1016/0016-7037\(80\)90040-X](https://doi.org/10.1016/0016-7037(80)90040-X).
- [67] I. Sadiktsis, C. Bergvall, C. Johansson, R. Westerholm, Automobile tires: a potential source of highly carcinogenic dibenzopyrenes to the environment, *Environ. Sci. Technol.* 46 (2012) 3326–3334, <https://doi.org/10.1021/es204257d>.
- [68] C.E. Cerniglia, Biodegradation of polycyclic aromatic hydrocarbons, *Biodegradation* 3 (1992) 351–368, <https://doi.org/10.1007/BF00129093>.
- [69] A. Lawal, P. Fantke, Polycyclic aromatic hydrocarbons. A review, *Cogent Environmental Science* 3 (1) (2017), <https://doi.org/10.1080/23311843.2017.1339841>.

- [70] M. Zander, Physical and chemical properties of polycyclic aromatic hydrocarbons, in: A. Bjorseth (Ed.), *Handbook of Polycyclic Aromatic Hydrocarbons*, Marcel Dekker Inc, NewYork, NY, 1983.
- [71] R. Kanaly, S. Harayama, Biodegradation of high-molecular-weight polycyclic aromatic hydrocarbons by bacteria, *J. Bacteriol.* 182 (2000) 2059–2067, <https://doi.org/10.1128/JB.182.8.2059-2067.2000>.
- [72] W. Xia, B. Liang, L. Chen, Y. Zhu, M. Gao, J. Chen, F. Wang, Y. Chen, M. Tian, Atmospheric wet and dry depositions of polycyclic aromatic compounds in a megacity of Southwest China, *Environ. Res.* 204 (2022) 112–151, <https://doi.org/10.1016/j.envres.2021.112151>.
- [73] R.J. Pruell, J.G. Quinn, Accumulation of polycyclic aromatic hydrocarbons in crankcase oil, *Environ. Pollut.* 49 (1988) 89–97, [https://doi.org/10.1016/0269-7491\(88\)902424](https://doi.org/10.1016/0269-7491(88)902424).
- [74] E. Stogiannidis, R. Laane, Source characterization of polycyclic aromatic hydrocarbons by using their molecular indices: an overview of possibilities, *Rev. Environ. Contam. Toxicol.* 234 (2014) 49–133, https://doi.org/10.1007/978-3-319-10638-0_2.
- [75] M.B. Yunker, C.L. Lachmuth, W.J. Cretney, B.R. Fowler, N. Dangerfield, L. White, P.S. Ross, Biota – sediment partitioning of aluminium smelter related PAHs and pulp mill related diterpenes by intertidal clams at Kitimat, British Columbia, *Mar. Environ. Res.* 72 (2011) 105–126. <https://doi.org/10.1016/j.marenvres.2011.06.004>.
- [76] A. Solanas, R. Pareš, J. Bayona, J. Albaigés, Degradation of aromatic petroleum hydrocarbons by pure microbial cultures, *Chemosphere* 13 (1984) 593–601, [https://doi.org/10.1016/0045-6535\(84\)90196-6](https://doi.org/10.1016/0045-6535(84)90196-6).
- [77] H. Huang, Z. Li, Z. Wen, D. Han, R. Pan, Biodegradation influence on alkylphenanthrenes in oils from Bongor Basin, SW Chad, *Sci. Rep.* 9 (1) (2019) 12960, <https://doi.org/10.1038/s41598-019-49495-1>.
- [78] A. Medić, M. Lješević, H. Inui, V. Beškoski, I. Kojić, K. Stojanović, I. Karadžić, Efficient biodegradation of petroleum n-alkanes and polycyclic aromatic hydrocarbons by polyextremophilic *Pseudomonas aeruginosa* strain with multi-degradative capacity, *RSC Adv.* 10 (2020) 14060–14070, <https://doi.org/10.1039/C9RA10371F>.
- [79] S. Lee, J. Kwon, Enhancement of toxic efficacy of alkylated polycyclic aromatic hydrocarbons transformed by *Sphingobium quisquiliarum*, *Int. J. Environ. Res. Publ. Health* 17 (2020) 6416, <https://doi.org/10.3390/ijerph17176416>.
- [80] P. Dimitriou-Christidis, R. Autenrieth, T. McDonald, A. Desai, Measurement of biodegradability parameters for single unsubstituted and methylated polycyclic aromatic hydrocarbons in liquid bacterial suspensions, *Biotechnol. Bioeng.* 97 (2007) 922–932, <https://doi.org/10.1002/bit.21268>.
- [81] M. Siddiqi, Z. Yuan, S. Honey, S. Kumar, H. Sikka, Metabolism of PAHs and methyl-substituted PAHs by *Sphingomonas paucimobilis* strain EPA 505, *Polycycl. Aromat. Comp.* 22 (2002) 621–630, <https://doi.org/10.1080/1040663029010379>.
- [82] B. Mahler, P. Van Metre, W. Foreman, Concentrations of polycyclic aromatic hydrocarbons (PAHs) and azaarenes in runoff from coal-tar- and asphalt-sealcoated pavement, *Environ. Pollut.* 188 (2014) 81–87, <https://doi.org/10.1016/j.envpol.2014.01.008>.
- [83] E. Nikiforova, N. Kasimov, N. Kosheleva, Polycyclic aromatic hydrocarbons in urban soils sealed under asphalt concrete, *Dokl. Earth Sci.* 491 (1) (2020) 171–174, <https://doi.org/10.1134/S1028334X20030125>.
- [84] M. Murakami, F. Nakajima, H. Furumai, Size- and density-distributions and sources of polycyclic aromatic hydrocarbons in urban road dust, *Chemosphere* 61 (6) (2005) 783–791, <https://doi.org/10.1016/j.chemosphere.2005.04.003>.
- [85] T. Nguyen, P. Loganathan, T.V. Nguyen, S. Vigneswaran, J. Kandasamy, D. Slee, G. Stevenson, R. Naidu, Polycyclic aromatic hydrocarbons in road-deposited sediments, water sediments, and soils in Sydney, Australia: comparisons of concentration distribution, sources and potential toxicity, *Ecotoxicol. Environ. Saf.* 104 (2014) 339–348, <https://doi.org/10.1016/j.ecoenv.2014.03.010>.
- [86] A. Azimi, A. Riahi Bakhtiari, R. Tauler, Polycyclic aromatic hydrocarbon source fingerprints in the environmental samples of Anzali - south of Caspian Sea, *Environ. Sci. Pollut. Control Ser.* 27 (2020) 32719–32731, <https://doi.org/10.1007/s11356-020-09588-1>.