AMERICAN UNIVERSITY OF BEIRUT

PARTICLE BOUND POLYCYCLIC AROMATIC HYDROCARBONS: SEASONAL VARIATION, SOURCE APPORTIONMENT AND CANCER RISK ESTIMATION

by
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AN ABSTRACT OF THE THESIS OF

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Title: Particle bound polycyclic aromatic hydrocarbons: seasonal variation, source apportionment and cancer risk estimation

Introduction: background and aims: Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous pollutants released into the atmosphere as a mixture of different congeners due to incomplete combustion and pyrolysis of organic matter. Many PAHs and their derivatives are strongly potent carcinogens or mutagens to humans; therefore, their quantification and source identification in the environment are continuing concerns. Some studies in Lebanon reported short-term PAH levels at different locations. However, no studies up to our knowledge, evaluated the annual average and the seasonal variation of the 16 PAHs defined by EPA as the most potent at an urban background site. Hence, this study establishes a baseline level of PAHs at an urban representative site in Lebanon, evaluates their seasonal variation, apportion their sources and ultimately estimates their lifetime cancer risk.

Methods: Every six days Particle bound PAHs (P-PAHs) were sampled using a high-volume sampler at a representative urban site like AUB. The desired analytes were then extracted using an optimized method and analyzed using gas chromatography-mass spectrometry (GC-MS)

Results: The results showed that PAH levels were highly variable between the seasons throughout the year of 2017. The Highest levels of total PAHs were detected during winter (13.85±2.32) ng/m^3 while lowest levels were detected in summer (6.32±0.74). Consistently, the group 1 carcinogen Benzo[a]pyrene (B[a]p) followed the same trend of seasonal variation with an annual mean (0.75±0.23) ng/m^3 lower than the annual recommended level determined by the European Union (1ng/m^3). Among the different congeners of PAHs, the five-member aromatic rings known as possible or probable carcinogens were the dominant PAH congeners in the urban site. Incremental lifetime cancer risk (ILCR) scenario estimation showed that out of 10^6 population, one individual at this urban site would develop cancer due to daily exposure to ambient PAHs levels. PAH congeners can be emitted by different sources. Among these, gasoline, diesel and incineration were found to be the three major sources of PAHs determined by source apportionment with a contribution of 55.5%, 31.9% and 12.6%, respectively.

Conclusion: In short, our study establishes a baseline level of P-PAHs with an annual average of 10.4±1.3 ng/m^3. This level and the seasonal averages can be used as a benchmark to assess the contribution of additional sources in the different urban areas. The results also show a strong seasonal variation in P-PAH levels which indicates the effect of meteorological conditions and source emissions on their ambient concentrations. Positive matrix factorization (PMF) proved to be successful into partitioning the contributing sources according to their PAH markers because of the high number of samples provided to the model (n=55). Among the different PAH sources identified by this study, gasoline was found to be the major contributing source. Incremental life time cancer risk (ILCR) estimation for PAH-induced cancer exceeded the commonly acceptable threshold of 10^{-6} and shows that there is a chance for an adult individual to develop cancer due to PAHs daily exposure.

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ABBRIVIATIONS

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
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
V-PAHs	Vapor phase polycyclic aromatic hydrocarbons
WHO	World health organization

Chapter I

POLYCYCLIC AROMATIC HYDROCARBONS IN AIRBONE PARTICULATE MATTER

A-Particulate Matter

Up to date, an extensive body of scientific evidence has shown that air pollution is linked to several ailments, due to the presence of toxic pollutants. In fact, exposure to these pollutants for either short or long term causes premature death and harmful effects on the human body, most of the time leading to many fatal diseases including cancer[1]. Even more, it is expected that by 2050, exposure to outdoor air pollution will take a lead among the environmental factors that cause premature mortality, thus surpassing malaria and water quality[2]. Recently, the World Health Organization (WHO) reported that in 2012, the indoor and outdoor air pollution led to 7 million premature deaths in the world, with 3.7 million deaths caused by outdoor air pollution[3]. Huge attention has been given to air pollution by scientists and great efforts have been made worldwide to reduce air pollution, especially after the establishment of Environmental Protection Agency (EPA) in 1970. Out of the many pollutants, EPA has defined National Ambient Air Quality Standards (NAAQS) for six principal pollutants-named "criteria" air pollutants. They are: Carbon Monoxide (CO), Sulfur Dioxide (SO_2), Nitrogen Dioxide (NO_2), Lead (Pb), ozone (O_3), and Particulate Matter (PM)[4]. Among these "criteria pollutants", PM has received a high attention due to their strong association with mortality and morbidity cases from respiratory, cardiovascular , and cancer diseases [5, 6].

PM is a widespread air pollutant, consisting of a mixture of solid particles and liquid droplets suspended in air. PM vary in sizes, they can range from few nanometers to several micrometers. Particles with diameters between 2.5 and 10 μm ($PM_{10-2.5}$) are known as coarse particles while those with a diameter between 2.5 μm and 0.25 μm ($PM_{2.5-0.25}$) are known as fine particles. Particles that are less than 0.25 μm in diameter are called ultrafine particulates (UFP)[7, 8]. Each PM mode has its own sources, chemical composition, respiratory penetration and atmospheric lifetimes. Coarse PMs mainly include crustal material, sea salts, and biological factors and are produced by mechanical processes unlike fine and ultrafine PMs which primarily contain elemental carbon, metals and organic compounds that are generated by combustion processes[8, 9].

