



Cite this: *Environ. Sci.: Processes Impacts*, 2021, 23, 1986

Poor regulation implications in a low and middle income country based on PAH source apportionment and cancer risk assessment†

Wiaam Jaafar, ^{†a} Vera Zaherddine, ^{†a} Fatima Hussein,^a Najat Aoun Saliba ^a and Nathalie Hayeck ^{*b}

Ambient particle-bound polycyclic aromatic hydrocarbons (PAHs) were collected for one year at an urban background site, and spatially and temporally compared to yearly averages in three coastal cities in Lebanon. The samples were quantified using gas chromatography-mass spectrometry (GC-MS) and source apportioned with an optimized robust method using positive matrix factorization (PMF). Three major sources were found to contribute to PAH emissions at the urban background site, namely, traffic (48%), diesel generators (23%), and incineration (29%). The cancer risk was found higher than what was measured at the same site in previous years with an increase of 35%. Improper regulations of the sources (incineration, power plant, diesel generators and traffic) identified in the different sites resulted in PAH intraurban variability. It is essential to study the chemical components of particulate matter (PM) in order to assess toxicity. In particular, particle-bound PAHs and their oxidation products are known for their carcinogenicity as well as their persistence in the atmosphere, which facilitate their transport to new locations. In the absence of law enforcement, unregulated sources and their total contribution to ambient PAHs present a major health risk. This calls for the attention of development funding agencies and their need to implement sustainable “carbon-free” funding strategies in support of urban development of low and middle-income countries (LMICs).

Received 11th July 2021
Accepted 27th October 2021

DOI: 10.1039/d1em00285f

rsc.li/epi

Environmental significance

Air pollution causes above three million premature deaths yearly, out of which 87% live in low and middle-income countries (LMICs). This study highlights how poor regulations of combustion sources contribute to high PAH emissions and high levels of cancer risk. Being chemically stable, PAH and their atmospheric products are able to contribute to the local and global pollution. It is hence of paramount importance to quantify and incorporate PAH emissions from LMICs into the long-range transportation models for more accurate predictions and mitigation measures.

Introduction

The increase in air pollution levels led to increased morbidity and mortality risk.¹ In Lebanon, the levels of air pollution, mainly particulate matter PM₁₀ and PM_{2.5} concentrations have long been shown to exceed by several folds the recommendations set by the World Health Organization (WHO).^{2–7}

PM₁₀ and PM_{2.5} are major carriers of polycyclic aromatic hydrocarbons (PAHs) in ambient air and have a significant role in spreading them. PAHs pose a threat on human life due to

their carcinogenicity, which is why their quantification and source identification in the environment is being continuously monitored. Their emissions are linked to natural and anthropogenic sources but anthropogenic sources dominate over natural sources.^{8–11} Many studies highlight the high PAH levels in Beirut and in cities outside Beirut.^{12–14} The exposure to such high levels of pollution is attributed to heavy traffic and the high dependence on diesel generators to provide electricity during daily power outages. According to Shihadeh *et al.*¹⁴ an increase, over the background, by 38% of the total emissions of PAHs into the atmosphere in Hamra, which is near our sampling site, was attributed to diesel generators. The biomarkers of a recent exposure to PAHs are the hydroxylated polyaromatic hydrocarbons (OHPAHs) that are formed by PAH *in vivo* hydroxylation reactions. In a study done by Hajir *et al.*,¹⁵ it was found that the exposure of the population in Lebanon to the high levels of PAHs leads to higher levels of OHPAHs in urine compared to other countries like Germany, Malaysia, and the US.

^aDepartment of Chemistry, Faculty of Arts and Sciences, American University of Beirut, Beirut, Lebanon

^bDepartment of Natural Sciences, Lebanese American University, Chouran, Beirut 1102-2801, Lebanon. E-mail: nathalie.hayeck@lau.edu.lb; Tel: +961 1 786456 ext. 3412

† Electronic supplementary information (ESI) available. See DOI: 10.1039/d1em00285f

* Contributed equally.

Furthermore, one of the specific markers of diesel generators and incineration, 1-hydroxypyrene (1-OHPYR), was associated with high risk of obstructive coronary artery disease.¹⁵ In addition to their health effect on local population, long-range transportation of PAHs makes them a trans-boundary threat due to their persistence in the atmosphere. Moreover, the oxygenated and nitrated oxidation products of PAHs (oxy-PAHs and nitro-PAHs) are classified as mutagenic and carcinogenic, and contribute to higher toxicity of PM.^{16,17}

While the various summarized studies have given a clear idea on the abundance of PAHs in the ambient atmosphere in different sites in Lebanon, these studies were limited in time and as such the collected data were insufficient to identify the percent contribution of the different sources based on a robust source apportionment method like the positive matrix factorization (PMF). In this study, the 55 particle samples collected over a whole year between November 2016 and November 2017 present a unique opportunity to identify the percent contribution of the various sources in one of the background sites in Beirut using the positive matrix factorization (PMF) model. The inter- and intra-comparison of PAH concentrations elucidate the variability in time and space and evaluate the cancer risk levels of each identified source. Being transported to new locations, the measured PAH concentrations in one LMIC where law enforcements are absent (*i.e.*, Lebanon) should be accounted for and included in the models that are used to study the long-range transportation.

Methodology

Sampling site

Ambient measurements of particle-bound PAHs were conducted at an urban site located at the rooftop of the chemistry department at the American University of Beirut (AUB) (33° 54' 4" N, 35° 28' 53" E, ~20 m above the ground) (Fig. 1). The sampling site is considered an urban background site since several sources contribute to the emission of PAHs with no source dominating over the other.^{18–23} The sampling site is embarked by the Mediterranean coastal road 100 m west, by Bliss Street 200 m east and it is 4.2 km far from Beirut harbor. The sampling site is surrounded from all sides by campus parking, pedestrian small roads and a highway that gets crowded by traffic from the schools close to AUB.

Sampling and analysis of PAHs

A high-volume sampler (HVS) (DH77, DIGITEL Elektronik AG, Hegnau, Switzerland), operating at a flow rate of 500 L min⁻¹ and equipped with a PM₁₀ impactor was used to sample particle-bound PAHs on quartz filters (Whatman, 150 mm), prebaked at 400 °C for 5 h to remove the absorbed organic compounds.²⁴ The samples were collected over 24 hours; once every six days between November 2016 and November 2017, for a total of 55 samples. After sampling, the filters were collected and wrapped in hexane-rinsed aluminum foil, then refrigerated at a temperature below 4 °C for up to 7 days before extraction.

The extraction and analysis method of the 16 PAHs were done using the EPA TO-13A²⁴ method with some modifications.

Prior to extraction, the collected filters were spiked with 2 µg of deuterated PAH standard (acenaphthene-D10, chrysene-D12, perylene-D12, and phenanthrene-D10 from Absolute Standards), and then extracted in 250 mL of toluene. The deuterated standards are used to quantify the PAHs. PAHs were extracted by sonication for 2 hours. After that, the extract was placed in a rotary evaporator at 45 °C and concentrated to a volume of 1 mL, without excessive loss of the desired analytes. The concentrate was then cleaned up on a HyperSep Silica SPE (Solid Phase Extraction) cartridge using 10 mL of hexane as an elution solvent and the cleaned sample was re-concentrated to 200 µL under a gentle flow of nitrogen. The sample is then injected into GC-MS for analysis.

