

AMERICAN UNIVERSITY OF BEIRUT

COMPARISON OF THE LEVELS OF PARTICLE BOUND
POLYCYCLIC AROMATIC HYDROCARBONS BETWEEN
PRE AND DURING ECONOMIC CRISIS IN BEIRUT

by
MOHAMMAD YEHYA AL HALLAK

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for the degree of Master of Science
to the Department of Chemistry
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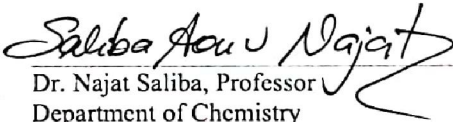
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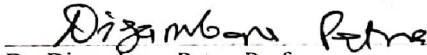
by
MOHAMMAD YEHYA AL-HALLAK

Approved by:


Dr. Najat Saliba, Professor
Department of Chemistry

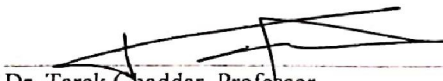
Signature

Advisor


Dr. Digambara, Patra, Professor
Department of Chemistry


Signature

Co-Advisor


Dr. Tarek Ghaddar, Professor
Department of Chemistry

Signature

Member of Committee


Dr. Issam Lakkis, Professor
Department of Mechanical Engineering

Signature

Member of Committee

Date of thesis defense: Wednesday Jan 24, 2024

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ABSTRACT OF THE THESIS OF

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Title: Comparison of the Levels of Particle Bound Polycyclic Aromatic Hydrocarbons between Pre and During Economic Crisis in Beirut

The presence of polycyclic aromatic hydrocarbons (PAHs) in urban areas due to human activities poses a significant risk to human health. A comparative study of three representative sites (AUB, BCD, and NSMU) in Beirut revealed varying levels of PAHs and PM_{2.5}, with AUB showing the lowest concentrations. The demand for electricity, particularly during the hot summer season, and stagnant weather conditions contribute to high concentration of PAHs, in summer as well as in winter and fall. The study also found that the cancer risk associated with PAH exposure exceeded acceptable thresholds set by the Environmental Protection Agency (EPA), in the three sites, emphasizing the need for effective emission regulations. Additionally, source apportionment analysis identified diesel generators, incinerators, and gasoline/vehicular emissions as significant contributors to PAH pollution. Diesel generators played a prominent role in high socio-economic areas (BCD), while vehicular and traffic emissions were more influencing in low-to-middle income areas (NSMU). Incinerators had a significant impact on pollution levels in AUB. These findings demonstrate the need for targeted mitigation strategies to reduce PAH emissions and improve air quality in urban environments.

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ABBREVIATIONS

ATSDR	Agency for Toxic Substances and Diseases Registry
AUB	American university of Beirut
AUH	American university hospital
B(a)p	Benzo(a)pyrene
CMB	Chemical mass balance
CO	Carbon monoxide
DNA	Deoxyribonucleic acid
EDL	Electricite Du Liban
EPA	Environmental protection agency
EU	European union
EPAQS	Expert Panel on Air Quality Standards
EHSRM	Environment and health safety risk management
EC	Elemental carbon
GC-MS	Gas chromatography-mass spectrometry
HPLC	High performance liquid chromatography
OH	Hydroxyl radical
IARC	International agency for research on cancer
IS	Internal standard
LOD	Limit of detection
LOQ	Limit of quantification
NAAQS	National ambient air quality standard
NO ₃	Nitrate radical

O ₃	Ozone
PAHs	Polycyclic aromatic hydrocarbons
PCA	Principle component analysis
P-PAHs	Particle bound polycyclic aromatic hydrocarbons
PM	Particulate matter
PM _{10-2.5}	Coarse particulate matter
PM _{2.5}	Fine particulate matter
PM _{0.1}	Ultrafine particulate matter
PUF	Polyurethane foam
PMF	Positive matrix factorization
QC	Quality control
QA	Quality assurance
R ²	Correlation coefficient
RSD	Relative standard deviation
RNA	Ribonucleic acid
S/N	Signal to noise ratio
SPE	Solid phase extraction
SOA	Secondary organic aerosol
TEF	Toxicity equivalence factor
UV	Ultraviolet
VPAHs	Vapor phase polycyclic aromatic hydrocarbons
WHO	World health organization

CHAPTER I

POLYCYCLIC AROMATIC HYDROCARBONS AND PARTICULATE MATTER

A. Particulate matter

Recent scientific evidence has overwhelmingly demonstrated the detrimental effects of air pollution on human health, linking it to various ailments due to the presence of toxic pollutants. Exposure to these pollutants, whether short or long term, has been found to result in premature death and a wide range of harmful impacts on the human body, including the development of fatal diseases such as cancer[1]. Disturbingly, projections indicate that by 2050, outdoor air pollution will become the leading environmental factor contributing to premature mortality, surpassing even malaria and water quality concerns.[2]

In light of this grave situation, the World Health Organization (WHO) reported that in 2012 alone, air pollution, both indoors and outdoors, led to a staggering 7 million premature deaths worldwide, with 3.7 million deaths attributed to outdoor air pollution specifically.[3] Consequently, a considerable amount of attention has been devoted to addressing air pollution, prompting significant global efforts, especially after the establishment of the Environmental Protection Agency (EPA) in 1970.

To regulate air quality, the EPA has defined National Ambient Air Quality Standards (NAAQS) for six principal pollutants known as "criteria" air pollutants. These pollutants include Carbon Monoxide (CO), Sulfur Dioxide (SO₂), Nitrogen Dioxide (NO₂), Lead (Pb), ozone (O₃), and Particulate Matter (PM). Among these pollutants, Particulate Matter

(PM) has garnered significant attention due to its strong association with respiratory, cardiovascular, and cancer-related morbidity and mortality cases.[4, 5]

PM, a pervasive air pollutant, consists of a mixture of solid particles and liquid droplets suspended in the air. These particles vary in size, ranging from a few nanometers to several micrometers. Coarse particles, with diameters between 2.5 and 10 μm ($\text{PM}_{10-2.5}$), primarily consist of crustal material, sea salts, and biological factors, generated through mechanical processes. In contrast, fine particles, with a diameter between 2.5 μm and 0.25 μm ($\text{PM}_{2.5-0.25}$), and ultrafine particulates (UFP) with a diameter less than 0.25 μm , predominantly contain elemental carbon, metals, and organic compounds resulting from combustion processes.[6, 7] The size and composition of these particles have been directly linked to their detrimental health effects.[7, 8]

Generally, smaller particles have a greater capacity to penetrate deeper into the respiratory tract.[9] Particles measuring less than 2.5 μm ($\text{PM}_{2.5}$) have been identified as the most impactful on human health. These fine particles have longer lifetimes in the air, ranging from days to weeks, compared to coarse particles (PM_{10}). Consequently, $\text{PM}_{2.5}$ can travel distances of up to 1000 km, two orders of magnitude farther than PM_{10} . [9, 10] While particles measuring approximately 5 to 10 μm tend to deposit in the upper respiratory tract, those smaller than 2.5 μm settle in the respiratory bronchioles and alveoli, where gas exchange occurs.[11, 12] Subsequently, fine and quasi-ultrafine particles can enter the bloodstream, delivering harmful chemicals that contribute to decreased lung function, aggravated asthma, cardiovascular diseases, oxidative stress, and cancer.[5, 13]

Although the precise mechanism by which PM impacts biological systems remains unclear, numerous studies have suggested that metals, particularly iron, act as possible

mediators of PM-induced airway injury and inflammation through the Fenton reaction.[14-16] Transition metals found in particles increase the production of reactive oxygen species (ROS) in vivo.[17] The release of ROS can lead to cellular and tissue damage, thereby initiating or exacerbating inflammation.[18] Additionally, a significant fraction of ambient fine PM, derived from combustion processes, contains substantial amounts (up to 80-90% of UFP mass) of elemental carbon (EC), also known as black carbon, and organic carbon (OC).[19, 20] Part of the OC includes polycyclic aromatic hydrocarbons (PAHs),[21] which exert their toxicity after being metabolized into toxic compounds that can covalently bind to cellular macromolecules such as proteins, Deoxyribo Nucleic Acid (DNA), and Ribonucleic Acid (RNA), causing cellular damage, mutagenesis, and carcinogenesis.[22]

B. Polycyclic aromatic hydrocarbons (PAHs)

PAHs are a group of organic compounds with at least two fused aromatic rings, and they are classified as semi volatile.[23] These compounds are widely found in the atmosphere, and there is growing concern about their presence in the environment due to their ability to cause cancer and mutations.[24] They are present throughout the atmosphere primarily because of human activities involving the incomplete combustion and pyrolysis of organic substances like paraffins, olefins, and aromatics. Generally, during combustion or pyrolysis processes where temperatures exceed 500°C, the organic compounds in the fuel break down into smaller, unstable free radicals. These radicals then undergo various reactions to form the initial aromatic ring. In high temperature and pressure conditions, this aromatic ring reacts with small molecules like acetylene, resulting in the expansion

of the aromatic system and the creation of larger, multi-ring structures that are resistant to thermal degradation as shown in figure 1.[25]

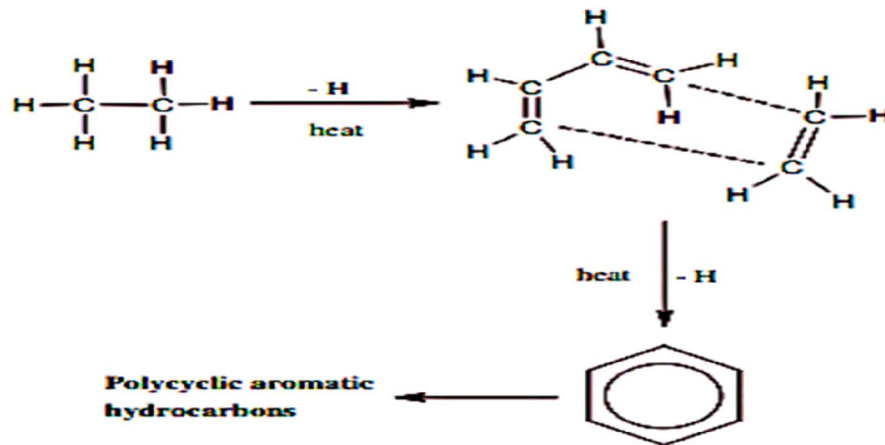


Figure 1: Pyrosynthesis of naphthalene starting with ethane

C. Sources of PAHs

In urban areas, the presence of PAHs in the air is predominantly a result of human-caused emissions originating from various sources. These sources include the burning of fossil fuels and biomass in power plants, as well as emissions from road transportation, such as diesel and gasoline vehicles. Other contributors include waste incinerators, domestic heating systems, diesel generators, and industrial activities like aluminum production. When compared to anthropogenic sources, the contribution of PAHs from natural sources like volcanic eruptions and forest fires is considered negligible.[25]

D. Physical properties of PAHs

PAHs are organic compounds that are partially volatile. They consist of ring systems that can have various configurations and substitution structures. [23] These compounds have low solubility in water and are highly lipophilic. Depending on their volatility, PAHs can

exist in both particulate and vapor phases at room temperature. PAHs with 2 to 3 aromatic rings are predominantly found in the vapor phase, while those with 4 rings or more are associated with particles.[23]

The partitioning of PAHs in the atmosphere involves the physical transformation between particles and vapor, which is influenced by various atmospheric conditions. Among these conditions, meteorological parameters such as temperature and relative humidity play a crucial role. For instance, a study conducted by Yamasaki and colleagues[26] focused on Fluoranthene, a PAH with a 3-member aromatic ring, to demonstrate the effect of temperature on PAH partitioning. They observed that lower temperatures resulted in a higher fraction of Fluoranthene existing in the particle phase. This phenomenon can be explained by the negative enthalpy of adsorption on particles. At lower temperatures, the equilibrium between the particle and vapor phases shifts towards PAH adsorption onto aerosols in the atmosphere.

In another study by Thibodeaux et al.[27] the impact of relative humidity on the partitioning of several PAHs was investigated. It was found that as relative humidity decreases to 0%, the sorption of PAHs increases. This increase is attributed to the desorption of water, which opens up surface sites for the sorption of organic compounds. In summary, both temperature and relative humidity significantly influence the distribution of PAHs between the vapor and particulate phases.

E. Transformation and degradation of PAHs in the troposphere

The transformation and fate of PAHs in the environment are greatly influenced by whether they exist in the vapor phase or are bound to particles.[28] Vapor phase PAHs (V-PAHs) with 2-3 aromatic rings are highly susceptible to tropospheric photochemical

reactions, where they react with hydroxyl (OH) and nitrate (NO₃) radicals, leading to degradation or transformation.[29] On the other hand, particle-bound PAHs (P-PAHs) are less susceptible to tropospheric photochemical reactions due to the protective effects of atmospheric organic compounds, which hinder their oxidation and promote their persistence in the troposphere.[30, 31]

Researchers such as Atkinson, Arey, and their colleagues have investigated the kinetics of chemical degradation for both V-PAHs and P-PAHs. They found that the reaction rate constants for V-PAHs with OH radicals are three orders of magnitude higher than those for P-PAHs. For instance, experimental data showed that naphthalene, a compound predominantly present in the vapor phase, has a higher rate constant (KOH) of 2.4E-11 compared to Benzo(a)pyrene, a compound mainly found in the particle phase, with a KOH of 1.1E-14. Consequently, P-PAHs are less likely to degrade and more persistent in the ambient air than V-PAHs, making them a focus of attention in atmospheric PAH studies.