The analysis of PAHs was accomplished using a Thermo-Finnigan Trace GC-Ultra Polaris ITQ 900 MS coupled with an AS 3000 II autosampler. Chromatographic separation was carried out on an Rtx-5MS column (60 m × 0.25 µm film thickness × 0.25 mm film ID). The carrier gas was helium of 99.99% purity with 1 mL min⁻¹ flow rate. The samples were injected in splitless mode at 280 °C. The GC oven was programmed from 80 °C (hold for 3 minutes) to 170 °C (10 °C min⁻¹, hold for 1 min), to 180 °C (3 °C min⁻¹, hold for 0 min), to 270 °C (10 °C min⁻¹, hold time 0 min), then ramped to 300 °C (3 °C min⁻¹, hold for 10 min). The mass spectrometer was operated in full scan mode (*m/z* range from 50 to 350). The ion source was set at 250 °C in electron impact mode (70 eV). The analytes were identified by their retention time and their mass spectrum. The sixteen PAHs quantified in this study were: naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flt), pyrene (Pyr), benzo[*a*]anthracene (BaA), chrysene (Chr), benzo[*k*]fluoranthene (BkF), benzo[*b*]fluoranthene (BbF), benzo[*a*]pyrene (BaP), benzo[*ghi*]perylene (BghiP), dibenz[*a,h*]anthracene (DahA), and indeno[1,2,3-*cd*]pyrene (IP).

Quality control and quality assurance (QC/QA)

The overall recovery of each PAH ranged between 85 and 118%. LOD/LOQ (limit of detection/limit of quantification) analysis was carried out using seven replicate extractions of a solution of the 16 PAHs at 0.1 µg mL⁻¹ spiked with 2 µg mL⁻¹ of deuterated standard. The results showed that ranges of detection and quantification limits of the 16 PAHs are 0.01–0.05 µg mL⁻¹ and 0.03–0.16 µg mL⁻¹ respectively. The results of six replicate standards for three concentrations (0.1, 4 and 8 µg mL⁻¹) revealed % RSD ranging between 4 and 8%. The deuterated standard calibration method was used to quantify the PAHs where it was found to be linear for the whole examined range of the 16 PAHs with a correlation coefficient >0.995. Concentrations of PAHs in the blanks were below the method detection limits during the analysis period.

Measurements of PM

Along with the PAH sampling, PM mass concentrations were measured using a real time portable monitor DustTrak DRX

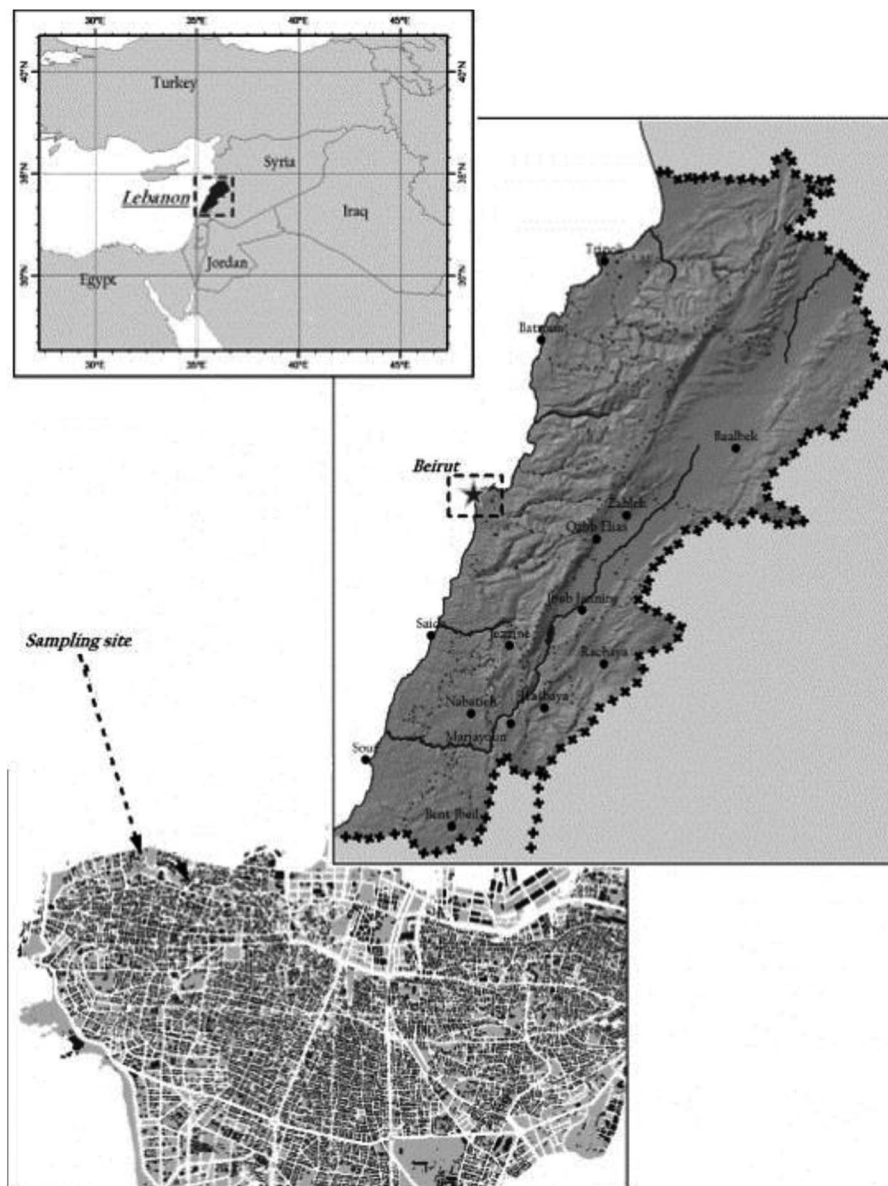


Fig. 1 Sampling site.

aerosol monitor 8533 for the size fractions $PM_{2.5}$, PM_{10} and total particulate matter (TPM). The DustTrak DRX was previously calibrated using a gravimetric analysis method. The DustTrak was placed to measure PM concentrations near two ChemComb (Thermo Scientific) cartridges. These cartridges were sampling PM_{10} and $PM_{2.5}$ aerosols using adequate impactors for 24 hours at 10 L min^{-1} flowrate. The PTFE (polytetrafluoroethylene) membrane filters (TISCH Scientific) used were pre-conditioned for 24-hours then weighed prior to sampling.²⁵ The sampled filters were then post-conditioned for 24 hours then weighed using a microbalance (Metler Toledo) to determine the mass of the collected $PM_{2.5}$ and PM_{10} . Following the calibration procedure developed by the DustTrak manufacturer, the PM concentrations obtained by the gravimetric method were compared to the concentrations determined by DustTrak to determine the two calibration factors needed to ensure an

accurate mass and size assignment for the measured aerosols, the factors being a photometric calibration factor (PCF) and a size calibration factor (SCF). The determined SCF and PCF factors were used during the DustTrak measurement performed in parallel to the HVS aerosol sampling for PAH determination.

Source apportionment using positive matrix factorization

Source apportionment for PAHs in this study was performed using the US EPA PMF 5.0 software. The Positive Matrix Factorization (PMF) methodology was previously detailed.^{26–29} Briefly, it is a receptor model based on a mathematical equation where it identifies and quantifies the contribution of different sources to a set of samples from the markers (fingerprints) of these sources.²⁹ More information on this model can be found in the ESI.†

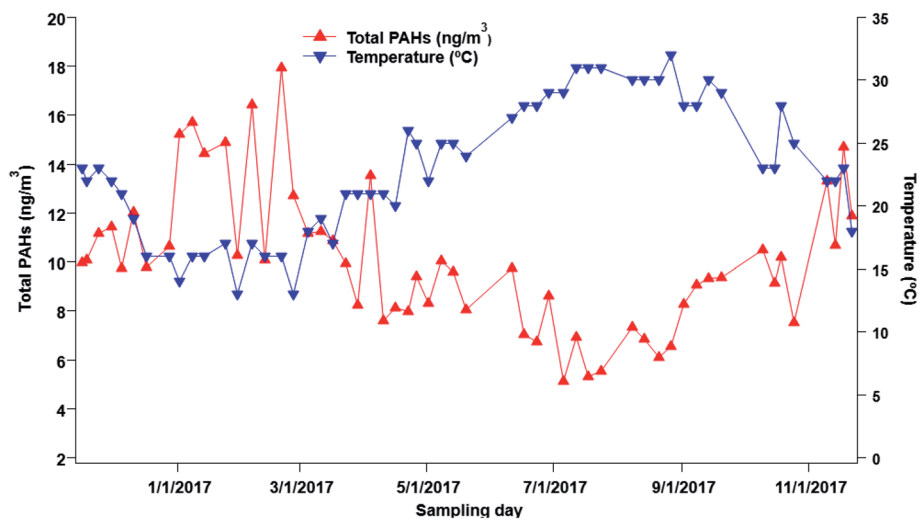


Fig. 2 Variation of the concentration of total PAHs with respect to temperature over the period extended between November 2016 and November 2017.

Cancer risk calculation

In this study, the carcinogenic potency of the measured PAHs was determined using the widely applied “toxic equivalence factor” (TEF) method.^{30–36} This approach, which is based on the procedures of the Office of Environmental Health Hazards Assessment of California Environmental Protection Agency (OEHHA-CalEPA), accounts for the toxicity of all PAHs in the form of BaP equivalence.^{34,37}

$$\sum \text{BaP}_{\text{eq.}} = \sum (C_i \times \text{TEF}_i) \quad (1)$$

where $\sum \text{BaP}_{\text{eq.}}$ is the total BaP equivalent concentrations, C_i is the concentration of each PAH in ng m^{-3} , and TEF_i is the toxicity equivalent factor of each PAH^{35–37} (refer to Table S2† for TEF values).

To determine the potential of contracting cancer by inhalation and exposure to particle-bound PAHs, the procedure from OEHHA was used. This widely applied procedure will allow the calculation of the lifetime excess cancer risk using the following equation:

$$\text{Excess Cancer Risk (ECR)} = \sum \text{BaP}_{\text{eq.}} \times \text{UR}_{\text{BaP}} \quad (2)$$

Table 1 Annual average concentrations of measured PAHs

	Beirut, Lebanon (this study)	Florence, Italy ³⁰	Shiraz, Iran ⁴⁶	Minnesota, USA ⁴⁹	Elche, Spain ⁵⁰	Saitama, Japan ⁵¹
Average PAH concentration (ng m^{-3})						
Naphthalene (Nap)	0.20 ± (0.02)	0.54	0.75	0.02	—	—
Acenaphthylene (Acy)	0.24 ± (0.02)	0.04	0.77	—	—	—
Acenaphthene (Ace)	0.28 ± (0.02)	0.06	1.89	—	—	—
Fluorene (Flu)	0.38 ± (0.03)	0.07	2.70	0.01	—	—
Phenanthrene (Phe)	0.31 ± (0.03)	0.13	3.57	0.02	0.12	—
Anthracene (Ant)	0.26 ± (0.02)	0.09	3.01	0.13	—	—
Fluoranthene (Flt)	0.59 ± (0.05)	0.13	0.49	0.28	0.17	—
Pyrene (Pyr)	0.54 ± (0.04)	0.20	2.58	0.23	0.22	0.18
Benzo[<i>a</i>]anthracene (BaA)	0.63 ± (0.05)	0.37	0.30	0.10	0.19	0.25
Chrysene (Chr)	0.66 ± (0.05)	0.19 ^a	0.28	0.16	0.35	—
Benzo[<i>k</i>]fluoranthene (BkF)	1.10 ± (0.09)	0.57 ^b	0.51	0.08	—	0.25
Benzo[<i>b</i>]fluoranthene (BbF)	0.86 ± (0.07)	0.57 ^b	0.46	0.16	0.57 ^c	0.50
Benzo[<i>a</i>]pyrene (BaP)	0.66 ± (0.05)	0.33	0.73	0.09	0.18	0.36
Benzo[<i>ghi</i>]perylene (BghiP)	1.30 ± (0.10)	0.5	0.23	0.15	0.13	0.64
Dibenz[<i>a,h</i>]anthracene (DahA)	1.00 ± (0.08)	0.30	0.26	0.02	—	—
Indeno[1,2,3- <i>cd</i>]pyrene (IP)	1.00 ± (0.08)	0.59	0.42	0.10	0.21	0.51
Total PAHs	10.00	4.68	19.28	1.55	2.14	2.69

^a Chrysene + triphenylene. ^b BbjkF: Benzo[*b + j + k*]fluoranthenes. ^c BkF + BbF.

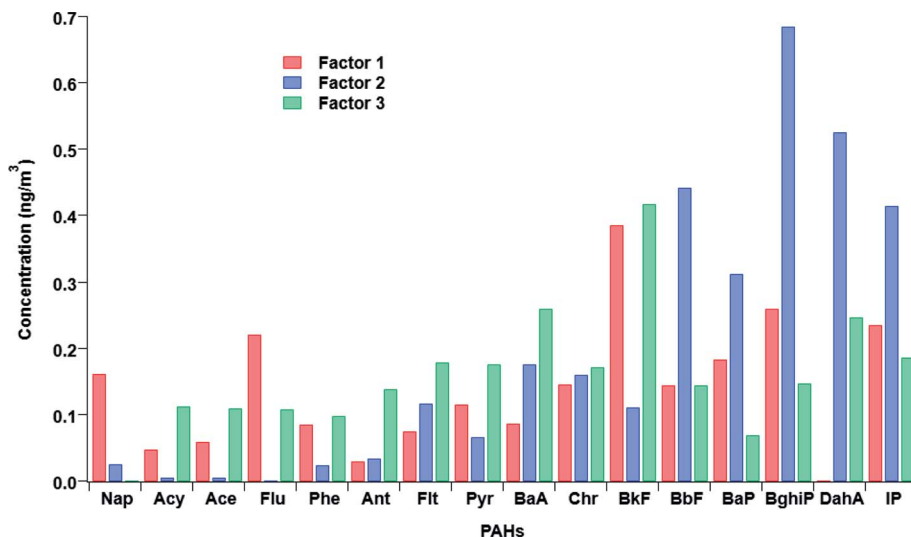


Fig. 3 Profiles of the three factors generated by the PMF model.

where UR_{BaP} is the number of people at risk of contracting cancer from inhalation of BaP equivalent concentration of 1 ng m^{-3} over a lifetime of 70 years.^{38,39} The value of UR_{BaP} used is 1.1×10^{-6} (0.11 cases per 100 000 people) according to OEHHA of the CalEPA.⁴⁰

Results and discussion

PM and PAH concentration

The yearly averages of PM_{10} and $PM_{2.5}$ were $68.13 \text{ } \mu\text{g m}^{-3}$ and $25.48 \text{ } \mu\text{g m}^{-3}$, respectively. The annual mean for the PAH sum was 10.04 ng m^{-3} with a maximum concentration of 17.94 ng m^{-3} measured on February 20, 2017, and a minimum of 5.12 ng m^{-3} measured on July 06, 2017, as shown in Fig. 2. PAHs show a high temporal variation throughout the year with higher concentrations during the period of low temperatures ($13 \text{ } ^\circ\text{C}$ to $21 \text{ } ^\circ\text{C}$) compared to the one of higher temperatures ($22 \text{ } ^\circ\text{C}$ to $32 \text{ } ^\circ\text{C}$) (Fig. 2). The average concentration of particle-bound PAHs was 14.0 ng m^{-3} during the cold season (from December to March) and 6.3 ng m^{-3} during the hot season (from April to September). The temporal variation of the PAH concentration agrees with other studies where previous PM_{10} and PAH measurements in Beirut have shown that PAH levels in winter were higher than those in summer. In those studies, the lower levels in the summer season were attributed to several factors including the evaporation of PAHs from the particulate to the gas phase, the low frequency of temperature inversions, the higher emissions in winter, and the photodegradation reactions of these compounds, which are known to increase in the summer leading to the decrease of PAH concentrations in the particulate phase.^{12,33,41–44} Such a behavior is attributed to the higher solar irradiation (April to September) that is estimated to double during the summer when compared to the winter, in Beirut.⁴⁵ Table S2 and Fig. S1 in the ESI† show the total PAHs with the recorded temperature, wind speed, and direction for each sampling day.