Among the various factors influencing the fate of V-PAHs in the environment, atmospheric photochemistry plays a crucial role in their degradation. These chemical reactions can be categorized into two groups based on the presence or absence of sunlight. During the daytime, tropospheric OH radicals are abundant due to the enhanced photolysis of ozone (O₃). (Figure 2)

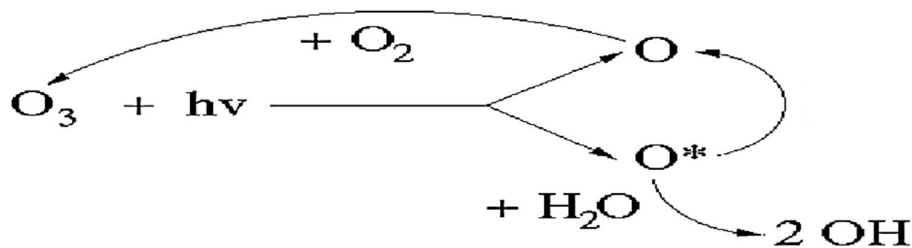


Figure 2: Photolysis of Ozone to produce OH radical.[32]

These OH radicals interact with V-PAHs, leading to their degradation or transformation into carboxylic acids, aldehydes, ketones, and quinones. The lifetime of V-PAHs in this process ranges from minutes to days, with approximately 40% of the products being degradation products. In contrast, during the nighttime when photolysis decreases, tropospheric O₃ interacts with NO₂ to form NO₃ radicals. These NO₃ radicals then interact with V-PAHs, resulting in the production of transformation products, mainly Nitro-PAH derivatives. The lifetime of V-PAHs in this nighttime process is similar to that during the daytime. It is important to note that these transformation products are highly mutagenic, stable, and persistent (with a lifetime of years), which can have significant impacts on both health and the environment. The reactions of naphthalene in the troposphere during day and night are represented in figure 3.

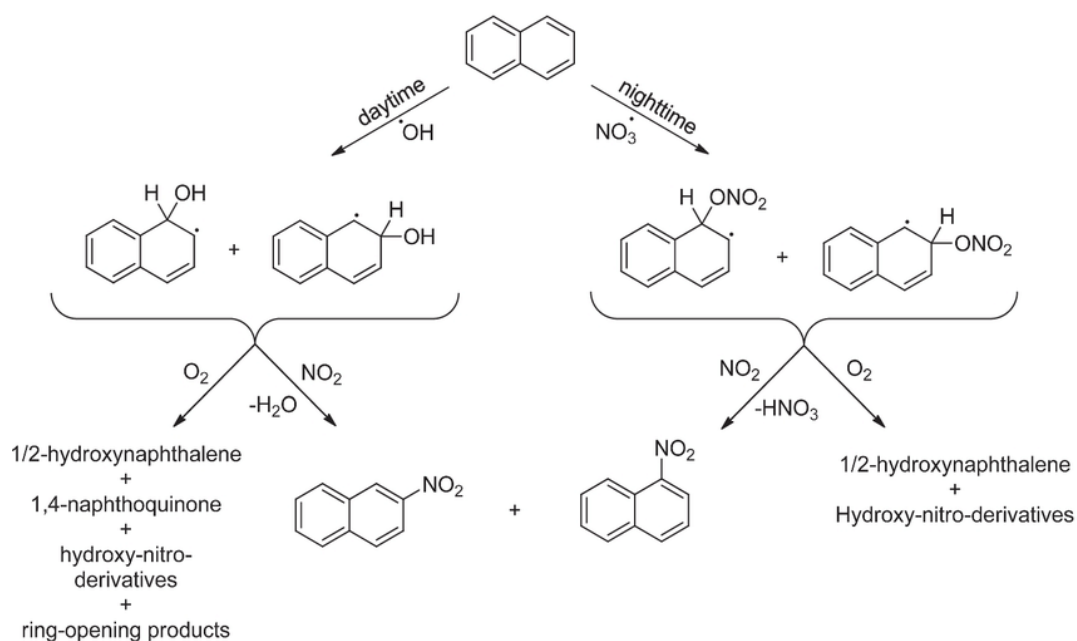


Figure 3: The decomposition of naphthalene during day time and formation of nitronaphthalene during night.[33]

F. Association of PAHs with particles in atmosphere

Studies have demonstrated that semi-volatile PAHs in ambient air exhibit a strong affinity for fine particulate matter (PM_{2.5}), which consists of small particles generated from diesel exhaust and incomplete combustion processes. These fine particles primarily consist of an amorphous carbon core (EC) to which organic compounds, particularly PAHs, adhere.[34, 35] The direct interaction between PAHs and carbonaceous particles results in the inhibition of PAH reactivity. This inhibitory effect is attributed to the slow diffusion of tropospheric oxidants (such as OH, NO₃ and O₃) and atmospheric oxidants into the bulk particle, unlike the case of vapor-phase PAHs mentioned earlier.

Furthermore, the oxidation of volatile organic compounds in the atmosphere leads to the formation of secondary organic aerosols (SOA), which can act as a protective shield for fine particles and trap PAHs within a highly viscous and hydrophobic medium. Once trapped, these PAHs are unable to evaporate and are shielded from atmospheric oxidation. This synergy between PAHs and SOA particles significantly increases their residence time in the atmosphere, resulting in longer-range transport.[36, 37] However, it is worth noting that the direct photolysis of particle-bound PAHs through ultraviolet (UV) sunlight radiation is also a potentially important process. The major degradation products resulting from this photolysis include epoxides and quinones.[33]

G. Toxicity of PAHs

The PAH (polycyclic aromatic hydrocarbon) family consists of over 100 compounds with diverse structures and toxicity levels. Assessing the toxicity of these numerous PAHs in the atmosphere is a complex task. To address this, the US Environmental Protection Agency (EPA) has identified 16 unsubstituted PAHs as priority pollutants based on their

toxicological profiles reported by the Agency for Toxic Substances and Disease Registry (ATSDR).(figure 4)[38] These 16 congeners were prioritized due to their suspected higher harm potential and their prevalence in air samples among the analyzed PAHs.[25] One prominent congener within this group is benzo[a]pyrene (B[a]P), which contains a five-member aromatic ring and is typically found in the particulate phase. B[a]P has been extensively studied and has been classified as a Group 1 human carcinogen by the International Agency for Research on Cancer (IARC).[24] In response to its carcinogenic properties, the European Union (EU) has set an air quality standard for B[a]P at 1 ng/m³. [39] In the United Kingdom, the Expert Panel on Air Quality Standards (EPAQS) recommends an annual average concentration of B[a]P not exceeding 0.25 ng/m³. [40] Additionally, other PAHs have been classified as Group 2A (probable human carcinogens) and Group 2B (possible human carcinogens), primarily found in the particulate phase.

Table 1 presents the IARC classification for the 16 priority PAHs and their corresponding Toxic Equivalency Factors (TEF). TEF indicates the relative toxicity of individual chemicals within the PAH family. The most toxic chemical, B[a]P, is assigned a TEF of 1, while less toxic chemicals are assigned TEFs of 0.1, 0.01, or 0.001 based on their relative toxicity compared to B[a]P. (Table 1)

PAHs can impact human health through various mechanisms, including genotoxicity, immunotoxicity, developmental toxicity, and carcinogenesis. Long-term exposure to PAHs can lead to epigenetic modifications. PAHs contribute to epigenetic changes through DNA methylation, histone modification, and microRNA silencing. [22, 41, 42] Reactive PAH metabolites enzymatically react with cellular proteins and DNA, forming PAH-DNA adducts of different structural conformations. These adducts can induce

mutations or inactivate tumor suppressor genes, ultimately causing DNA damage and carcinogenesis (figure 5). [22, 41, 42]

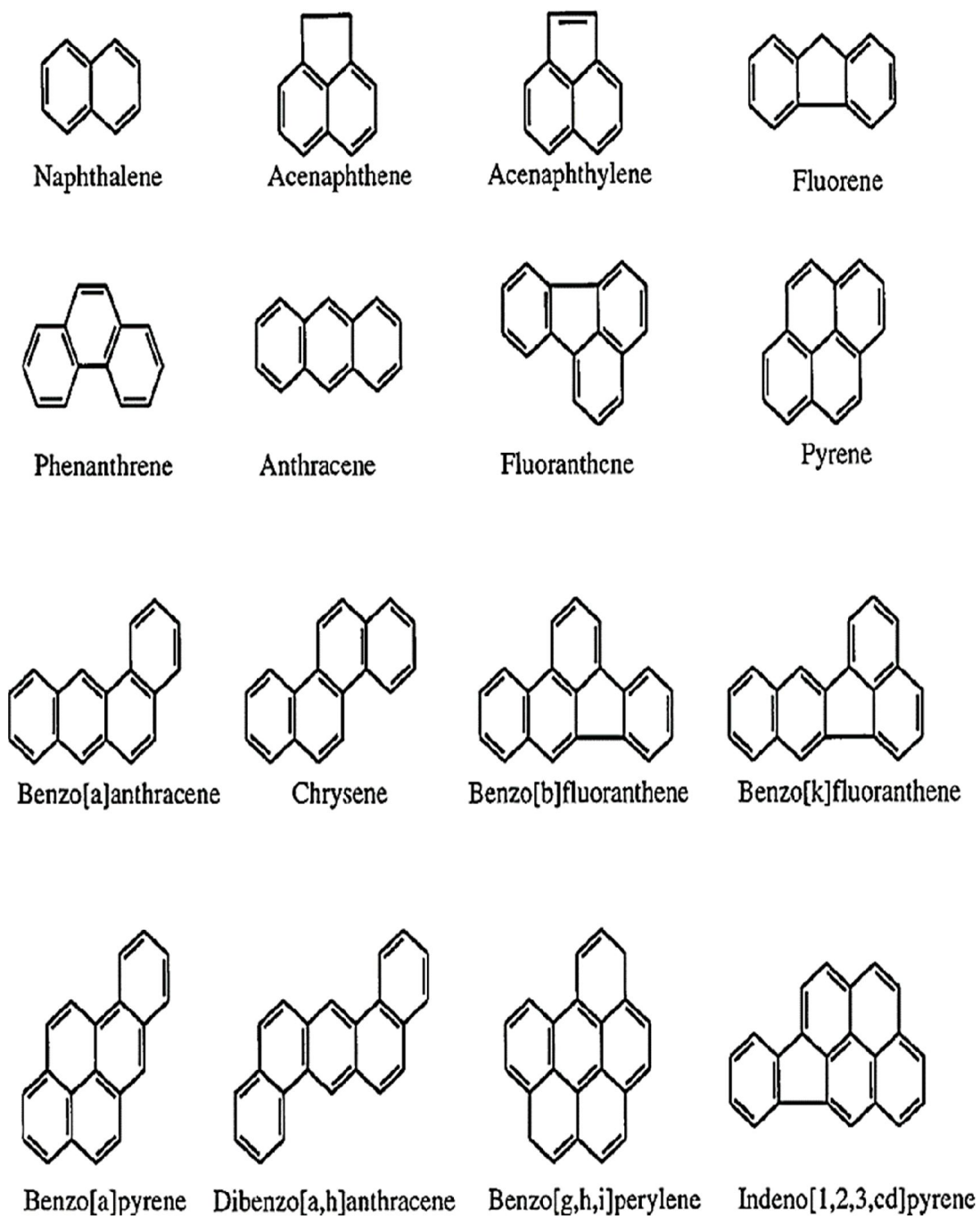


Figure 4: The 16 PAHs identified by the environmental protection agency (EPA)

Table 1: The 16 EPA priority PAHs, their acronym, their phase distribution at ambient temperature, their IARC classification and TEF values

Polycyclo Aromatic Hydrocarbons	Acronym	Molecular Weight (g)	Gas/Particle Phase	IARC	TEF
Naphtalene	Nap	128	Gas phase	2B	0.0001
Acenaphtylene	Acy	152	Gas phase		0.001
Acenaphtene	Ace	153	Gas phase	3	0.001
Fluorene	Flu	165	Gas phase	3	0.001
Phenanthrene	Phe	178	Particle and Gas Phase	3	0.001
Anthracene	Ant	178	Particle and Gas Phase	3	0.01
Fluoranthene	Flt	202	Particle and Gas Phase	3	0.001
Pyrene	Pyr	202	Particle and Gas Phase	3	0.001
benzo[a]anthracene	BaA	228	Particle Phase	2B	0.1
Chrysene	Chr	228	Particle Phase	2B	0.01
Benzo[k]fluoranthene	BkF	252	Particle Phase	2B	0.1
Benzo[b]fluoranthene	BbF	252	Particle Phase	2B	0.1
Benzo[a]pyrene	BaP	252	Particle Phase	1	1
Benzo[g,h,i]perylene	BghiP	276	Particle Phase	3	0.01
Dibenz[a,h]anthracene	DahA	278	Particle Phase	2A	1
Indeno[1,2,3-cd]pyrene	IP	276	Particle Phase	2B	0.1

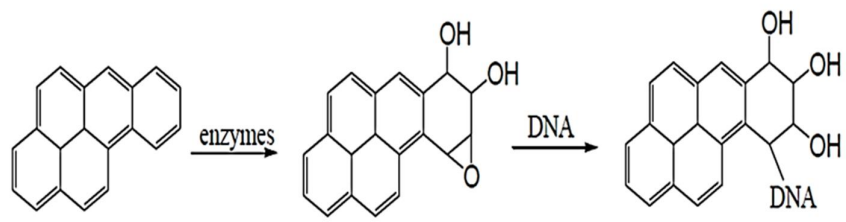


Figure 5: Formation of BaP-DNA adduct leading to DNA mutation[42]

CHAPTER II

COMPREHENSIVE STUDY OF THE SITUATION IN LEBANON AND SYSTEMATIC REVIEW

Air pollution is a significant environmental concern worldwide. With particular attention polycyclic aromatic hydrocarbons (PAHs), understanding the presence and distribution of specific PAH markers can provide valuable insights into pollution sources, transport mechanisms, and potential health risks associated with exposure. In this context, this study aims to conduct a systematic review of existing literature shed light on the situation in Lebanon especially after studies performed before crisis in 2017 and 2015.

A. PAHs and diesel generators: Systematic review

A systematic review conducted to better understand the markers of PAH associated with diesel generators. The main goal of this review was to gather insights from previous studies and use them to analyze the main research study. This review, is titled "Power Plant Shortage and Urban Air Pollution: Exploring the Impact of Diesel Generators on PAH Levels." and aimed to learn from the experiences of others and examine how diesel generators affect PAH levels in urban areas.

1. Methodology

a. The Search Method

On June 20th, 2023, a literature search on PubMed, Web of Science, and SciFinder databases with no time restriction was conducted using the following terms: (((air) OR (atmospher*)) AND ("polycyclic aromatic hydrocarbon*" OR PAH*)) AND (urban)) AND (diesel)

b. Inclusion Criteria

Publications were included if the original data established a relation between the use of diesel generators and increased levels of PAHs.

c. Exclusion Criteria

Publications were excluded if they did not report any significant impact of the use of diesel generators on PAHs levels. Furthermore, articles that were not peer-reviewed and were not written in English were not included.

d. Study Selection and Data Extraction

To determine a record's eligibility, two reviewers (MH and FHM) independently looked over its title and abstract. Studies that met the inclusion criteria were then collected for full-text reading and data extraction. Both reviewers gathered to cross-validate records' selection and discuss the extracted data.

2. Results

a. The Included Studies

The search resulted in 1028 records across three databases. Following removing duplicates, a total of 839 records were screened by titles and abstracts for inclusion. A total of 710 records were removed at this stage and the full texts of the remaining 129 articles were scanned. Accordingly, a total of 18 articles were included in the review.

Figure 6 shows the PRISMA diagram that summarizes the steps of the selection process.

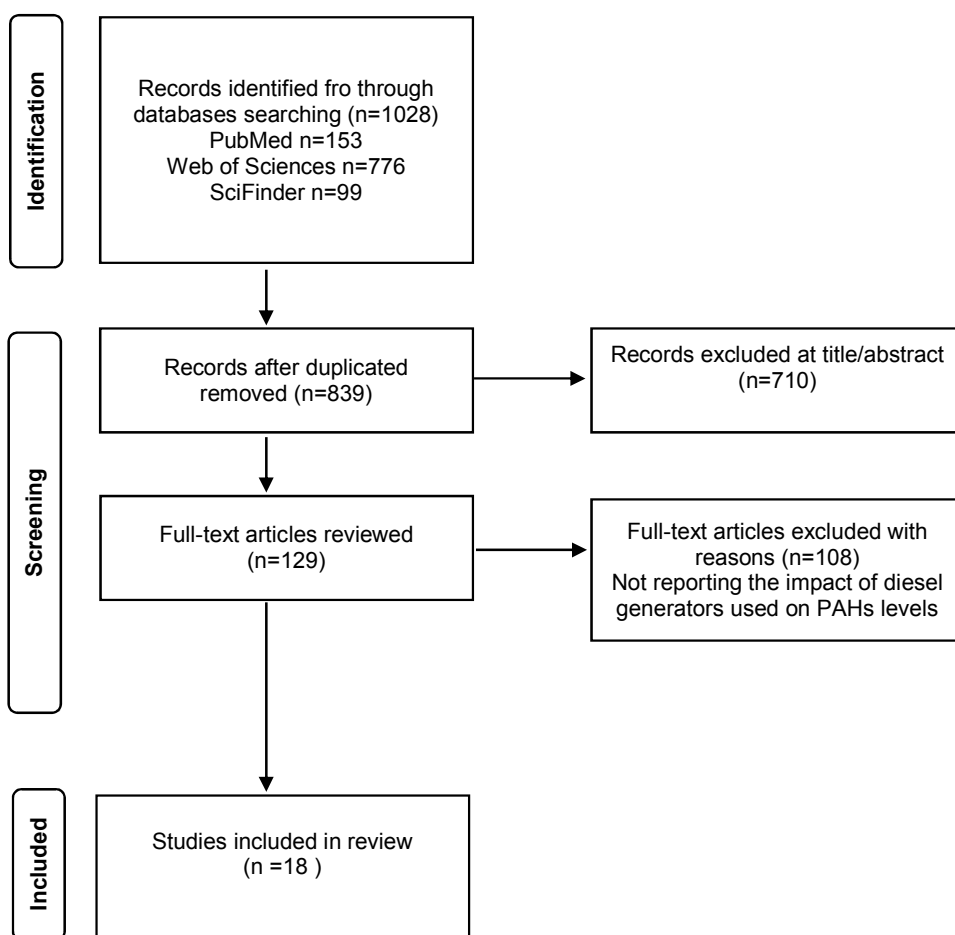


Figure 6: PRISMA diagram summarizing the selection process

3. Discussions

Generally, the situation of a region or a country plays a significant role in the use of diesel generators. Economic downturns or periods of financial instability combined with high population results a reduction in the investments in infrastructure development, including power generation and distribution, leading to a greater reliance on diesel generators. The 18 articles resulted represents the different sources of pollution and its contribution on PAHs and other pollutants in the following countries/cities: Nepal, India (Agra, Kanpur and Coimbatore), Lebanon (Beirut, Zouk Mikael, Dora and Hamra), Cambodia, Naples, Pakistan, Chile, Belgrade(Serbia) and Erzurum (Turkey).

In this investigation, it is observed that larger generators exhibited higher concentrations of PAHs compared to smaller ones, which can be attributed to their higher fuel consumption rates. Total PAH (TPAH) levels measured, are comprising both gas phase (GPAH) and particle phase (PPAH). Notably, the TPAHs were predominantly composed of low molecular weight (LMW) PAHs, [43-50] characterized by 2 or 3 benzene rings, which tend to exist in the vapor gas phase.

Regarding medium molecular weight (MMW) PAHs containing 4 benzene rings, they were found to be present between the gas and particle phases. In contrast, high molecular weight (HMW) PAHs, consisting of 5 or more benzene rings, were detected mainly in the particle phase. HMW PAHs, due to their lower vapor pressures, tend to adhere to fine particles in areas with high emission sources, [47-53] leading to variations in the PAH composition based on seasonal and geographical factors.

However, there are typical markers for diesel combustion which are Phenanthrene, Pyrene, Fluoranthrene and Chrysene.[49-51] Interestingly, the smaller engines exhibited

higher PAH toxicity in terms of BaP_{eq} (benzo[a]pyrene equivalent), primarily attributable to the presence of heavier PAHs in the particle phase [47-54].

Furthermore, ratios were found [43-46] indicative of a diesel source in selected ranges:

- 1) $\frac{Flt}{Flt+Pyr} > 0.4$,(Flt: Fluoranthene and Pyr: Pyrene)
- 2) $0.3 \leq \frac{BaA}{BaA+Chy} \leq 0.6$,(BaA: Benzo(a)anthracene and Chy: Chrysene)
- 3) $\frac{BaA}{BaA+BaP} \leq 0.5$,(BaA: Benzo(a)anthracene and BaP: Benzo(a)pyrene)
- 4) $0.35 \leq \frac{IcP}{IcP+BghiP} < 0.7$, (IcP:Indeno[1,2,3-cd]pyrene and BghiP: Benzo[ghi]perylene)

B. Air Quality in Lebanon

The Mediterranean region is renowned for experiencing frequent episodes of high pollution due to its enclosed geographical location. It is situated between the Sahara Desert in Africa and the densely populated and industrialized European continent, making it susceptible to the accumulation of aerosols. Additionally, being at the crossroads of air masses from Africa, Asia, and Europe further contributes to its unique characteristics. The Mediterranean basin is characterized by high humidity, long summers, and stagnant winds originating from eastern Europe. Moreover, the intense solar radiation in this area leads to significant photochemical reactions, resulting in the formation and transformation of pollutants. The eastern side of the Mediterranean basin experiences higher levels of these photochemical reactions and pollutant accumulation compared to the western side, primarily due to dry summers and minimal precipitation. Furthermore, the eastern side is prone to dust outbreaks from the Saharan and Arabian deserts during the fall and spring seasons, making it a region of concern in terms of pollution.[55-59]

Among the cities in the eastern Mediterranean, Beirut (35°28'790"E, 33°54'139"N), the capital of Lebanon, stands out with a population density of 7800 persons per square kilometer. Geographically located between the Mediterranean coast and the Mount Lebanon range, the city is home to approximately 88% of the country's 6 million population. The city faces significant traffic congestion throughout the day, leading to delays of up to 30 minutes at certain intersections.[60] Construction activities are also prevalent in Beirut due to a high urban population growth rate of 3.2%, exceeding the global average of 2.1%.[61] The construction aims to accommodate the increasing city population and maintain the country's outdated infrastructure.[62] Furthermore, Lebanon faces inadequate power production capacity, resulting in a rotating power outage regime implemented by the national electric company, Electricité du Liban (EDL).[63] As a result, citizens have resorted to privately owned diesel generators to compensate for the electricity demand.[64, 65]

It is important to note that Lebanon lacks heavy industrial facilities, with only a few thermal power plants and low-duty industrial factories situated away from the main cities. Over the past decade, numerous studies have been conducted in Beirut to assess the levels, seasonal variation, and composition of atmospheric particulate matter. These studies consistently report that ambient levels of PM (particulate matter) in the greater Beirut area exceed the guidelines set by the World Health Organization (WHO) by up to 273% for PM₁₀ and around 100% for PM_{2.5}. [55-59, 66] The high concentrations of PM₁₀ and PM_{2.5} have been associated with increased emergency hospital admissions for respiratory and cardiovascular issues. [67] Table 2 provides a comprehensive overview of PM_{2.5} levels in Beirut that have been investigated by different studies. Besides, it compares PM_{2.5} levels in Beirut with different countries and WHO standard.

Furthermore, investigations into reactive oxygen species in Beirut have revealed that the intrinsic toxicity of roadside PM_{2.5}, gram for gram, is relatively higher than that observed in roadside PM_{2.5} in Los Angeles [68], Italy[69] and less than in Saudi Arabia.[70]

Table 2: PM_{2.5} Levels in Beirut: Investigated Studies and International Comparisons

Location	Year	PM _{2.5} level in $\mu\text{g}/\text{m}^3$	Reference	
Beirut	BCD	2022-2023	18.33	Our study
	AUB	2022-2023	14.27	Our study
	NSMY	2022-2023	22.59	Our study
	Annual average	2022-2023	17.19	Our study
Beirut	2016-2017	25.48	[50]	
Beirut	2010	40.95	[44]	
Beirut	2007	22.5-67.05	[61]	
Beirut	2004	40	[53]	
Saudi Arabia	2018	45	[58]	
Rome	2020	15.6	[57]	
WHO annual standard	-	5		

While these studies provide insights into the levels of particulate matter, the long-term tracking of ambient carcinogenic composition, specifically Polycyclic Aromatic Hydrocarbons (P-PAHs), influenced by various emissions, remains unclear. For instance, a study by Shihadeh et al. examined P-PAH emissions from private diesel generators during a 3-hour electricity power outage in the Hamra area of Beirut between January 2010 and January 2012. They reported an increase of approximately 40% in airborne P-PAH levels compared to the local background level.[56, 71] Another study conducted by Daher et al. in 2012, over a two-month period in the summer, measured P-PAH levels near a major road in Beirut as 11.5 ng/m³, while levels were below the detection limits at the American University of Beirut (AUB).[66, 72] Moreover, Baalbaki et al. investigated gas and particle PAHs during winter and summer in 2015 at three different urban sites, reporting PAH values ranging between 13.15 and 91.88 ng/m³. [73] In 2017, Jaafar W et

al.[50] ,in annual study, investigated the PAHs levels in AUB and found an average of 10 ng/m³, whereas in another study conducted after Beirut Port explosion in August, 2020[74] for few months, the levels fell into less than 1 ng/m³. Another factor of pollution, mentioned by Jaafar et al., which is the incinerators spreaded, especially after a crisis in 2015, all over Lebanon.

C. Economic crisis and Electricity

Since 2019, Lebanon has been grappling with a severe and prolonged crisis, including an economic and financial downturn. The economic crisis has led to a significant decline in Gross domestic product (GDP), disposable income, and purchasing power, pushing a large portion of the population into poverty [75]. The depletion of foreign exchange reserves has resulted in fuel shortages, impacting the national electric grid. As a consequence, the public electricity supply has been highly unreliable, with frequent rolling blackouts. The average daily supply of electricity is limited to only one to two hours, leading to a heavy reliance on alternative power sources, such as diesel generators, to meet the energy needs of businesses and households. The scarcity of fuel items has not only affected the electricity sector but has also hindered access to essential services like healthcare and clean water. Additionally, the disruption to supply chains caused by fuel shortages has further exacerbated the challenges faced by food suppliers, transport service providers, and telecom network operators. The huge reliance on diesel generators highlights the struggle to maintain a consistent power supply and the dire consequences of the power generation shortage on various aspects of daily life in Lebanon.[76-79]

D. Study Objectives

The objective of this study is to assess the impact of the economic crisis and increased usage of diesel generators, following 24-hour power shortages in Lebanon, on the levels of Polycyclic Aromatic Hydrocarbons (PAHs) and fine particulate matter (PM_{2.5}) in three different areas of Beirut. The study aims to examine and quantify the concentrations of PAHs and PM_{2.5} in an urban background site, a high socio-economic area, and a low socio-economic area. Additionally, the study will employ source apportionment techniques, specifically Positive Matrix Factorization (PMF), to identify and quantify the major sources contributing to PM_{2.5} pollution in these areas.

By conducting source apportionment through PMF, the study aims to differentiate between various pollution sources. This analysis will allow for a comprehensive understanding of the specific contributions of each source to the observed PM_{2.5} levels in the selected areas, considering their respective economic conditions and prevalence of diesel generator usage. Moreover, the study seeks to evaluate any correlations between the identified pollution sources and the concentrations of PAHs, enabling a better understanding of the potential health risks associated with specific emission sources.

Through this investigation, the study aims to contribute to the understanding of the environmental consequences of the economic crisis and the increased reliance on diesel generators for power generation, particularly regarding air pollution and public health risks associated with PAHs and PM_{2.5}. The findings will provide valuable insights for policymakers and stakeholders in designing targeted interventions to mitigate the adverse effects of power shortages and diesel generator usage on air quality and public health in Beirut.

E. Study Area

Ambient measurements were carried out in three different sites in Beirut as represented in Figure 7. The first site is situated on the rooftop of the chemistry department at AUB and considered an urban background site since all reviewed studies have used this site as a background site. AUB is surrounded by dense greenery and separated from the sea by a road-way experiencing relatively light traffic.

The second site is Beirut Central District (BCD), also called Downtown Beirut (DT), on the rooftop of building 157 (33° 54' 54" N, 35° 30' 20" E, 16.5m above the ground).

The third site is nursing school of Makassed University (NSMU) (33° 52' 31" N, 35° 30' 12" E, 15m above the ground). The sites of the Nursing School of Makassed University and the Beirut Central District represent two distinct socio-economic areas with contrasting characteristics.