The annual average concentrations of the 16 PAHs and their sum are presented in Table 1. Also, in Table 1 a comparison of the concentration of PAHs with different urban cities is presented. Findings from this study indicate that some PAHs and the total PAHs in the AUB site show higher concentrations than that in other cities with more enforced regulations like Florence (Italy), Minnesota (USA), Elche (Spain), and Saitama (Japan) with a percent difference of approximately 36%, 72%, 51%, and 45%, respectively. In particular, the yearly BaP average of 0.66 ng m^{-3} is less than the 1 ng m^{-3} annual guideline set by the European Union Directive 2004/107/EC but greater by 33%, 76%, 57%, and 29% compared to the cities mentioned above. It should be noted that the sampling site in Saitama is similar to that of the sampling site in Beirut (roof of a university near a highway), but the level of BaP in Beirut was higher by 29% which shows higher level of pollution. In addition, BghiP and DahA, which are markers for traffic, are higher in Beirut by approximately 70% and 60% than in Shiraz (Iran), respectively.⁴⁶ This could be attributed to the higher average age of gasoline vehicles in the two corresponding countries (19 years in the case of Lebanon⁴⁷ versus less than 10 years for Iran⁴⁸). The higher average age of gasoline vehicles along with the percent difference in BaP and PAHs is an indicator that there are poor applications of regulations in Lebanon.

Source apportionment

Factor identification. The profiles for the three factors are displayed in Fig. 3.

Factor 1, which was dominated by high-molecular weight (HMW) PAHs like BkF, BghiP, BaP, IP, and Chr, and was assigned to waste incineration, was in good accordance with the profile of PAHs of a medical waste incinerator.^{52–55} Factor 2 corresponds to traffic emissions marked by PAHs like BghiP, DahA, BbF, IP, and BaP as the dominant components.^{37,56–60} Factor 3 shows high levels of low molecular weight (LMW) PAHs such as Pyr, Flt, Ant, and Phe congeners that are considered to

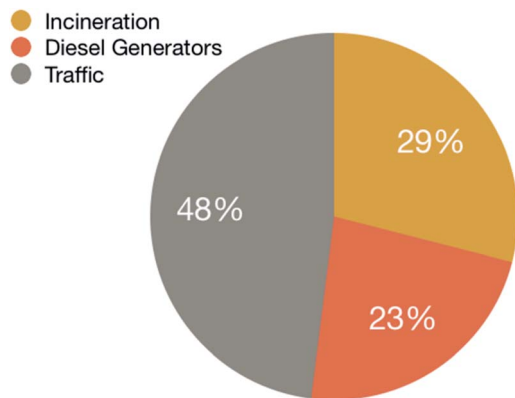


Fig. 4 Total contribution of the three sources.

represent emissions from diesel generators.^{39,54} In addition, factor 3 has a substantial loading of BaA, Chr, BkF, BbF and some BaP compared to factor 2 (attributed to vehicle emissions) where the concentrations of IP and BghiP contribute the most.^{61,62} Further differentiation between diesel and gasoline emission factors is based on the diagnostic ratios. In particular, a ratio of $(\text{BaP}/(\text{BaP} + \text{Chr})) = 0.3 < 0.5$ supports the association of factor 3 with diesel emissions⁶³ whereas the IP/BghiP ratios of 0.6 and 1.26 confirm the assignment of the gasoline vehicle (factor 2) and diesel generator emissions (factor 3), respectively, with IP/BghiP > 1 being more typical of diesel generator emissions (factor 3).⁶⁴ The contribution of each of the identified factors, traffic, diesel, and incineration, to PAH concentrations was 48, 23 and 29%, respectively, as shown in Fig. 4.

The primary source of PAHs at the sampling site was traffic emissions with a total contribution to the total PAH emissions of 48%. The site, which overlooks a coastal road, is surrounded by two large schools and a university, and as such heavy traffic from low duty vehicles is observed mostly during the academic year. A high contribution to the PAH annual average concentration (29%) was also attributed to incineration mainly due to a nearby hospital incinerator. The usage of diesel generators contributes to the total PAH emissions by 23%. The interruption of the national electricity supply (Electricite du Liban – EDL) for three hours per day in Beirut, forced citizens to use diesel generators during the cut-off periods. The density of diesel generators to buildings in the capital reaches 50% indicating that there is one generator between every two buildings.⁴⁷ The incineration and diesel generators are uncommon urban emission sources. Those sources might have contributed to the annual PM₁₀ and PM_{2.5} concentrations that exceed the WHO standards⁶⁵ and to a relatively high level of toxicity in PMs.¹³

A comparison was done on the sources that emit PAHs into the atmosphere between countries with different Gross National Incomes (GNIs). It was found that in low-income countries the main source of PAH emission was vehicular emission (both diesel and gasoline vehicles) like in Rwanda.⁶⁶ In middle and high-income countries, sources like industrial processes, and coal combustion predominate in addition to vehicular emission (both diesel and gasoline vehicles).^{67–70}

Lebanon was one of the few countries that showed incineration and diesel generators to account for almost 50% of PAH emissions into the atmosphere. The results in this study highlight how traffic emissions, incineration, and diesel generators highly influence and affect residents nearby. In addition, previous studies^{2,3,7,12,47} performed around the city of Beirut showed that these sources were widespread in Beirut and are the cause of the levels of the emitted PM. Our study confirms this, but it also shows that incineration in addition to vehicle and diesel emissions dominates on this site.

In 2015, Baalbaki *et al.* studied the sources that contribute to the total PAH emissions in three cities along the coastal line and it was found that the sites possess a heterogeneous temporal and spatial intra- and inter-urban variability.¹² The study also shows that the coefficient of divergence (COD) for most PAHs was greater than 0.2 which shows that the heterogeneity is due to the variation of the sources and their contribution in each site.¹² To further support the inter- and intra-urban variability in Beirut, another study by Massoud *et al.*³ in AUB and two other sites (Lycée Abel Kader and Grand Lycée Franco Libanais) is in agreement with Baalbaki *et al.*'s conclusions. It is apparent that due to improper application of regulations in Lebanon that while the three sites share common sources, each site has at least one heavy contributor to the total PAH emissions. According to Baalbaki *et al.*, because the sites are less than 10 km apart, the heterogeneity in emissions at each site is attributed to intra-urban variations and not due to PAH transportation.¹² For example, the AUB site has a waste incinerator, Dora site has traffic and petroleum reserves, and Zouk Mikael has a power plant that uses heavy fuel oil for electricity production. The three sites are heavily populated and the presence of these sources poses some health risks.