Figure 7: The three different sites in Great Beirut Area (GBA) using Google earth

The BCD site is situated in a high socio-economic area while the NSMU is relatively lower socio-economic area. Despite the economic disparity, the sites share similar features including the presence of diesel generators, high-traffic roads, and various activities. However, it is important to consider that the impact and distribution of these factors can vary depending on the economic status of different regions. Factors such as the concentration of diesel generators and the volume of vehicular emissions may differ based on varying economic capacities and levels of infrastructure development in each area.

CHAPTER III

SAMPLING AND ANALYTICAL METHOD

A. Sample Collection

The campaign involved of collecting samples over 24 hours and once every six day. It started in March 2022 and ended in July 2023. The sampling in BCD was done from March 2022 to May 2022 and from September 2022 till October 2022 whereas in AUB from June2022 to August 2022 and December 2022 till March 2023. Finally, it ended in NSMU during the period of April-July2023.

B. Sampling method for PM_{2.5}

Sampling was conducted on a 24-hour basis every sixth day, utilizing a low volume sampler operating at a consistent flow rate of 16.7 L/min. The low volume sampler consisted of pump and Harvard cartridge (CHEMCOMB 3500) (Figure 8) equipped with a PM_{2.5} impactor. To collect the samples, PTFE (polytetrafluoroethylene) membrane filters (Figure 9) (TISCH Scientific) were employed.

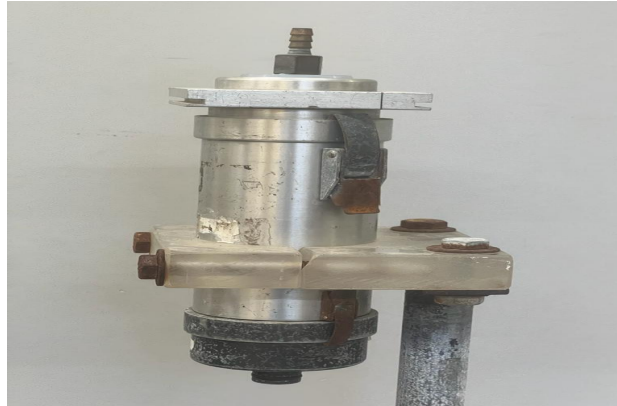


Figure 8: Cartridge equipped with PM_{2.5} impactor



Figure 9: PTFE filter before the sampling

C. Gravimetric Analysis for PM_{2.5}

To collect PM_{2.5} particles, PTFE (polytetrafluoroethylene) membrane filters from TISCH Scientific were employed. Gravimetric analysis of PM_{2.5} involved measuring the mass difference between the pre and post-sampling Teflon membrane filters using a micro balance (Balance XPR2U). The filters were equilibrated under controlled humidity (40-50%) and temperature (20-22°C) conditions before the measurements were taken. The levels of PM_{2.5} were reported in micrograms per cubic meter ($\mu\text{g}/\text{m}^3$) using the following equation:

$$PM_{2.5}level = \frac{\bar{m}_{after} - \bar{m}_{before} \text{ (mg)}}{flow\ rate\ (L/min) \times sampling\ time\ (min)} \times 10^6$$

D. Sampling method for PAHs

The sampling method was based on the US Environmental Protection Agency (EPA) TO-13A compendium method (USEPA 1999). In brief, active sampling was performed using a high volume air sampler (HVS) (DIGITEL enviro-sense DH77) operating at a flow rate of 0.25m³/min. It consists of a sampling probe designed as a single-stage impactor with a “cut-point” of an aerodynamic particle of 2.5 μm diameter. Particles larger than 2.5 μm in diameter are removed through impaction in the buffer chamber as shown in figure 10. A quartz fiber filter (Whatman, 150 mm) collects particle-bound compounds were baked in a furnace oven at 400 °C for 5 hours to remove adsorbed organic compounds. Post-sampling, the filter are wrapped in baked aluminum foils and stored at -20 °C before analysis.



Figure 10: The high volume sampler (HVS)

E. Extraction method for PAHs samples

1. Materials

The experiment utilized a 16 PAH standard from Absolute Standards, which was dissolved in methylene chloride at a concentration of $2000\mu\text{g}/\text{mL}$. The 16 PAH standard consists of the 16 polycyclic aromatic hydrocarbons (PAHs).

Additionally, four deuterated internal standards (Acenaphthene-D10, Chrysene-D12, Perylene-D12, and Phenanthrene-D10) were obtained from Absolute Standards. These internal standards were also dissolved in methylene chloride at a concentration of $2000\mu\text{g}/\text{mL}$. HPLC-grade toluene and hexane solvents were procured from Sigma Aldrich for use in the experiment. Solid Phase Extraction cartridges (SPE) Silica (1000 mg/6 mL HyperSep SI) were obtained from Thermo Scientific to facilitate the extraction

process whereas quartz filters and teflon membrane filters were purchased from Whatman International for filtration purposes.

2. Filter extraction

The extraction and analysis method of the 16 PAHs was done using the EPA TO-13A method[80, 81] with some modifications.

Prior to extraction, the collected filters are half-cut. A half filter is spiked with 1 µg/mL of deuterated PAH standard, then extracted in 10 mL of Toluene/Hexane (4:1 v/v) by ultrasonication for 90 min at 40°C.

3. Sample Concentration (first round)

Sample concentration is a critical requirement to increase PAH concentrations. Our aim is to concentrate the sample down to 1 mL. The extract is to be concentrated into 1 mL under Nitrogen (N₂) flow fixed at 10 L/min.

4. Solid phase extraction (SPE)

To minimize interference from other compounds present in the sample, it is essential to employ a clean-up procedure that purifies the sample specifically for the Polycyclic Aromatic Hydrocarbons (PAHs). Among various clean-up techniques, solid-phase extraction (SPE) is the most suitable method. The general procedure involves conditioning the SPE cartridge, loading the sample, and then eluting the desired analytes. To activate the functional groups on the silica surface, the cartridge was initially washed with 10 mL of hexane, as per the manufacturer's instructions. Subsequently, a concentrated sample of 1 mL was loaded onto the SPE cartridge, followed by elution using 10 mL of hexane as the mobile phase.

5. Final Concentration Step

Upon completing the solid-phase extraction (SPE) procedure, it is necessary to perform a nitrogen evaporation step to concentrate the sample, ensuring improved precision in quantifying the desired analytes. This step holds significance since Polycyclic Aromatic Hydrocarbons (PAHs) are expected to be present in low parts per million (ppm) concentrations in ambient air. A concentration volume of 150 μL was deemed suitable for precise PAH quantification without excessively reducing the final sample volume. Both the flow rate and temperature during evaporation were explored. The vapor pressures of the 16 PAHs at 25 $^{\circ}\text{C}$ ranged between 2.1×10^{-11} and 8.9×10^{-2} Pa, while that of toluene was 3.8 kPa. Consequently, sample concentration was conducted at room temperature and atmospheric pressure, where PAHs are relatively less volatile compared to toluene. With the entire sample preparation procedure optimized, the sample is now ready for GC-MS analysis.

F. Instrumental analysis

The analysis of PPAHs was accomplished by Thermo-Finnigan Trace GC-Ultra Polaris ITQ 900 MS coupled with AS 3000 II autosampler. Chromatographic separation was carried out on an Rxi-17 Sil MS column (30 m \times 0.25 μm film thickness \times 0.25 mm film ID).

The carrier gas was helium of 99.999% purity with 1 mL/min flow rate. Injection mode was splitless and set at 280 $^{\circ}\text{C}$. The GC oven was programmed from 80 $^{\circ}\text{C}$ (hold for 3 minute) to 170 $^{\circ}\text{C}$ (10 $^{\circ}\text{C}/\text{min}$, hold for 1 min), to 180 $^{\circ}\text{C}$ (3 $^{\circ}\text{C}/\text{min}$, hold for 0 min), to 270 $^{\circ}\text{C}$ (10 $^{\circ}\text{C}/\text{min}$, hold time 0 min), then ramped to 300 $^{\circ}\text{C}$ (3 $^{\circ}\text{C}/\text{min}$, hold for 10 min).

The mass spectrometer was operated in full scan mode (50-350). The ion source temperature was 250 °C in electron impact mode (70 eV). The analytes were identified by their mass spectrum in which PAHs and IS have a relatively intense molecular ion (mass-to-charge ratio (m/z)).

The linearity was evaluated by building an 7-point calibration curve in the range from 0.1 to 4 µg/mL, good linearity was observed with correlation coefficients (R^2) > 0.996 for most of the 16 PAHs

G. Quantification of PAHs

To prepare the calibration curve, ten different concentrations of PAHs ranging from 0.0134 µg/mL to 4 µg/mL were created in a 150 µL solvent mixture of Toluene and Hexane using a standard containing 16 PAHs. These solutions were then spiked with deuterated PAH internal standards at a concentration of 1 µg/mL. Subsequently, the prepared solutions were directly analyzed using GC-MS.

The quantification process is based on a regression equation, $y = ax + b$, where y represents the ratio of the area of the standard to the area of the internal standard, x denotes the concentration, and a and b represent the slope and intercept, respectively. The unknown concentration (x) was calculated using the formula $x = (y' - b) / a$, where y' represents the ratio of the area of the unknown sample to the area of the internal standard. The concentration (C) obtained from GC-MS was expressed in µg/mL. Multiply C by 0.150 mL to obtain the mass of half-filter in µg, and multiply the mass of the filter by 2 to determine the mass of the filter in µg.

The following equation represents the final step to calculate the concentration of the individual PAHs reported in ng/m³.

$$\frac{\text{Mass of filter in } (\mu\text{g})}{500 \text{ (L/ min)} \times 24 \times 60 \text{ min}} \times 10^6 = \text{Concentration in ng/m}^3$$

H. Method Validation

Validation plays a crucial role in maintaining quality control (QC) and quality assurance (QA) standards by assessing the dependability, consistency, and precision of a method. The main factors considered in this evaluation include linearity, limit of detection, limit of quantification, recovery, and repeatability.

1. Linearity

Linearity evaluation confirms that the response of PAHs is directly proportional to their concentration within a specific range. Typically, this is assessed by examining the correlation coefficient of the calibration curve. In this study, a direct calibration curve was employed, where PAH standards ranging from 0.1 to 4 $\mu\text{g/mL}$ were prepared and spiked with a constant amount of deuterated internal standards (1 $\mu\text{g/mL}$).

The relationship between the ratio of the analytes' signal to the IS signal and the analyte standard concentrations exhibited linearity across the entire range of the 16 PAHs tested, with a correlation coefficient greater than 0.996 as shown in Figure 10.

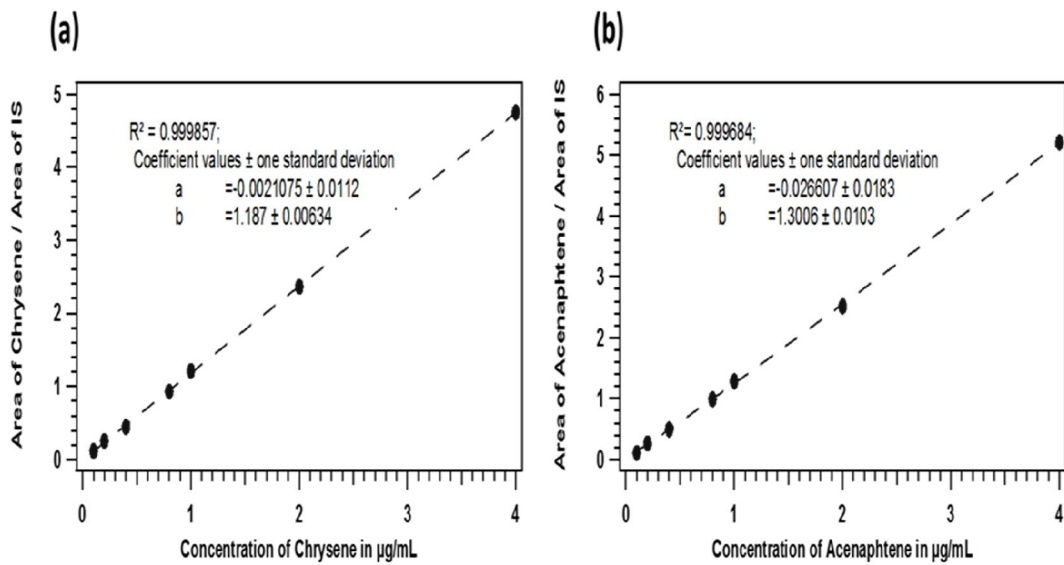


Figure 11: Examples of direct calibration curve of (a) chrysene and (b) acenaphthene

2. Limit of Detection

The limit of detection (LOD) refers to the minimum concentration of the analyte that can be detected, although not necessarily quantified. It is determined based on the standard deviation response and slope, and the LOD can be calculated using the following formula:

$$\text{LOD} = 3\sigma/s$$

Here, σ represents the standard deviation of the ratio of the analytes' signal to the IS signal obtained from seven replicates of analytes prepared at a low concentration, and s denotes the slope of the direct calibration curve. In this study, LOD analysis was conducted by performing seven replicate extractions of a solution containing 0.1 $\mu\text{g/mL}$ of the analytes spiked with 1 $\mu\text{g/mL}$ of the deuterated internal standard. The results revealed that the detection limits for the 16 PAHs ranged from 0.01 to 0.09 $\mu\text{g/mL}$.

3. Limit of Quantification

The limit of quantification (LOQ) refers to the minimum concentration of the analyte that can be reliably measured with an acceptable level of accuracy and precision. It is determined based on the standard deviation response and slope, and the LOQ can be calculated using the following formula:

$$\text{LOQ} = 10\sigma/s$$

Here, σ represents the standard deviation of the response obtained from seven replicate extractions of a solution containing 0.1 $\mu\text{g/mL}$ of the analytes, and s denotes the slope of the calibration curve. In this study, the quantification limits of the 16 PAHs were analyzed by performing seven replicate extractions of a solution with a concentration of 0.1 $\mu\text{g/mL}$. The results indicated that the LOQ ranged between 0.034 and 0.131 $\mu\text{g/mL}$.

I. Repeatability

Repeatability refers to the degree of agreement among a series of measurements conducted under identical operating conditions, involving the same operator, equipment, and day.

It is quantified by the percent relative standard deviation (%RSD) of analytical results obtained from a minimum of five measurements at three distinct concentrations (low, medium, and high).

The acceptance criteria for repeatability are determined based on the nature of the analysis, complexity of the sample matrix, and the concentration level being tested.

Analysis of six replicate standards at three concentrations (0.1, 1, and 4 $\mu\text{g/mL}$) demonstrated %RSD within the range of 3 to 7%.

J. Recovery

To ensure a reliable extraction process, it is important to achieve a high percentage of analyte recovery. The recovery is determined by comparing the concentration of the analytes extracted from a sample following the complete extraction procedure to that of a sample with the same concentration directly analyzed on GC-MS.

In this study, the recovery was evaluated by performing six extraction measurements at three concentration levels encompassing the working range of 0.1, 1, and 4 µg/mL. The obtained recovery values fell within the acceptable range of 90% to 108%.

Consequently, all the quality control (QC) and quality assurance (QA) requirements were met, indicating that the method is well-suited for the accurate measurement of PPAHs in ambient air.

K. Blank analysis

Field blanks, which were taken along with the samples to the sampling sites, were utilized to identify any potential background contamination. The analysis method employed for the blanks was the same as that used for the samples.

Throughout the analysis period, the concentrations of PAHs detected in the blanks were consistently below the method's detection limits.

CHAPTER IV

RESULTS AND DISCUSSION

Polycyclic aromatic hydrocarbons (PAHs) and fine particulate matter (PM_{2.5}) are significant air pollutants that have garnered considerable attention due to their impact on human health and the environment. PAHs undergo various processes, including dilution, evaporation, accumulation in sediments or water, and photodegradation, which can influence their levels in the atmosphere. Photodegradation, in particular, involves the breakdown of lighter PAHs into intermediate products and is influenced by sunlight intensity.

The depletion processes mentioned above, along with seasonal variations in environmental conditions such as rainfall, temperature, and wind speed, play a role in the rate at which PAHs are reduced and subsequently affect their distribution patterns in the atmosphere. Furthermore, the extent of PAH pollution can vary depending on the specific sampling location and the presence of different pollution sources.

In order to gain a comprehensive understanding of the behavior of PAHs and PM_{2.5} in our local environment, we conducted a study examining the spatial and temporal variations of PAHs and PM_{2.5} in three distinct sites in Beirut. By investigating the influence of environmental factors, including rainfall, temperature, and wind speed, we aim to enhance our understanding of the dynamics of these pollutants and their potential implications for air quality management and human health. Also, the aim of this study is to assess the change of PAHs levels post-economic crisis.

A. Assessment of PM_{2.5}

Figure 12 shows the PM_{2.5} box plot that represents the means and standard deviations of PM_{2.5} levels at the three sites (referred to as BCD, AUB, and NSMU).

The mean PM_{2.5} level at BCD was found to be 18.33 µg/m³, with a standard deviation of 6.78 µg/m³. The maximum recorded value was 32.13 µg/m³ because of sand and dust storm (SDS) measured on April 2022, while the minimum was 11.4 µg/m³ in March 2022. Similarly, AUB site exhibited a mean PM_{2.5} level of 14.27 µg/m³, accompanied by a standard deviation of 6.03 µg/m³. The highest and lowest values observed (because of rain) and measured in February 2023 at AUB were 25.66 µg/m³ and 2.4 µg/m³, respectively .

NSMU displayed an average PM_{2.5} level of 22.59 µg/m³, with a relatively higher standard deviation of 13.71 µg/m³. The maximum and minimum values recorded at this site were 60.32 µg/m³ in April 2023 and 8.3 µg/m³ in May 2023, respectively.

The annual PM_{2.5} level in Beirut, exhibited the 17.19 µg/m³, was found to exceed the recommended WHO value (5 µg/m³)[82] by 243.8% . In addition, across all sites, 52% of all PM_{2.5} measurements exceeded the daily limit. Specifically, at BCD, 60% of the data points exceeded 15 µg/m³, indicating a prolonged period of elevated PM_{2.5} levels. AUB site exhibited a lower percentage, with 39.3% of measurements surpassing the daily limit. In contrast, Site of NSMU demonstrated the highest proportion, with 75% of measurements exceeding 15 µg/m³, highlighting a more significant concern for air quality deterioration. In the analysis of PM_{2.5} and in order to determine if there is a significant difference between the means , t-tests conducted to compare the values between groups AUB and BCD, as well as between groups AUB and NSMU, since AUB is the background site. Notably, all t-test results yielded p-values below the critical threshold of

0.05. T-test of AUB-BCD was 0.0305 while 0.0362 for AUB-NSMU. These values are indicating statistically significant differences between $PM_{2.5}$ values from the sites. This suggests that the variables under investigation exhibit significant variation between both AUB and BCD, as well as AUB and NSMU. Additionally, we performed an analysis of variance (ANOVA) test, which also yielded a p-value 0.0417 which is below 0.05. This indicates that there are significant differences among the values when considering all variables collectively.

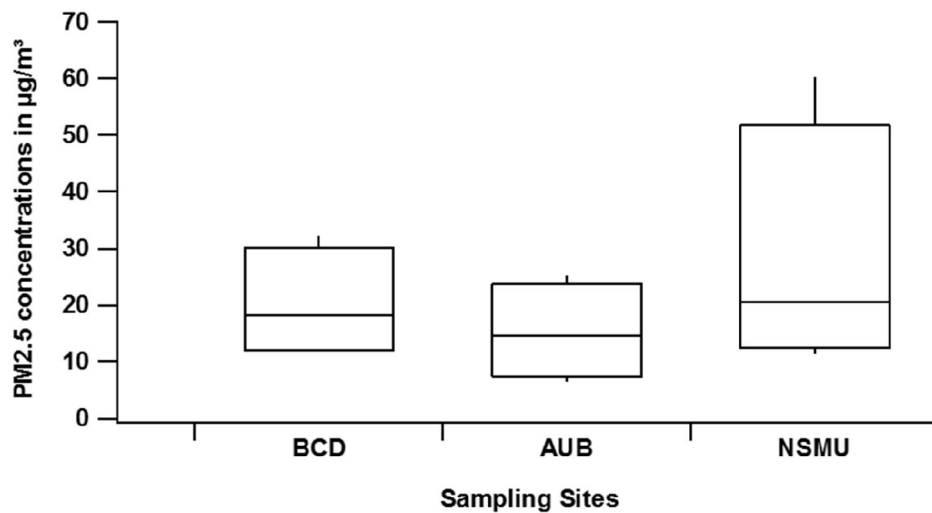


Figure 12: Box plots of $PM_{2.5}$ concentrations measured at BCD, AUB and NSMU. Whisker bottom, box bottom, box top and whisker top represent 10, 25, 75 and 100 concentration percentiles.

Figure 13 represents comparison of $PM_{2.5}$ mean recorded in Beirut in rainy and clear days. Analyzing this data, we can observe the impact of precipitation on $PM_{2.5}$ concentrations.

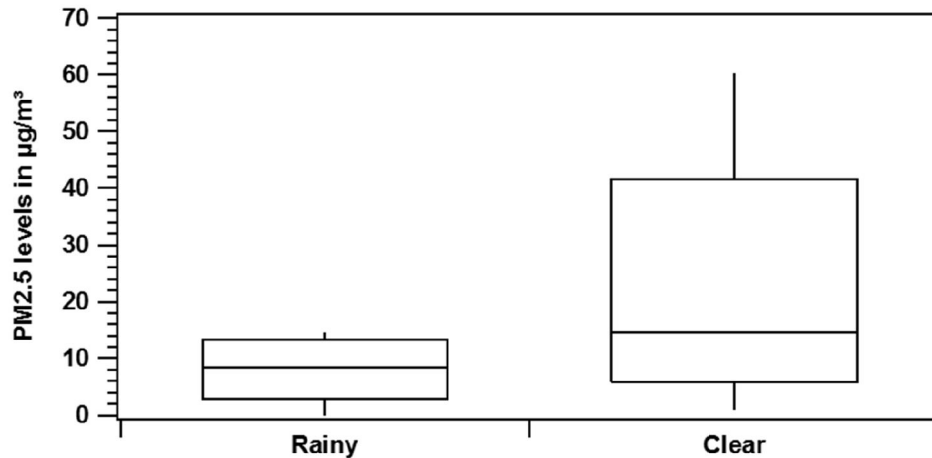


Figure 13: Box plots of PM_{2.5} concentrations measured in Beirut in rainy and clear days. Whisker bottom, box bottom, box top and whisker top represent 10, 25, 75 and 100 concentration percentiles.

On rainy days, the mean PM_{2.5} level is measured at 9.98 µg/m³. This indicates that when it rains, the concentration of PM_{2.5} in the air tends to be lower due to the cleansing effect of precipitation, which effectively removes these fine particles from the atmosphere.

On clear days without rainfall, the mean PM_{2.5} level is significantly higher, recorded at 19.42 µg/m³. This indicates that without the cleansing effect of rain, the concentration of PM_{2.5} particles remains higher in the air.

For instance, let's consider the specific example of January 2, 2023, which was a rainy day. On this day, the PM_{2.5} level was measured at 2.41 µg/m³. This low level suggests that the rain effectively washed away a significant portion of the PM_{2.5} particles present in the air.

In contrast, on January 3, 2023, which was a clear day without rainfall, the PM_{2.5} level increased to 14.41 µg/m³. This higher concentration indicates that without precipitation to remove the particulate matter, the air quality was compromised, and the PM_{2.5} levels rose.

Overall, these observations highlight the positive impact of precipitation, especially rain, on air quality. Rainwater acts as a natural purifier, helping to reduce the concentration of PM_{2.5} and other pollutants in the air, leading to cleaner and healthier atmospheric conditions.

B. Investigation of PAHs

1. Inter sites: Spatial and temporal comparison

The analysis of the Total 16 EPA PAHs concentration in three distinct locations, namely BCD, AUB, and NSMU, has provided intriguing findings that offer insights into the temporal variations and potential environmental impact of these compounds. The results presented in Table 3 indicate that the average concentration of the Total 16 EPA PAHs in BCD was determined to be 12.44 ng/m³. The highest recorded concentration of 28.39 ng/m³ was observed on April 2, 2022, while the lowest concentration of 5.40 ng/m³ was observed on April 20, 2022.

Similarly, in AUB, the average concentration of the Total 16 EPA PAHs was found to be 11.01 ng/m³, with a peak concentration of 22.05 ng/m³ noted on November 29, 2022, and a minimum concentration of 5.19 ng/m³ observed on February 28, 2023. Additionally, NSMU exhibited an average concentration of 12.39 ng/m³, with a maximum

concentration of 30.26 ng/m³ observed on May 10, 2023, and a minimum concentration of 4.97 ng/m³ on June 22, 2023, as depicted in Table 3.

These findings provide valuable information about the varying levels of Total 16 EPA PAHs in different locations over time. The recorded concentrations highlight the potential environmental impact of these compounds and suggest the presence of sources contributing to their presence in the air.

The varying concentrations of PAHs suggest the presence of different pollution sources at each location. Identification and understanding of these sources can be valuable for environmental management and remediation efforts. Further investigation, such as source apportionment studies, can help identify specific emission sources contributing to the PAH concentrations.

Table 3: Concentrations, in ng/m³, of individual and total 16 PAHs in the three Beirut sites during the campaign

PAHs	Acr	BCD			AUB			NSMU		
		Avg	Max	Min	Avg	Max	Min	Avg	Max	Min
Naphtalene	Nap	0.45	0.71	0.33	0.45	0.56	0.34	0.65	2.72	0.34
Acenaphthylene	Acy	0.23	0.33	0.14	0.22	0.29	0.16	0.29	1.13	0.12
Acenaphthene	Ace	0.26	0.58	0.08	0.34	1.13	0.10	0.25	0.35	0.08
Fluorene	Flu	0.36	0.98	0.24	0.26	0.28	0.24	0.32	0.92	0.25
Phenanthrene	Phe	0.54	1.09	0.24	0.44	0.65	0.31	0.52	1.04	0.21
Anthracene	Ant	0.46	0.89	0.13	0.47	0.57	0.38	0.48	1.01	0.31
Fluoranthene	Flt	0.98	2.82	0.24	0.80	1.47	0.37	0.86	1.80	0.12
Pyrene	Pyr	1.34	3.04	0.42	1.04	2.45	0.46	1.23	3.00	0.10
benzo[a]anthracene	BaA	1.20	2.73	0.45	0.82	1.94	0.22	0.98	3.04	0.24
Chrysene	Chr	1.92	3.81	0.73	1.52	3.43	0.45	1.62	4.23	0.41
Benzo[k]fluoranthene	BkF	1.97	6.00	0.61	2.03	4.92	0.40	2.10	9.02	0.68
Benzo[b]fluoranthene	BbF	0.95	2.51	0.29	0.99	2.34	0.28	1.03	4.81	0.38
Benzo[a]pyrene	BaP	1.46	5.21	0.50	1.36	3.51	0.34	1.57	9.25	0.58
Benzo[g,h,i]perylene	BghiP	0.08	0.29	0.00	0.05	0.11	0.01	0.13	2.28	0.02
Dibenz[a,h]anthracene	DahA	0.14	0.23	0.02	0.12	0.16	0.10	0.18	1.03	0.10
Indeno[1,2,3-cd]pyrene	IP	0.10	0.25	0.02	0.10	0.20	0.05	0.18	1.26	0.05
Total 16 PAHs	TPAHs	12.44	28.39	5.40	11.01	22.05	5.19	12.39	30.26	4.97

Among the high-concentration PAHs, Pyrene (Pyr) exhibits relatively high concentrations across all three locations. The concentrations are as follows: BCD - 1.34 ng/m³, AUB - 1.04 ng/m³, NSMU - 1.23 ng/m³. Benzo[a]anthracene (BaA) also shows higher concentrations compared to some other PAHs. The concentrations are as follows:

BCD - 1.20 ng/m³, AUB - 0.82 ng/m³, NSMU - 0.98 ng/m³. Chrysene (Chr) demonstrates relatively high concentrations across all locations. The concentrations are as follows: BCD - 1.92 ng/m³, AUB - 1.52 ng/m³, NSMU - 1.62 ng/m³. Benzo[k]fluoranthene (BkF) consistently exhibits higher concentrations. The concentrations are as follows: BCD - 1.97 ng/m³, AUB - 2.03 ng/m³, NSMU - 2.10 ng/m³. Additionally, Benzo[a]pyrene (BaP) also shows higher concentrations compared to some other PAHs. The concentrations are as follows: BCD - 1.46 µg/m³, AUB - 1.36 µg/m³, NSMU - 1.57 µg/m³.