The health risks are attributed to the components and toxicity of PM which are expressed, for example, in cancer risk calculation using PAH concentration. The type and concentrations of the PM components increase or decrease the PM toxicity. The chemical composition of PM was assessed by Daher *et al.*¹³ and it was found that the chemical content of an equal mass of particles in Lebanon usually shows higher toxicity than other places, like Los Angeles. Relying solely on PM concentration does not fully encompass toxicity since sites can possess similar PM concentrations but due to a different chemical composition one site can have higher toxicity than another. For example, an urban site in Shiraz (Iran) having multiple sources contributing to PAH emissions (highest percent contribution was vehicular emissions) showed a PM₁₀ concentration of 62.73 $\mu\text{g m}^{-3}$ with a mean PAH sum of 19.28 ng m^{-3} .⁴⁶ The average concentration of PM₁₀ reported in this study is 68.13 $\mu\text{g m}^{-3}$ and a mean PAH sum of 10.04 ng m^{-3} . This shows the importance of components of PM when assessing toxicity especially in urban sites where multiple sources are found and no one source dominates over another.

In this study, the increase in the PM toxicity is illustrated in the calculation and comparison of the cancer risk related to PAH exposure. The major concern related to the toxic effect of PAHs is their ability to cause mutations, developmental malformations, tumors and cancers.^{71,72} Occupational studies of

workers have shown that exposure to PAH mixtures is carcinogenic to humans causing skin, lungs, bladder and gastrointestinal cancers. Other laboratory studies have shown animal exposure to PAH for long periods to cause lung cancer from inhalation.⁷³

Based on the presented data, the estimated cancer risk for AUB using eqn (1) and (2) is 2.25×10^{-6} . The three major sources identified, traffic, diesel generators and incineration, seemed to contribute 58%, 25% and 17%, respectively. This value is above the threshold for acceptable cancer risk set by EPA (10^{-6}),⁷⁴ and also higher than those obtained in some European cities such as Greece (0.58×10^{-6}),³⁷ Grenoble (1.64×10^{-6}),⁷⁵ Florence (1.53×10^{-6}) and Athens (4.73×10^{-7}).³⁰ The lower ECR levels in these European cities are attributed to the effective environmental regulations which are not enforced in Lebanon, the cleaner energy resources, waste export and recycling.³³ However, the ECR found in this study is lower than those found in some Chinese cities like Beijing (10^{-5} to 10^{-3})³³ and Xi'an (18.7×10^{-6}).³²

The cancer risk calculated for AUB in 2017 (this study) showed an increase over the value that was calculated for 2015 (1.05×10^{-6}), confirming thereby the lack of regulations to reduce or contain emissions. In the other two cities, Dora and Zouk Mikael, where emissions are expected to be higher due to the presence of major polluting sources like heavy traffic and a power plant, the estimated cancer risks of 4.45×10^{-6} and 3.10×10^{-6} , respectively,¹² are higher than those of AUB in 2015 and 2017. High PAH levels have been shown to be associated with morbidities like cardiovascular diseases (CVD).⁷⁶⁻⁷⁸ In particular, a recent study conducted in our lab has shown that even non-smoking individuals who reported to a medical hospital for catheterization in Beirut showed high levels of PAH metabolites in their urine samples. The measured levels of 1-hydroxypyrene were found to be associated with coronary artery disease (CAD).¹⁵

In addition to their direct health effect at the local level, PAHs are also known for their resistance to degradation, their persistence in the atmosphere and hence their qualification as persistent organic pollutants (POPs).^{79,80} Long-range transport of PAHs was identified early in 1977 when PAHs were found in Norway and were identified as originating from France/England and England/Scotland.⁸¹ Evidence of PAH long-range transport continued to emerge with more measurements in the sub-Arctic region showing that fossil fuel and wood combustion emissions are transported from Asia, continental North America, and north Europe to sub-Arctic Canada.⁸²

The understanding of the ability of PAHs to withstand the photodegradation and heterogeneous reactions with ozone was recently explained by the presence of viscous organic compounds in PM creating a shield to protect BaP and other PAHs. Modeling results have shown that the shielding effect is more efficient in the middle/high latitudes compared to tropics due to the variability in the organic aerosol properties and the fast chemical degradation of BaP in the tropics.⁸³ In addition, the oxidation products of PAHs, the oxygenated PAHs (oxy-PAHs) and nitrated PAHs (nitro-PAHs), are more toxic than their parent PAHs due to their mutagenicity and

carcinogenicity¹⁶ and might contribute to the high toxicity of particulate matter.¹⁷

Being in the middle latitude zone, Lebanon might be contributing to the long-range transport of PAHs. This contribution should be accounted for, first by providing annual measurement of their concentrations and second by including these concentrations in the long-range transportation models. The results obtained from this study are part of the efforts that are needed to increase the number of PAH studies in the middle east region.

In summary, the levels of ambient PAHs are due to poor enforcement of regulations and unregulated sources. Levels have shown to increase over time and are expected to have increased at least 8 folds in the past year due to the economic collapse of the country and the complete shutdown of the major power plants. This poses a major health risk to the population in Lebanon and to other cities where PAHs and their oxidation products are transported. The lack of mitigation and reduction strategies from the part of the local governments calls for sustainable “carbon-free” plans from the part of the funding agencies and supporting organizations to aid the urban development of LMIC cities.

Abbreviations

ECR	Excess cancer risk
HQ	Hazard quotient
AUB	American University of Beirut
OHPAHs	Hydroxylated polycyclic aromatic hydrocarbons
PAHs	Polycyclic aromatic hydrocarbons
1-OHPYR	1-Hydroxypyrene
HVS	High volume sampler
HMW	High molecular weight
LMIC	Low and middle-income countries
LMW	Low molecular weight
OEHHA-	Office of Environmental Health Hazards
CalEPA	Assessment of California Environmental Protection Agency
TEF	Toxicity equivalent factor
CVD	Cardiovascular disease
Nap	Naphthalene
Acy	Acenaphthylene
Ace	Acenaphthene
Flu	Fluorene
Phe	Phenanthrene
Ant	Anthracene
Flt	Fluoranthene
Pyr	Pyrene
BaA	Benzo[<i>a</i>]anthracene
Chr	Chrysene
BkF	Benzo[<i>k</i>]fluoranthene
BbF	Benzo[<i>b</i>]fluoranthene
BaP	Benzo[<i>a</i>]pyrene
BghiP	Benzo[<i>ghi</i>]perylene
DahA	Dibenz[<i>a,h</i>]anthracene
IP	Indeno[1,2,3- <i>cd</i>]pyrene

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We would like to thank WHO for providing funding and the research team at the analytical and atmospheric laboratory (AAL) for the fruitful discussions on PAHs.

References

- 1 C. A. Pope, N. Coleman, Z. A. Pond and R. T. Burnett, Fine particulate air pollution and human mortality: 25+ years of cohort studies, *Environ. Res.*, 2020, **183**, 108924.
- 2 M. Borgie, A. Garat, F. Cazier, A. Delbende, D. Allorge, F. Ledoux, D. Courcot, P. Shirali and Z. Dagher, Traffic-related air pollution. A pilot exposure assessment in Beirut, Lebanon, *Chemosphere*, 2014, **96**, 122–128.
- 3 R. Massoud, A. L. Shihadeh, M. Roumié, M. Youness, J. Gerard, N. Saliba, R. Zaarour, M. Abboud, W. Farah and N. A. Saliba, Intraurban variability of PM₁₀ and PM_{2.5} in an Eastern Mediterranean city, *Atmos. Res.*, 2011, **101**, 893–901.
- 4 Z. Nasser, P. Salameh, H. Dakik, E. Elias, L. Abou Abbas and A. Levêque, Outdoor Air Pollution and Cardiovascular Diseases in Lebanon: A Case-Control Study, *J. Environ. Public Health*, 2015, **2015**, e810846.
- 5 N. A. Saliba and R. Massoud, in *Urban Airborne Particulate Matter: Origin, Chemistry, Fate and Health Impacts*, ed. F. Zereini and C. L. S. Wiseman, Springer, Berlin, Heidelberg, 2011, pp. 3–17.
- 6 N. A. Saliba, H. Kouyoumdjian and M. Roumié, Effect of local and long-range transport emissions on the elemental composition of PM_{10–2.5} and PM_{2.5} in Beirut, *Atmos. Environ.*, 2007, **41**, 6497–6509.
- 7 A. Waked, C. Afif and C. Seigneur, An atmospheric emission inventory of anthropogenic and biogenic sources for Lebanon, *Atmos. Environ.*, 2012, **50**, 88–96.
- 8 B. Garban, H. Blanchoud, A. Motelay-Massei, M. Chevreuil and D. Ollivon, Atmospheric bulk deposition of PAHs onto France: trends from urban to remote sites, *Atmos. Environ.*, 2002, **36**, 5395–5403.
- 9 M. Howsam and K. C. Jones, in *PAHs and Related Compounds: Chemistry*, ed. A. H. Neilson, Springer, Berlin, Heidelberg, 1998, pp. 137–174.
- 10 B. Maliszewska-Kordybach, Sources, Concentrations, Fate and Effects of Polycyclic Aromatic Hydrocarbons (PAHs) in the Environment. Part A: PAHs in Air, *Pol. J. Environ. Stud.*, 1999, **8**, 131–136.
- 11 E. Terzi and C. Samara, Gas-Particle Partitioning of Polycyclic Aromatic Hydrocarbons in Urban, Adjacent Coastal, and Continental Background Sites of Western Greece, *Environ. Sci. Technol.*, 2004, **38**, 4973–4978.
- 12 R. Baalbaki, J. Nassar, S. Salloum, A. L. Shihadeh, I. Lakkis and N. A. Saliba, Comparison of atmospheric polycyclic aromatic hydrocarbon levels in three urban areas in Lebanon, *Atmos. Environ.*, 2018, **179**, 260–267.
- 13 N. Daher, N. A. Saliba, A. L. Shihadeh, M. Jaafar, R. Baalbaki and C. Sioutas, Chemical composition of size-resolved particulate matter at near-freeway and urban background sites in the greater Beirut area, *Atmos. Environ.*, 2013, **80**, 96–106.
- 14 A. Shihadeh, K. Makdisi, N. Farajalla and R. E. Hajj, Effect of distributed electric power generation on household exposure to airborne carcinogens in Beirut, *Electr. Power Gener.*, 2013, **15**, 4.
- 15 S. Hajir, L. Al Aaraj, N. Zgheib, K. Badr, H. Ismaeel, A. Abchee, H. Tamim and N. A. Saliba, The association of urinary metabolites of polycyclic aromatic hydrocarbons with obstructive coronary artery disease: A red alert for action, *Environ. Pollut.*, 2021, **272**, 115967.
- 16 J. Kielhorn, International Programme on Chemical Safety and Inter-Organization Programme for the Sound Management of Chemicals, *Selected Nitro- and Nitro-oxy-polycyclic Aromatic Hydrocarbons*, World Health Organization, Geneva, 2003.
- 17 Y. Kawanaka, E. Matsumoto, N. Wang, S.-J. Yun and K. Sakamoto, Contribution of nitrated polycyclic aromatic hydrocarbons to the mutagenicity of ultrafine particles in the roadside atmosphere, *Atmos. Environ.*, 2008, **42**, 7423–7428.
- 18 A. Bigi, G. Ghermandi and R. M. Harrison, Analysis of the air pollution climate at a background site in the Po valley, *J. Environ. Monit.*, 2012, **14**, 552–563.
- 19 V. Crenn, I. Fronval, D. Petitprez and V. Riffault, Fine particles sampled at an urban background site and an industrialized coastal site in Northern France - Part 1: Seasonal variations and chemical characterization, *Sci. Total Environ.*, 2017, **578**, 203–218.
- 20 G. Grivas, S. Cheristanidis, A. Chaloulakou, P. Koutrakis and N. Mihalopoulos, Elemental Composition and Source Apportionment of Fine and Coarse Particles at Traffic and Urban Background Locations in Athens, Greece, *Aerosol Air Qual. Res.*, 2018, **18**, 1642–1659.
- 21 J.-P. Putaud, L. Pozzoli, E. Pisoni, S. Martins Dos Santos, F. Lagler, G. Lanzani, U. Dal Santo and A. Colette, Impacts of the COVID-19 lockdown on air pollution at regional and urban background sites in northern Italy, *Atmos. Chem. Phys.*, 2021, **21**, 7597–7609.
- 22 O. Ramirez, A. M. Sánchez de la Campa, F. Amato, R. A. Catacolí, N. Y. Rojas and J. de la Rosa, Chemical composition and source apportionment of PM₁₀ at an urban background site in a high-altitude Latin American megacity (Bogota, Colombia), *Environ. Pollut.*, 2018, **233**, 142–155.
- 23 A. Waked, O. Favez, L. Y. Alleman, C. Piot, J.-E. Petit, T. Delaunay, E. Verlinden, B. Golly, J.-L. Besombes, J.-L. Jaffrezo and E. Leoz-Garziandia, Source apportionment of PM₁₀ in a north-western Europe regional urban background site (Lens, France) using positive matrix factorization and including primary biogenic emissions, *Atmos. Chem. Phys.*, 2014, **14**, 3325–3346.