Benzo[ghi]perylene (BghiP) demonstrates lower concentrations in all the sites. The concentrations are as follows: BCD - 0.08 ng/m³, AUB - 0.05 ng/m³, NSMU - 0.13 ng/m³. Indeno[1,2,3-cd]pyrene (IP) also tends to have lower concentrations across all locations. The concentrations are as follows: BCD - 0.10 ng/m³, AUB - 0.10 ng/m³, NSMU - 0.18 ng/m³.

When comparing the locations, BCD generally exhibits higher concentrations of Benzo[a]anthracene (BaA) (BCD - 1.20 ng/m³, AUB - 0.82 ng/m³, NSMU - 0.98 ng/m³), Chrysene (Chr) (BCD - 1.92 ng/m³, AUB - 1.52 ng/m³, NSMU - 1.62 ng/m³), and Benzo[k]fluoranthene (BkF) (BCD - 1.97 ng/m³, AUB - 2.03 ng/m³, NSMU - 2.10 ng/m³) when compared to AUB and NSMU.

On the other hand, NSMU exhibits higher concentrations of Benzo[b]fluoranthene (BbF) (BCD - 0.95 ng/m³, AUB - 0.99 ng/m³, NSMU - 1.03 ng/m³) compared to BCD and AUB.

a. Temporal variation of TPAHs

The data shows a high temporal variation throughout the year as shown in figure 14 . The maximum sum of PPAHs of 30.25 ng/m³ was measured on May 10th, 2023 in NSMU whereas the lowest of 4.96 ng/m³ measured on June 22th, 2023 in the same site. The high

difference in concentration can be attributed to high variation in the meteorological conditions.

As an example on meteorological conditions difference, the TPAHs concentration, on April 20th, 2022, with parameters such as temperature (19°C), relative humidity (33%) and wind speed (5mph) measured 5.40 ng/m³ whereas on July 12th, 2023 with parameters such as temperature (35°C), relative humidity (69%) and wind speed (2.1mph) measured 28.43 ng/m³.

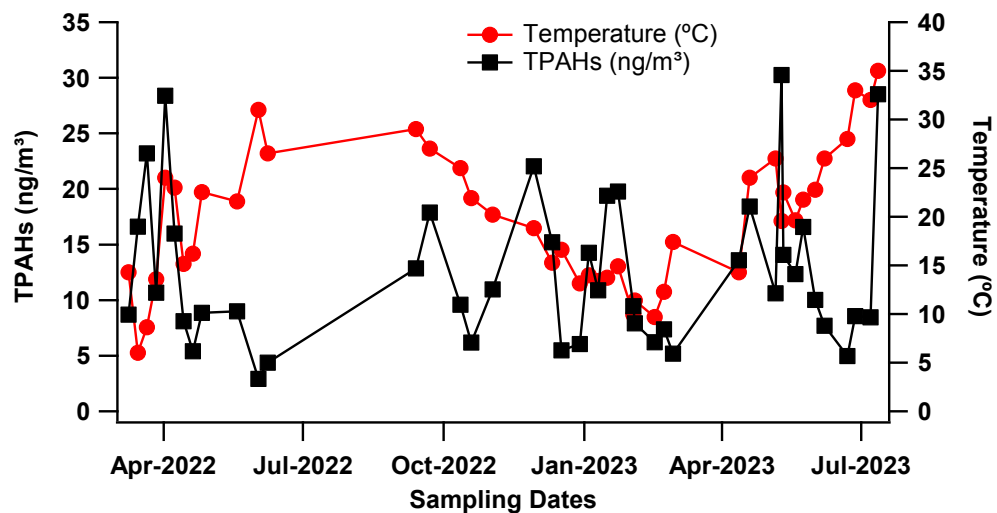


Figure 14: Temporal variation of TPAHs during the campaign started in March, 2022 and ended in July, 2023.

b. Seasonal variation of individual P-PAHs

Figures 15-18 show the levels of the individual P-PAHs during the four seasons. A strong seasonal variation of P-PAHs was observed. During the spring and the summer seasons, the standard deviation of the individual P-PAHs was high. This high deviation is mainly attributed to changing the sites, which makes the different pollution

sources and the contribution in every site an important factor; especially that Beirut is a small urban city.

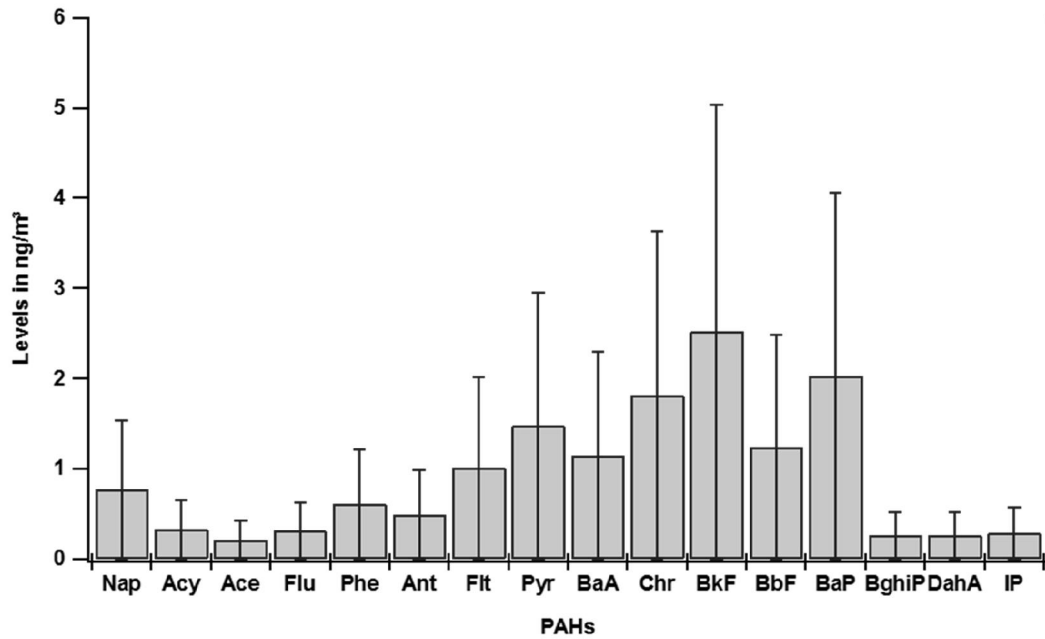


Figure 15: The average concentration of the 16 PAHs during the spring season.

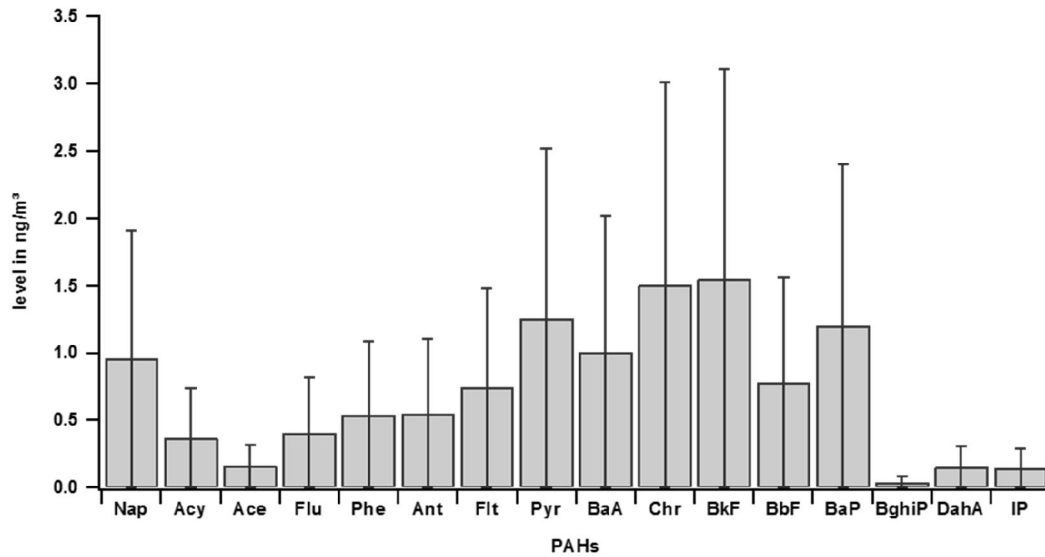


Figure 16: The average concentration of the 16 PAHs during the summer season

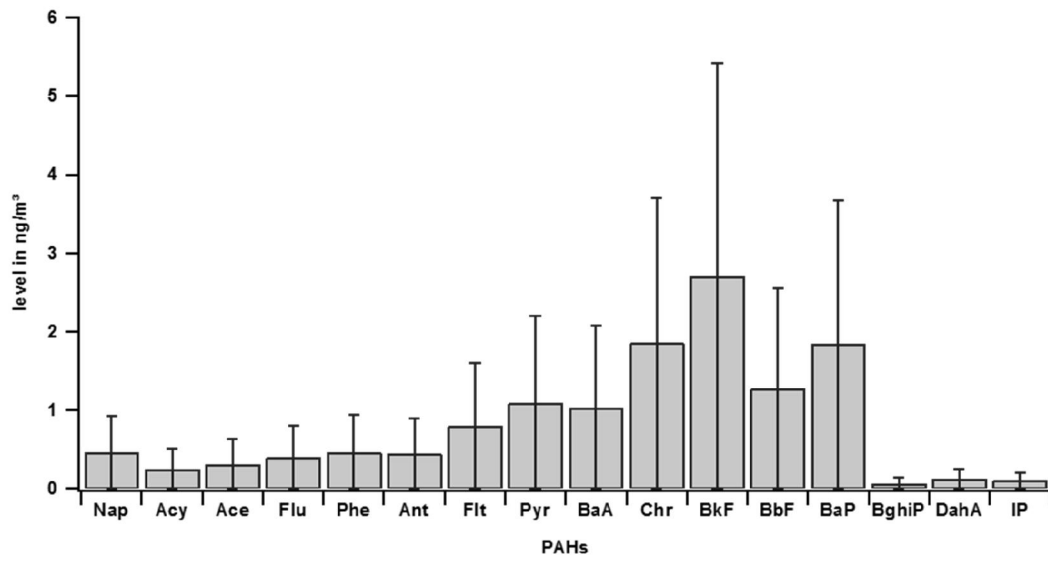


Figure 17: The average concentration of the 16 PAHs during the fall season.

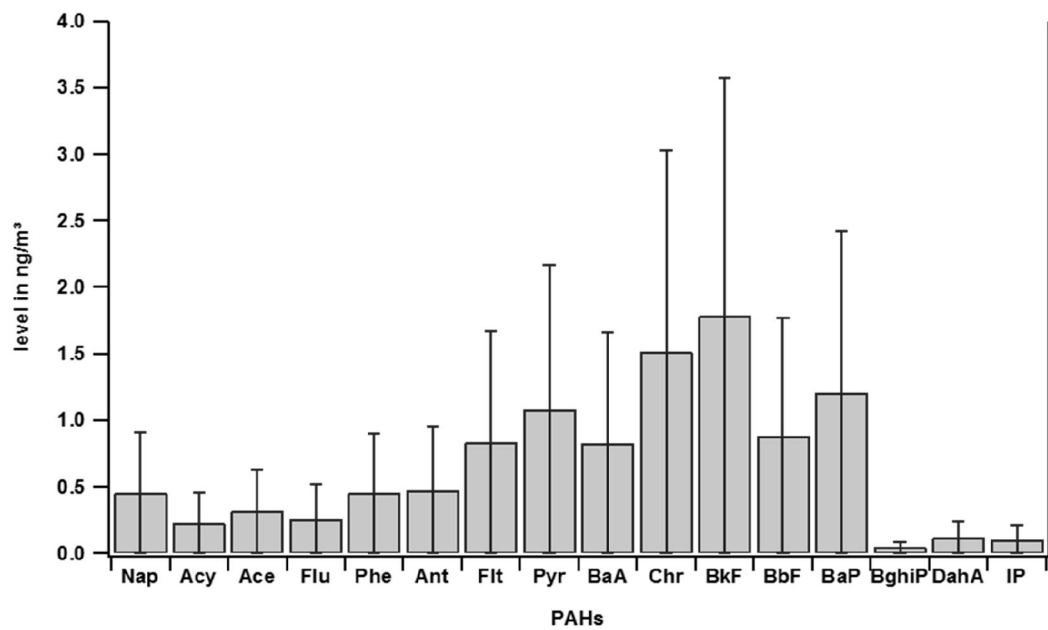


Figure 18: The average concentration of the 16 PAHs during the winter season.

c. PAHs levels in Beirut

Table 4 represents the mean on individual P-PAHs and total P-PAHs in Beirut area compared to the recent annual study represented by Jaafar et al.[50] investigated the P-PAHs at AUB between 2017 and 2018.

Table 4: Average concentration of PAHs in this study in Beirut compared to recent study

Polycyclic Aromatic Hydrocarbons	Acronym	This study in Beirut	Zhao Y. et al, 2021 in Beirut	Jaafar W. et al, 2017 in AUB,Beirut	Baalbaki R.et al.2015 in AUB,Beirut
PAHs	Acr	Avg	Avg	Avg	Avg
Naphtalene	Nap	0.66	0.17	0.2	1.75
Acenaphtylene	Acy	0.29	0.001	0.24	1.12
Acenaphtene	Ace	0.25	0.02	0.28	ND
Fluorene	Flu	0.32	0.02	0.38	3.25
Phenanthrene	Phe	0.53	0.27	0.31	9.75
Anthracene	Ant	0.49	0.0002	0.26	1.07
Fluoranthene	Flt	0.89	0.07	0.59	1.7
Pyrene	Pyr	1.27	0.1	0.54	3.17
benzo[a]anthracene	BaA	1.02	0.03	0.63	2.2
Chrysene	Chr	1.69	0.07	0.66	1.65
Benzo[k]fluoranthene	BkF	2.19	0.2	1.1	0.6
Benzo[b]fluoranthene	BbF	1.07	0.06	0.86	ND
Benzo[a]pyrene	BaP	1.64	0.17	0.66	0.79
Benzo[g,h,i]perylene	BghiP	0.14	0.18	1.3	0.55
Dibenz[a,h]anthracene	DahA	0.18	0.1	1	ND
Indeno[1,2,3-cd]pyrene	IP	0.19	0.25	1	0.44
Total 16 PAHs	TPAHs	12.82	1.7112	10	

C. Discussion of Results

The levels of P-PAHs in the air vary depending on the time of year, as both seasonal emission sources and meteorological conditions differ. Many studies[35, 83-87]have reported an increase in P-PAHs during winter and fall. In colder seasons, the rise in PAH concentrations can be attributed to emissions from domestic heating, which are absent

during warmer seasons. Additionally, the inversion layer frequently occurs during long, cold winter nights. This phenomenon occurs when the ground surface cools rapidly at a faster rate than the radiation received from the sun, resulting in excessive nocturnal cooling.[40, 88-90] The inversion layer restricts the upward vertical mixing and dispersion of PAHs, trapping them near the ground below the inversion layer.

The cold period is characterized by low ambient temperature, reduced solar radiation, and high relative humidity, all of which limit the physical and chemical decomposition of P-PAHs, leading to increased persistence in the atmosphere.[88, 91]

On the other hand, high temperatures in summer, along with intense solar radiation and low humidity, promote thermo-, photo-, and chemical oxidation processes for decomposing atmospheric P-PAHs. However, in a city, like Beirut, has an increasing demand for electricity especially from residential, commercial and others (including schools, hospitals, governmental buildings) activities [92] and increase in electricity consumption in the summer because of need for electricity during the hot season [93]. Also, in summer there are stagnant weather conditions with minimal dilution contrary to what is expected to happen in winter. All these mentioned reasons resulted in this study that TPAHs levels are also concentrated in summer and sunny days.

D. Cancer risk calculation

Benzo[a]pyrene (B(a)p) is recognized as one of the most potent polycyclic aromatic hydrocarbons (PAHs) with well-documented carcinogenic and mutagenic properties. [1, 82]. Box plot of figure 19 represented that the BaP levels in NSMU were the highest in average and day to day measurements. As shown in table 3, Bap average concentration in NSMU was 1.5 ± 0.63 ng/m³ higher than that in BCD (1.46 ± 0.45 ng/m³) and in AUB (1.37 ± 0.30 ng/m³). In particular, the yearly BaP average of 1.64 ng/m³ (Table 4) is

exceeding the annual guideline set by the European Union Directive 2004/107/EC (1 ng/m³). The average of BaP in this study is much higher compared to the previous studies (0.17±0.10 ng/m³ in 2020-2021 [74], 0.66±0.05 ng/m³ in 2016-2017[50] and 0.9±0.02 ng/m³ in 2014-2015[43]).

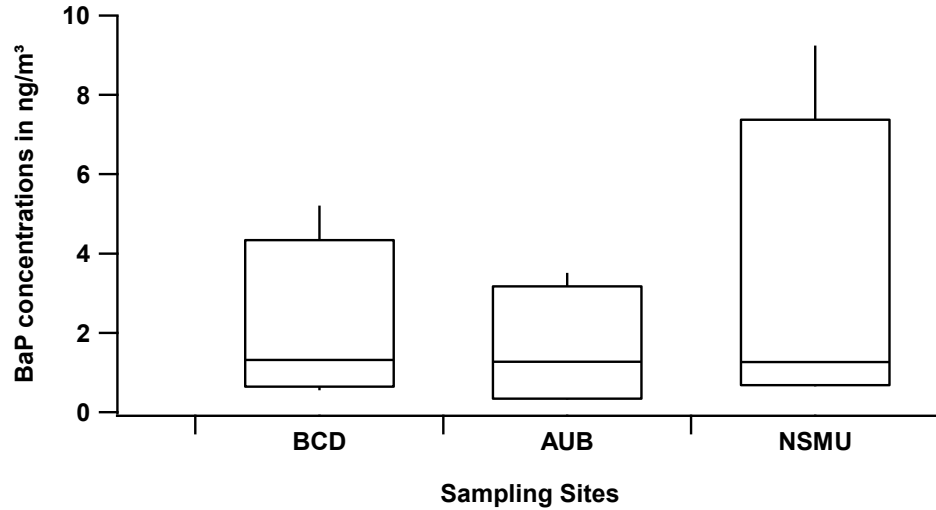


Figure 19: Box plots of BaP concentrations measured in BCD, AUB and NSMU. Whisker bottom, box bottom, box top and whisker top represent 10, 25, 75 and 100 concentration percentiles.

In this study, the widely utilized "toxic equivalence factor" (TEF) method was employed to assess the carcinogenic potency of the PAHs measured.[94-97] The TEF method, following the procedures of the Office of Environmental Health Hazards Assessment of California Environmental Protection Agency (OEHHA-CalEPA), takes into account the toxicity of all PAHs by expressing them in terms of BaP equivalence.[98-100]

$$\text{Equation 1: } \sum BaP_{eq} = \sum (C_i \times TEF_i)$$

Where $\sum BaP_{eq}$ is the total BaP equivalent concentrations, C_i is the concentration of each PAH in ng/m³, and TEF_i is the toxicity equivalent factor of each PAH. [98-100]

To evaluate the potential risk of developing cancer through inhalation and exposure to particle-bound PAHs, the OEHHA procedure was utilized. This established approach allows for the calculation of the lifetime excess cancer risk using the following equation:

$$\text{Equation 2: Excess Cancer Risk (ECR)} = \sum BaPeq \times UR_{BaP}$$

The equation takes into consideration the UR_{BaP} value, which represents the number of individuals at risk of developing cancer from inhaling a BaP equivalent concentration of 1 ng/m^3 over a 70-year lifetime.[101, 102] The value of UR_{BaP} utilized in this study was 1.1×10^{-6} (equivalent to 0.11 cases per 100,000 people), as determined by the OEHHA of the CalEPA.

Based on the presented data in table 4, the estimated cancer risk for AUB using equation 1 and 2 is 3.45×10^{-5} . The calculated value is higher than the calculated one for AUB in 2016-2017 (2.25×10^{-6})[50] and in 2015 (1.05×10^{-6}) [43]. Over and above that, the cancer risk calculated for BCD and NSMU estimated (2.49×10^{-5}) and (3.97×10^{-5}) respectively whereas the estimated cancer risk for Beirut is 1.04×10^{-4} . The cancer risk calculated, in this study, showed an increase and exceeded the threshold for acceptable cancer risk set by EPA (10^{-6})[103]. Based on the assumption, ECRs for diesel generators and traffic were calculated to assess the exposure risks in current and predicted scenarios. In 2017, diesel generators in Beirut were operated for 3 hours per day whereas since 2021 generators were running for longer periods as the electricity shortage was caused by the grid shut down. Such high values are confirming thereby the lack of regulations to reduce or contain emissions and describing how the air quality in Beirut is getting worse year after year.

CHAPTER V

SOURCE APPORTIONMENT FOR P-PAHS

A. General introduction

After conducting measurements and analysis for PAHs, the process of source apportionment becomes crucial to understand the specific origins and contributions of these pollutants. By employing advanced data analysis techniques such as Positive Matrix Factorization (PMF), source apportionment can provide valuable insights into the major pollution sources and guide effective mitigation strategies. By applying PMF to PAH measurements and analysis, researchers can identify the major sources of PAH pollution and estimate their relative contributions.

B. Positive Matrix Factorisation (PMF)

PMF Receptor model is based on the Chemical Mass Balance (CMB) equation that considers a single sample taken at a single location and time period, can be expressed as:

$$X_{ij} = \sum_{k=1}^p g_{ik} f_{kj} + e_{ij}$$

Where:

X_{ij} represents the concentration of ambient measured species j in sample i

P is the number of factors (sources) contributing to the measured sample and is provided to the model by the user.

f_{kj} is the fractional concentration of species j in the emissions from factor profile k .

g_{ik} is the relative contribution of factor k to sample i .

e_{ij} is the residual of the measured concentration of species j in sample i that cannot be explained by the model.

In brief, the input matrix provided by the user is factorized into three matrices: factor contribution(**G**), factor profile(**F**), and residual (**E**).

The objective of solving this equation is to determine the optimal values of g_{ik} , f_{kj} , and p that can accurately reproduce the observed X_{ij} values. The process involves adjusting g_{ik} and f_{kj} iteratively until the minimum value of the robust goodness of fit parameter, Q_{robust} , is achieved for a given p . Q_{robust} is calculated by excluding outliers from the analysis. However, it is also important to consider the true goodness of fit parameter, Q_{true} , which incorporates all the collected data. To obtain a stable and reliable solution, Q_{robust} and Q_{true} should be reasonably similar. The expression for Q_{robust} is as follows:

$$Q_{robust} = \sum_{i=1}^n \sum_{j=1}^m \left[\frac{x_{ij} - \sum_{k=1}^p g_{ik} f_{kj}}{u_{ij}} \right]^2$$

Thus the function Q_{robust} is basically the residues divided by uncertainties or is the weighted sum of squares of differences between the PMF output and the original data set. This means that in order to obtain a minimum Q that would give a feasible and robust solution, it is important that the residues which is the fraction that cannot be explained by the model to be low. [104]

C. Optimization and Validation of PMF

Determining the appropriate number of factors and sources is a major step in PMF modeling. During the optimization process, it is essential to consider and evaluate five parameters to accurately estimate the number of factors. By achieving an optimal estimation, a more stable, robust, and dependable solution can be obtained.

The five parameters that should be taken into account are as follows: signal to noise ratio, closeness of Q_{robust} to Q_{true} , residual analysis, correlation coefficients between observed and estimated concentrations, and bootstrap mapping.

The range of factors considered was between 3 and 7, and the number of factors closest to the optimal value was determined. Based on the aforementioned parameters, a 3-factor solution yielded the lowest Q_{robust} value of 1450, which was close to the Q_{true} value of 1459 ($Q_{\text{robust}}/Q_{\text{true}} = 0.993$), indicating a high level of accuracy.

Additionally, this solution demonstrated a favorable range of scaled residuals, strong correlation coefficients, and satisfactory bootstrap mapping.

1. *Signal to noise ratio (S/N):*

S/N indicates whether the variations observed in the measurements are genuine or simply due to random fluctuations in the data. If the data falls within the noise range, it suggests that our measurements are either close to or below the detection limits. To determine this, we compare our data to the provided calculated uncertainties. There are several methods[105, 106] to calculate uncertainties, with one common approach being based on the analytical method's limit of detection.

The two equations are as follow:

Equation 1: $U_{ij} = 0.2X_{ij} + LOD/3$

Equation 2: $U_{ij} = 0.1X_{ij} + LOD/3$

In case of this study, Equation 2 was employed to calculate the uncertainties since our measurements for the 16 PAHs were above the detection limit in all samples.

To assess the strength of each species, we calculate their signal-to-noise (S/N) ratio. Species are considered strong if their S/N ratio exceeds 1, weak if it falls between 0.5 and 1, and poor if it is below 0.5. Based on our input data, all the species exhibited strengths higher than 5.8, which are considered strong. Consequently, none of the 16 PAHs were excluded from the model.

2. Observed/ predicted scatter plots:

Scatter plots are used to compare the observed (input data) values with the predicted (modeled) values for each species, allowing us to assess how well the model fits each individual species. In the case of PMF, a minimum acceptable correlation coefficient (R^2) for a species is set at 0.6[104].

3. Residual analysis

This analysis indicates how much points were excluded from the solution of the model. If all residuals of the whole species are between +3 and -3 and they are normally distributed then this species is well modeled. If the residuals' range of a specie has a high scale and are non-normally distributed, it may be an indication of a poor fit. For the 16 PAHs, 87% of the scaled residuals estimated by PMF were normally distributed. Those

which were beyond this range should be treated in caution while interpreting the output profiles[104].

4. Bootstrap mapping

Bootstrap mapping indicates whether the number of factors is an approximation or needs to be optimized[107-110]. A bootstrap model involves running at least 100 bootstraps. The mapping percentage of each assigned bootstrap factor to the base factor reveals the uniqueness of the different factor profiles. If a significant number of bootstrapped factors overlap with more than one base factor, it suggests that the factor profiles are not distinct, and the number of factors may need to be optimized. In this study, the mapping percentage between the three base factors and the three bootstrap factors exceeded 83%, indicating that the chosen number of factors is appropriate.

Once most of the PMF validation parameters were satisfied, it was concluded that three factors are the appropriate number of factors influencing the receptor site in our study.

D. PMF output results

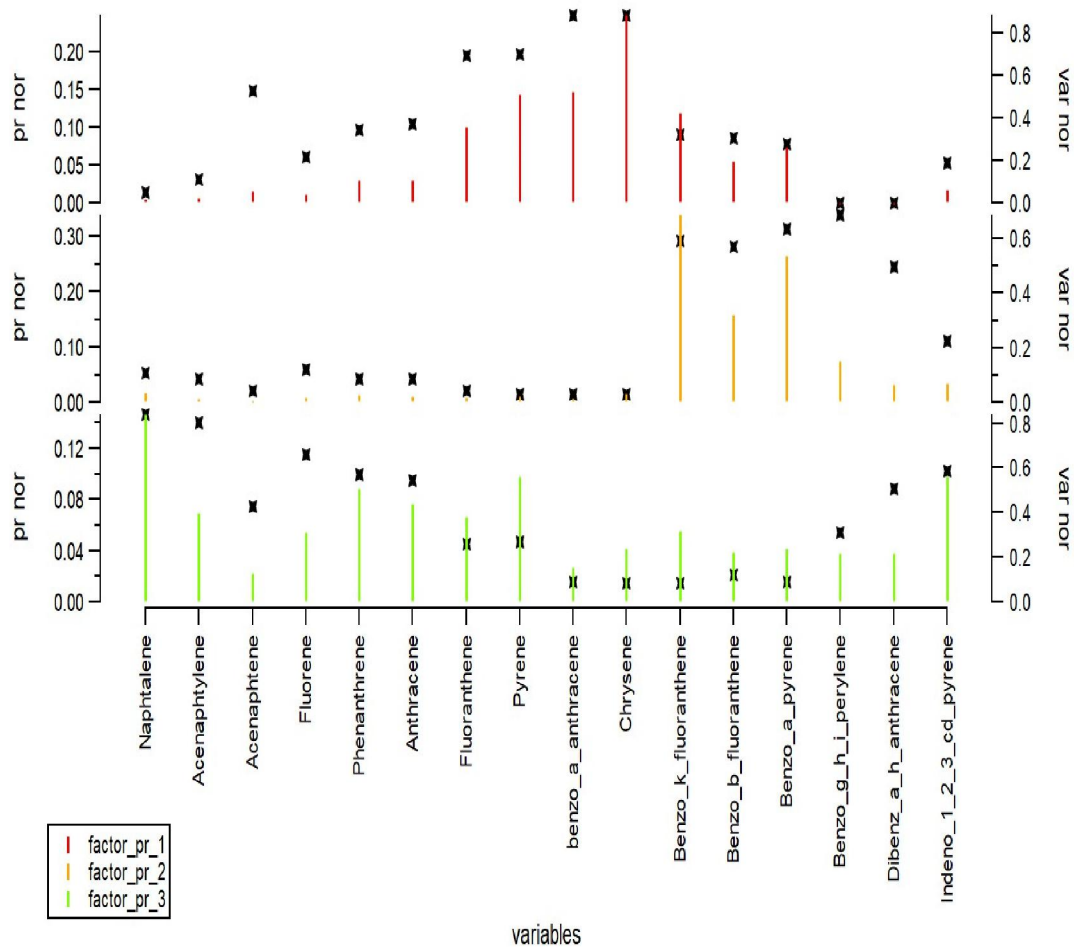


Figure 20: The three factor profiles for factors 1,2 and 3 determined by PMF and the fraction of the species in each.