- 24 O. US EPA, *Compendium Method TO-13A, Determination of Polycyclic Aromatic Hydrocarbons (PAHs) in Ambient Air Using Gas Chromatography/Mass Spectrometry (GC/MS)*, <https://www.epa.gov/amtic/compendium-methods-determination-toxic-organic-compounds-ambient-air>, accessed 9 October 2021.
- 25 Environmental Protection Agency, *40 CFR Appendix L to Part 50 - Reference Method for the Determination of Fine Particulate Matter as PM_{2.5} in the Atmosphere*, https://www.law.cornell.edu/cfr/text/40/appendix-L_to_part_50, accessed 17 September 2021.
- 26 European Commission. Joint Research Centre, *European Guide on Air Pollution Source Apportionment with Receptor Models: Revised Version 2019*, Publications Office, LU, 2019.
- 27 P. Chen, S. Kang, C. Li, Q. Li, F. Yan, J. Guo, Z. Ji, Q. Zhang, Z. Hu, L. Tripathi and M. Sillanpää, Source Apportionment and Risk Assessment of Atmospheric Polycyclic Aromatic Hydrocarbons in Lhasa, Tibet, China, *Aerosol Air Qual. Res.*, 2018, **18**, 1294–1304.
- 28 G. Norris, R. Duvall, S. Brown and S. Bai, *EPA Positive Matrix Factorization (PMF) 5.0 Fundamentals and User Guide*, 2014, vol. 136.
- 29 P. Paatero, Least squares formulation of robust non-negative factor analysis, *Chemom. Intell. Lab. Syst.*, 1997, **37**, 23–35.
- 30 C. A. Alves, A. M. Vicente, D. Custódio, M. Cerqueira, T. Nunes, C. Pio, F. Lucarelli, G. Calzolari, S. Nava, E. Diapouli, K. Eleftheriadis, X. Querol and B. A. Musa Bandowe, Polycyclic aromatic hydrocarbons and their derivatives (nitro-PAHs, oxygenated PAHs, and azaarenes) in PM_{2.5} from Southern European cities, *Sci. Total Environ.*, 2017, **595**, 494–504.
- 31 N. Ramirez, A. Cuadras, E. Rovira, R. M. Marcé and F. Borrull, Risk Assessment Related to Atmospheric Polycyclic Aromatic Hydrocarbons in Gas and Particle Phases near Industrial Sites, *Environ. Health Perspect.*, 2011, **119**, 1110–1116.
- 32 B. A. M. Bandowe, H. Meusel, R. Huang, K. Ho, J. Cao, T. Hoffmann and W. Wilcke, PM_{2.5}-bound oxygenated PAHs, nitro-PAHs and parent-PAHs from the atmosphere of a Chinese megacity: Seasonal variation, sources and cancer risk assessment, *Sci. Total Environ.*, 2014, **473–474**, 77–87.
- 33 A. Elzein, R. E. Dunmore, M. W. Ward, J. F. Hamilton and A. C. Lewis, Variability of polycyclic aromatic hydrocarbons and their oxidative derivatives in wintertime Beijing, China, *Atmos. Chem. Phys.*, 2019, **19**, 8741–8758.
- 34 S. Taghvaei, M. H. Sowlat, M. S. Hassanvand, M. Yunesian, K. Naddafi and C. Sioutas, Source-specific lung cancer risk assessment of ambient PM_{2.5}-bound polycyclic aromatic hydrocarbons (PAHs) in central Tehran, *Environ. Int.*, 2018, **120**, 321–332.
- 35 I. C. T. Nisbet and P. K. LaGoy, Toxic equivalency factors (TEFs) for polycyclic aromatic hydrocarbons (PAHs), *Regul. Toxicol. Pharmacol.*, 1992, **16**, 290–300.
- 36 Md. A. Bari, G. Baumbach, B. Kuch and G. Scheffknecht, Particle-phase concentrations of polycyclic aromatic hydrocarbons in ambient air of rural residential areas in southern Germany, *Air Qual., Atmos. Health*, 2010, **3**, 103–116.
- 37 I. Tsiodra, G. Grivas, K. Tavernaraki, A. Bougiatioti, M. Apostolaki, D. Paraskevopoulou, A. Gogou, C. Parinos, K. Oikonomou, M. Tsagkaraki, P. Zampas, A. Nenes and N. Mihalopoulos, Annual exposure to PAHs in urban environments linked to wintertime wood-burning episodes, *Clouds and Precipitation/Field Measurements/Troposphere/Physics (Physical Properties and Processes)*, 2021.
- 38 Y. Jia, D. Stone, W. Wang, J. Schrlau, S. Tao and S. L. Massey Simonich, Estimated Reduction in Cancer Risk due to PAH Exposures If Source Control Measures during the 2008 Beijing Olympics Were Sustained, *Environ. Health Perspect.*, 2011, **119**, 815–820.
- 39 February 2015, Air Toxics Hot Spots Program Risk Assessment, 231.
- 40 OEHHA, *Benzo[a]pyrene*, <https://oehha.ca.gov/chemicals/benzoapyrene>, accessed 9 October 2021.
- 41 N. A. Saliba, S. Moussa, H. Salame and M. El-Fadel, Variation of selected air quality indicators over the city of Beirut, Lebanon: Assessment of emission sources, *Atmos. Environ.*, 2006, **40**, 3263–3268.
- 42 J. Zalzal, I. Alameddine, M. El-Fadel, S. Weichenthal and M. Hatzopoulou, Drivers of seasonal and annual air pollution exposure in a complex urban environment with multiple source contributions, *Environ. Monit. Assess.*, 2020, **192**, 415.
- 43 I. J. Keyte, R. M. Harrison and G. Lammel, Chemical reactivity and long-range transport potential of polycyclic aromatic hydrocarbons – a review, *Chem. Soc. Rev.*, 2013, **42**, 9333.
- 44 D. Kim, B. M. Kumfer, C. Anastasio, I. M. Kennedy and T. M. Young, Environmental aging of polycyclic aromatic hydrocarbons on soot and its effect on source identification, *Chemosphere*, 2009, **76**, 1075–1081.
- 45 C. Hajjar, Masters Degree in Human Geography, Faculty of Letters and human sciences, Lebanese University, 2020, 15.
- 46 S. Shahsavani, M. Hoseini, M. Dehghani and M. Fararouei, Characterisation and potential source identification of polycyclic aromatic hydrocarbons in atmospheric particles (PM₁₀) from urban and suburban residential areas in Shiraz, Iran, *Chemosphere*, 2017, **183**, 557–564.
- 47 A. Baayoun, W. Itani, J. El Helou, L. Halabi, S. Medlej, M. El Malki, A. Moukhadder, L. K. Aboujaoude, V. Kabakian, H. Mounajed, T. Mokalled, A. Shihadeh, I. Lakkis and N. A. Saliba, Emission inventory of key sources of air pollution in Lebanon, *Atmos. Environ.*, 2019, **215**, 116871.
- 48 H. Shahbazi, M. Reyhanian, V. Hosseini and H. Afshin, The Relative Contributions of Mobile Sources to Air Pollutant Emissions in Tehran, Iran: an Emission Inventory Approach, *Emiss. Control Sci. Technol.*, 2016, **2**, 44–56.
- 49 G. C. Pratt, C. Herbrandson, M. J. Krause, C. Schmitt, C. J. Lippert, C. R. McMahon and K. M. Ellickson, Measurements of gas and particle polycyclic aromatic hydrocarbons (PAHs) in air at urban, rural and near-roadway sites, *Atmos. Environ.*, 2018, **179**, 268–278.

- 50 M. Varea, N. Galindo, J. Gil-Moltó, C. Pastor and J. Crespo, Particle-bound polycyclic aromatic hydrocarbons in an urban, industrial and rural area in the western Mediterranean, *J. Environ. Monit.*, 2011, **13**, 2471–2476.
- 51 T. Naser, Y. Yoshimura, K. Sekiguchi, Q. Wang and K. Sakamoto, Chemical Composition of PM_{2.5} and PM₁₀ and Associated Polycyclic Aromatic Hydrocarbons at a Roadside and an Urban Background Area in Saitama, Japan, *Asian J. Atmos. Environ.*, 2008, **2**, 90–101.
- 52 W.-J. Lee, M.-C. Liow, P.-J. Tsai and L.-T. Hsieh, Emission of polycyclic aromatic hydrocarbons from medical waste incinerators, *Atmos. Environ.*, 2002, **36**, 781–790.
- 53 T. Okuda, K. Okamoto, S. Tanaka, Z. Shen, Y. Han and Z. Huo, Measurement and source identification of polycyclic aromatic hydrocarbons (PAHs) in the aerosol in Xi'an, China, by using automated column chromatography and applying positive matrix factorization (PMF), *Sci. Total Environ.*, 2010, **408**, 1909–1914.
- 54 B. R. T. Simoneit, P. M. Medeiros and B. M. Didyk, Combustion Products of Plastics as Indicators for Refuse Burning in the Atmosphere, *Environ. Sci. Technol.*, 2005, **39**, 6961–6970.
- 55 K. Yasuda and M. Takahashi, The Emission of Polycyclic Aromatic Hydrocarbons from Municipal Solid Waste Incinerators during the Combustion Cycle, *J. Air Waste Manage. Assoc.*, 1998, **48**, 441–447.
- 56 G. Valotto, G. Rampazzo, F. Gonella, G. Formenton, S. Ficotto and G. Giraldo, Source apportionment of PAHs and n-alkanes bound to PM₁ collected near the Venice highway, *J. Environ. Sci.*, 2017, **54**, 77–89.
- 57 B. Zielinska, J. Sagebiel, J. D. McDonald, K. Whitney and D. R. Lawson, Emission Rates and Comparative Chemical Composition from Selected In-Use Diesel and Gasoline-Fueled Vehicles, *J. Air Waste Manage. Assoc.*, 2004, **54**, 1138–1150.
- 58 H. Guo, Particle-associated polycyclic aromatic hydrocarbons in urban air of Hong Kong, *Atmos. Environ.*, 2003, **37**, 5307–5317.
- 59 P. Masclat, G. Mouvier and K. Nikolaou, Relative decay index and sources of polycyclic aromatic hydrocarbons, *Atmos. Environ.*, 1986, **20**, 439–446.
- 60 M. G. Perrone, C. Carbone, D. Faedo, L. Ferrero, A. Maggioni, G. Sangiorgi and E. Bolzacchini, Exhaust emissions of polycyclic aromatic hydrocarbons, n-alkanes and phenols from vehicles coming within different European classes, *Atmos. Environ.*, 2014, **82**, 391–400.
- 61 E. Manoli, D. Voutsas and C. Samara, Chemical characterization and source identification/apportionment of fine and coarse air particles in Thessaloniki, Greece, *Atmos. Environ.*, 2002, **36**, 949–961.
- 62 M. Iakovides, E. G. Stephanou, M. Apostolaki, M. Hadjicharalambous, J. S. Evans, P. Koutrakis and S. Achilleos, Study of the occurrence of airborne Polycyclic Aromatic Hydrocarbons associated with respirable particles in two coastal cities at Eastern Mediterranean: Levels, source apportionment, and potential risk for human health, *Atmos. Environ.*, 2019, **213**, 170–184.
- 63 M. Cerqueira and J. Matos, A one-year record of particle-bound polycyclic aromatic hydrocarbons at an urban background site in Lisbon Metropolitan Area, Portugal, *Sci. Total Environ.*, 2019, **658**, 34–41.
- 64 A. M. Caricchia, S. Chiavarini and M. Pezza, Polycyclic aromatic hydrocarbons in the urban atmospheric particulate matter in the city of Naples (Italy), *Atmos. Environ.*, 1999, **33**, 3731–3738.
- 65 *Ambient (outdoor) air pollution*, [https://www.who.int/news-room/fact-sheets/detail/ambient-\(outdoor\)-air-quality-and-health](https://www.who.int/news-room/fact-sheets/detail/ambient-(outdoor)-air-quality-and-health), accessed 8 October 2021.
- 66 E. Kalisa, E. G. Nagato, E. Bizuru, K. C. Lee, N. Tang, S. B. Pointing, K. Hayakawa, S. D. J. Archer and D. C. Lacap-Bugler, Characterization and Risk Assessment of Atmospheric PM_{2.5} and PM₁₀ Particulate-Bound PAHs and NPAHs in Rwanda, Central-East Africa, *Environ. Sci. Technol.*, 2018, **52**, 12179–12187.
- 67 M. Akyüz and H. Çabuk, Particle-associated polycyclic aromatic hydrocarbons in the atmospheric environment of Zonguldak, Turkey, *Sci. Total Environ.*, 2008, **405**, 62–70.
- 68 S. Gupta, K. Kumar, A. Srivastava, A. Srivastava and V. K. Jain, Size distribution and source apportionment of polycyclic aromatic hydrocarbons (PAHs) in aerosol particle samples from the atmospheric environment of Delhi, India, *Sci. Total Environ.*, 2011, **409**, 4674–4680.
- 69 P. Pant, A. Shukla, S. D. Kohl, J. C. Chow, J. G. Watson and R. M. Harrison, Characterization of ambient PM_{2.5} at a pollution hotspot in New Delhi, India and inference of sources, *Atmos. Environ.*, 2015, **109**, 178–189.
- 70 M. S. Callén, A. Iturmendi and J. M. López, Source apportionment of atmospheric PM_{2.5}-bound polycyclic aromatic hydrocarbons by a PMF receptor model. Assessment of potential risk for human health, *Environ. Pollut.*, 2014, **195**, 167–177.
- 71 *List of Classifications – IARC Monographs on the Identification of Carcinogenic Hazards to Humans*, <https://monographs.iarc.who.int/list-of-classifications>, accessed 8 October 2021.
- 72 H. I. Abdel-Shafy and M. S. M. Mansour, A review on polycyclic aromatic hydrocarbons: Source, environmental impact, effect on human health and remediation, *Egypt. J. Pet.*, 2016, **25**, 107–123.
- 73 ATSDR, *Polycyclic Aromatic Hydrocarbons (PAHs)*, 1995, Agency Toxic Subst. Dis. Regist., vol. 2.
- 74 D. Bussard, *Exposure Factors Handbook*, 2011, p. 1436.
- 75 S. Tomaz, P. Shahpoury, J.-L. Jaffrezo, G. Lammel, E. Perraudin, E. Villenave and A. Albinet, One-year study of polycyclic aromatic compounds at an urban site in Grenoble (France): Seasonal variations, gas/particle partitioning and cancer risk estimation, *Sci. Total Environ.*, 2016, **565**, 1071–1083.
- 76 X. Xu, H. Hu, G. D. Kearney, H. Kan and D. S. Sheps, Studying the effects of polycyclic aromatic hydrocarbons on peripheral arterial disease in the United States, *Sci. Total Environ.*, 2013, **461–462**, 341–347.
- 77 I. Burstyn, H. Kromhout, T. Partanen, O. Svane, S. Langård, W. Ahrens, T. Kauppinen, I. Stücker, J. Shaham, D. Heederik,

- G. Ferro, P. Heikkilä, M. Hooiveld, C. Johansen, B. G. Randem and P. Boffetta, Polycyclic aromatic hydrocarbons and fatal ischemic heart disease, *Epidemiol.*, 2005, **16**, 744–750.
- 78 X. Xu, R. L. Cook, V. A. Ilacqua, H. Kan, E. O. Talbott and G. Kearney, Studying associations between urinary metabolites of polycyclic aromatic hydrocarbons (PAHs) and cardiovascular diseases in the United States, *Sci. Total Environ.*, 2010, **408**, 4943–4948.
- 79 United Nations, Economic Commission for Europe, Executive Body for the Convention on Long-range Transboundary Air Pollution, *Protocol on Persistent Organic Pollutants (POPs)*|UNECE, <https://unece.org/environment-policy/air/protocol-persistent-organic-pollutants-pops>, accessed 8 October 2021.
- 80 *Quality Status Report 2000*, ed. OSPAR Commission, London, 2000.
- 81 G. Lunde and A. Bjorseth, Polycyclic aromatic hydrocarbons in long-range transported aerosols, *Nature*, 1977, **268**, 518–519.
- 82 U. M. Sofowote, H. Hung, A. K. Rastogi, J. N. Westgate, P. F. Deluca, Y. Su and B. E. McCarty, Assessing the long-range transport of PAH to a sub-Arctic site using positive matrix factorization and potential source contribution function, *Atmos. Environ.*, 2011, **45**, 967–976.
- 83 M. Shrivastava, S. Lou, A. Zelenyuk, R. C. Easter, R. A. Corley, B. D. Thrall, P. J. Rasch, J. D. Fast, S. L. M. Simonich, H. Shen and S. Tao, Global long-range transport and lung cancer risk from polycyclic aromatic hydrocarbons shielded by coatings of organic aerosol, *Proc. Natl. Acad. Sci. U. S. A.*, 2017, **114**, 1246–1251.