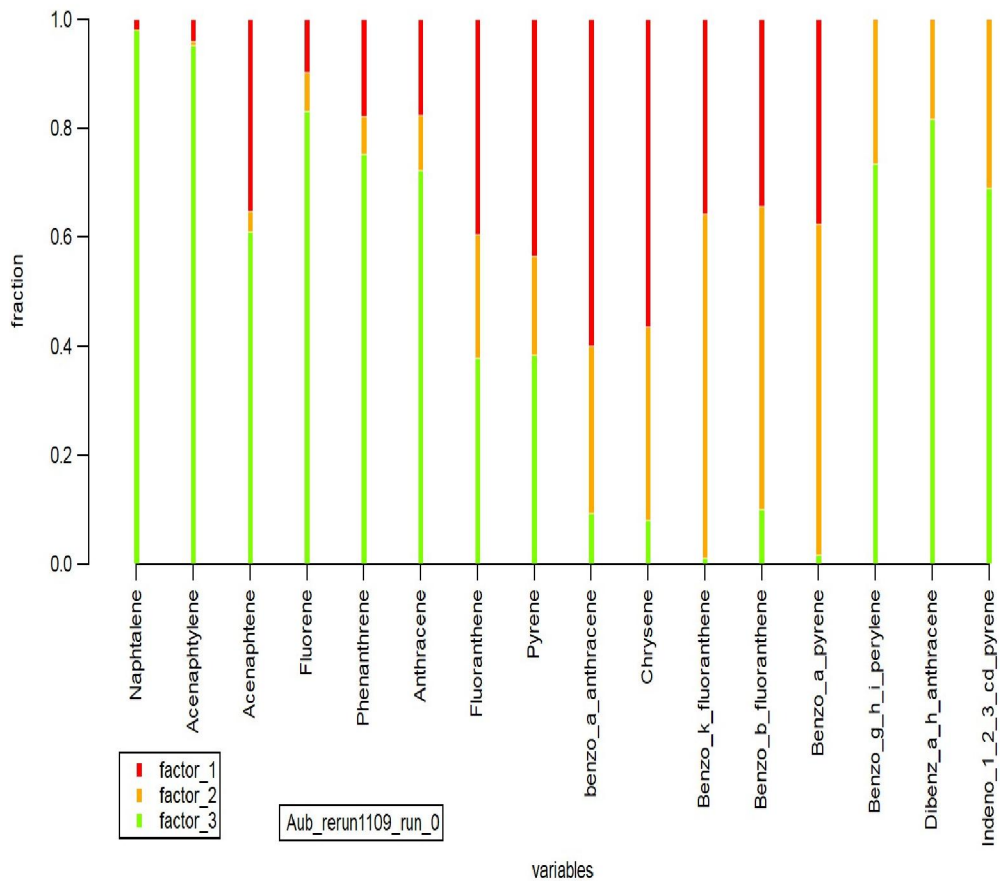


Figure 21: Fingerprints (PAH markers) of the three factor profiles according to PMF results.

After conducting measurements and analysis for PAHs, the process of source apportionment becomes crucial to understand the specific origins and contributions of these pollutants. By employing advanced data analysis techniques such as Positive Matrix Factorization (PMF), source apportionment can provide valuable insights into the major pollution sources and guide effective mitigation strategies. By applying PMF to PAH measurements and analysis, researchers can identify the major sources of PAH pollution and estimate their relative contributions.

E. Results and identification of factors

A three-factor model associated to P-PAHs gave the best fit in the PMF analysis. Figure 21 represented the contribution of every factor in the three sites in Beirut. Following the markers of PAHs associated with diesel generators extracted from the systematic review, in factor 1 the medium molecular weight compounds (MMW, containing 4 benzene rings) Fluoranthene, Pyrene, benzo[a]anthracene and Chrysene were dominating alongside with Benzo[k]fluoranthene which make this factor influenced by diesel engines and generators emissions.

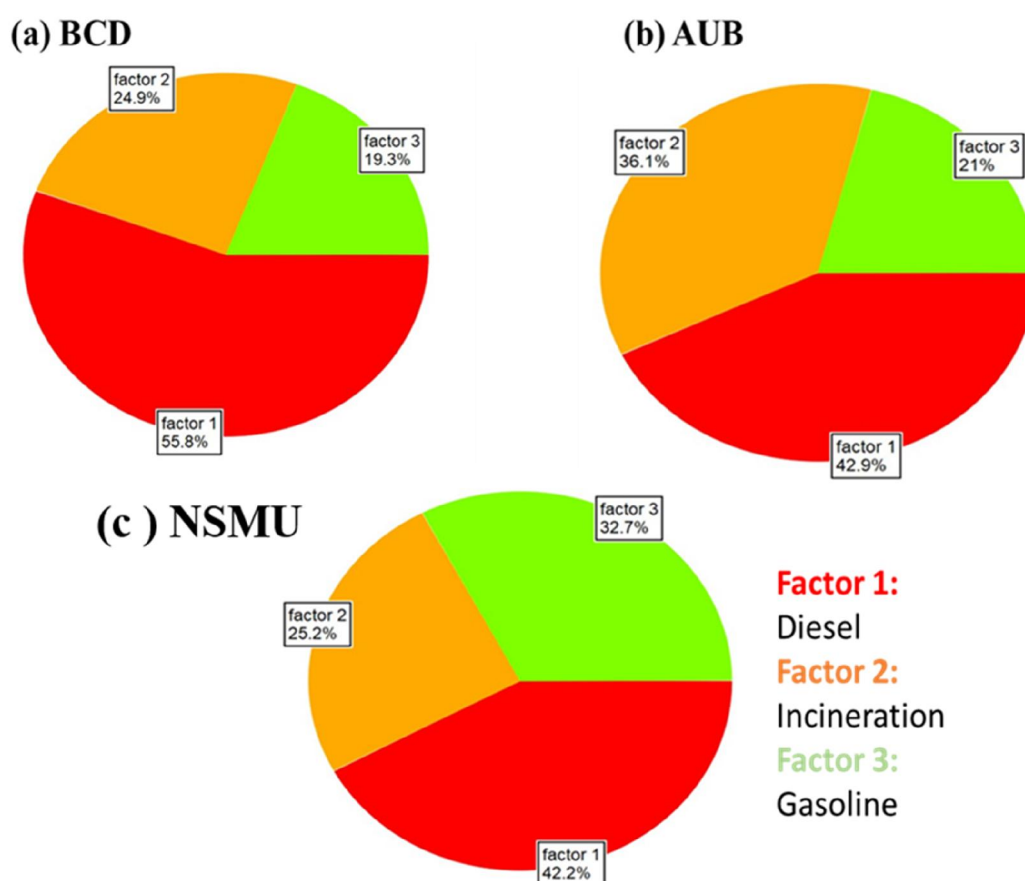


Figure 22: The portion contribution of the three factors to the total ambient P-PAH

Next, Factor highly consists of Benzo[k]fluoranthene, Benzo[b]fluoranthene, Benzo[a]pyrene, Benzo[g,h,i]perylene, Dibenz[a,h]anthracene and Indeno[1,2,3-cd]pyrene). As reported by Zhao et al, Dibenz[ah]anthracene and the remaining of high molecular weight PAHs are highly released by incinerators and especially the medical ones[111]. In fact, the reduction in the levels of Benzo[g,h,i]perylene, Dibenz[a,h]anthracene and Indeno[1,2,3-cd]pyrene in this study compared to the study performed between 2016-2017 when the country suffered of a spread of incinerators[50] is logically accepted.

In factor three high loadings of Dibenz[a,h]anthracene and Indeno[1,2,3-cd]pyrene and moderate loading of benzo[ghi]perylene are observed. Also, the low molecular weight PAHs are present in high values especially naphthalene. Indeed, this kind of profile is usually attributed to gasoline emissions. [43-50] The primary source of PAHs from gasoline is the on-road vehicles. In fact, Beirut, suffers from high number of vehicles and traffics, thus, no wonder why gasoline contributes in the high pollution levels.

F. Discussions of results

A comparative analysis was conducted on the sources responsible for emitting PAHs into the atmosphere across countries with varying Gross National Incomes (GNIs). The studies revealed that in low-income countries, the primary contributor to PAH emissions was vehicular exhaust from both diesel and gasoline vehicles, as observed in Rwanda.[112] On the other hand, middle and high-income countries exhibited a dominance of sources such as industrial processes and coal combustion, alongside vehicular emissions from both diesel and gasoline vehicles.[113-115]

Notably, Lebanon stood out among the few countries where incineration and diesel generators accounted between 67% and 81% of PAH emissions into the atmosphere. These findings underscore the significant impact of traffic emissions, incineration, and diesel generators on the well-being of residents in close proximity to these sources. By going deeply into the properties of every site, percent of contribution of diesel generators in the low-to-middle income area (NSMU) (42.2%) was the lowest compared to high economic area (BCD) (55.8%) and urban background area (AUB) surrounded by high economic area (42.9%). In contrast NSMU is the highest site influenced by vehicular and traffic emissions with a 32.7% which is higher than that in AUB (21%) and BCD (19.3%). On the other side, incinerators are highly attributed to the pollution in AUB with a percentage of contribution (36.1%) more than that in BCD (24.9%) and NSMU (25.2%).

To gain insights into the case of AUB, it is necessary to conduct a comparative analysis for the difference of contribution of the three factors of pollution in AUB between this study and the recent study in 2016-2017.

The percentage of contribution of diesel increased from 23% into 42.9%. Based on the assumption, ECRs for diesel generators and traffic were calculated to assess the exposure risks in current and predicted scenarios. In 2017, diesel generators in Beirut were operated for 3 hours per day generators were running for longer periods as the electricity shortage was caused by the grid shut down since 2021. In the other side, contribution of gasoline decreased from 48% into 21%, while that of incineration increased from 29% into 36.1%. In fact, the medical waste incinerator of the American university hospital (AUH) located nearby AUB has an impact on the amount of factor two in the AUB site. is influenced by the medical waste incinerator at the AUH. Based on the information provided by the

department of environment and health risk management (EHSRM) at AUB, about 3.5 % of cytotoxic medical waste generated by the hospital is incinerated. The incinerator is known to operate for a maximum of six times per month with few hours at night.[81]

CHAPTER VI

CONCLUSIONS

Polycyclic aromatic hydrocarbons (PAHs) are present widely in the air we breathe, including in urban areas due to human activities. These compounds have detrimental effects on human health, as they are known to cause adverse health effects. While PAHs can originate from natural sources, anthropogenic emissions play a significant role in their presence in populated urban areas.

To understand the spatial distribution of PAHs and PM_{2.5} (particulate matter with a diameter of 2.5 micrometers or less), three representative sites (AUB, BCD, and NSMU) were studied. The results revealed how local emissions at each sampling location influenced the levels of PAHs and PM_{2.5}. AUB, representative of an urban background site, had the lowest concentrations of PAHs and PM_{2.5}. On the other hand, BCD, characterized by a high economic activity and numerous diesel generators, and NSMU, a low-income area affected by diesel generators and heavy vehicular traffic, exhibited higher levels of PAHs and PM_{2.5}.

In cities like Beirut, the demand for electricity is constantly increasing, driven by residential, commercial, and institutional activities such as schools, hospitals, and governmental buildings. This heightened demand is particularly pronounced during the hot summer season. Additionally, stagnant weather conditions during the summer limit the dispersion of pollutants, contrary to what is typically observed in winter. Consequently, this study found that PAH levels, including total PAHs (TPAHs), tend to be concentrated during summer as well as in winter and fall.

The study also calculated the cancer risk associated with exposure to PAHs, and the results indicated that the risk exceeded the acceptable threshold set by the Environmental Protection Agency (EPA). These findings highlight the absence of sufficient regulations to mitigate or control emissions, underscoring the worsening air quality in Beirut year after year.

Furthermore, a systematic review was conducted to identify markers specifically associated with diesel generators, which are one of the significant sources of PAH emissions. The study employed the Positive Matrix Factorization (PMF) technique for source apportionment and identification of PAH sources. Three factors were identified: factor one represented diesel generators, factor two corresponded to incinerators, and factor three represented gasoline and vehicular emissions. In AUB the contribution of diesel emissions increased from 23% to 42.9%, while gasoline emissions decreased from 48% to 21%. The contribution from incineration sources increased from 29% to 36.1%. Upon closer examination of each site, the percentage of contribution from diesel generators in the low-to-middle income area (NSMU) was found to be the lowest at 42.2% compared to the high socio-economic area (BCD) at 55.8% and the urban background area (AUB) surrounded by a high socio-economic region at 42.9%. In contrast, NSMU had the highest percentage of contribution from vehicular and traffic emissions at 32.7%, surpassing AUB (21%) and BCD (19.3%). On the other hand, incinerators were found to have a significant impact on pollution levels in AUB, with a contribution percentage of 36.1%, higher than that in BCD (24.9%) and NSMU (25.2%).

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