The size and composition of these particles has been directly linked to being the main cause of health problems[10]. Generally speaking, the smaller a particle is, the deeper will penetrate to deposit on the respiratory tract at an increasing rate. To date, particles that have the most impact on human health have been acknowledged to those less than 2.5 μm ($PM_{2.5}$). These particles have longer lifetimes in air ranging from days to weeks compared to coarse particles (PM_{10}) which have a lifetime of minutes to hours. Accordingly, the fine particles ($PM_{2.5}$) can travel distances up to 1000 km higher by two orders of magnitude than coarse particles(PM_{10})[11]. While particles between approximately 5 and 10 μm are most likely deposited in the tracheobronchial tree (upper respiratory track), those less than 2.5 μm are deposited in the respiratory bronchioles and the alveoli (pulmonary interstitial sites) where gas exchange occurs[12, 13] (Figure.1). Eventually, those of the fine and quasi-ultrafine mode particles will escape into the blood stream and deliver harmful chemicals to the blood system to cause significant health problems including decreased lung function, aggravated asthma, cardiovascular diseases, oxidative stress, and ultimately cancer [6, 14].

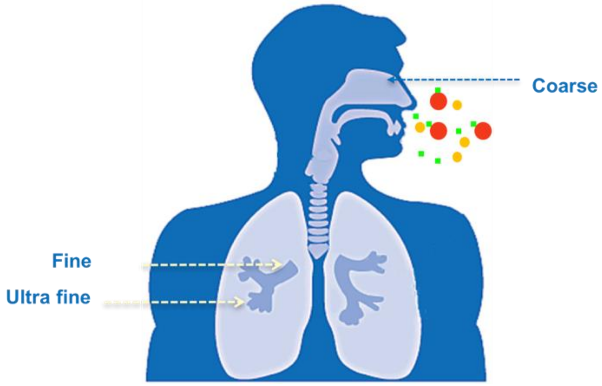

Figure 1. The different sizes of particulate matter and their different penetration pathways into the respiratory system.

Although the mechanism by which PM affects biological systems is still unclear, many studies has reported that metals act as possible mediators of PM induced airway injury and inflammation through the Fenton reaction[15-17]. Transition metals present in particles, especially iron, increase production of reactive oxygen species (ROS) in vivo[18]. As the release of ROS can result in cellular and tissue damage, it can thus initiate or exacerbate inflammation[19, 20]. However, a large fraction of ambient fine PM in many areas is derived from combustion processes and as such, contains significant amounts (up to 80–90% of UFP mass) of elemental carbon (EC) also called black carbon and organic carbon (OC)[21-24]. Part of the OC are polycyclic aromatic hydrocarbons (PAHs)[25]. PAHs are known to exert their toxicity after their biotransformation into toxic metabolites, which can be bound covalently to cellular macromolecules such as protein, Deoxyribo Nucleic Acid (DNA) and Ribonucleic Acid (RNA), causing cell damage, mutagenesis and carcinogenesis[26].

B-Polycyclic aromatic hydrocarbons(PAHs)

PAHs are a class of semi volatile organic compounds, composed of at least two fused aromatic rings[27]. These compounds are widely distributed in the atmosphere and exhibit an increasing concern about their occurrence in the environment due to their carcinogenicity and mutagenicity[28]. Their ubiquitous presence in the atmosphere is mainly due to anthropogenic activities related to pyrolysis and incomplete combustion of organic matter such as paraffins, olefins, and aromatics. In general, during combustion or pyrolysis, where temperature exceeds 500°C, the organic compounds present in the fuel are cracked into smaller unstable free radicals, which in turn produce the first aromatic ring via several reaction mechanisms. Further reaction of this aromatic ring under high temperature and pressure conditions with small molecules such as acetylene (C_2H_2), ultimately leads to the growth of the aromatic system and the formation of larger multi-ring structures that are resistant to thermal degradation[Figure 2][29, 30].

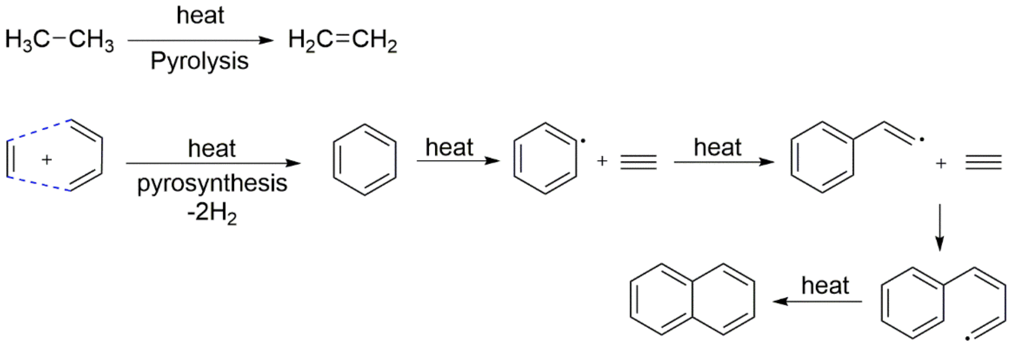

Figure 2. Pyrolysis followed by Pyrosynthesis of naphthalene starting with ethane

C-Sources of PAHs

In the ambient air of urban areas, PAH’s occurrence is largely a result of anthropogenic emissions from many sources including fossil and biomass fuel burning power plants, road transport including diesel, and gasoline vehicles, waste incinerators, domestic heating, diesel generators, and industrial activities such as aluminum industry. The ambient existence of PAHs from biogenic sources including volcanic eruptions and forest fires is considered of negligible importance when compared to anthropogenic sources [29]. Different PAH emission sources usually produce different congeners. High levels of Fluorine, flouranthene, and pyrene along with moderate levels of high molecular weight PAHs benzo[b]fluoranthene and indeno[1,2,3-cd]pyrene mark the existence of oil combustion[29, 31, 32]. High factor loading of fluoranthene, benzo[ghi]perylene, benzo[a]anthracene, benzo[a]pyrene, and indeno[1,2,3-cd]pyrene is known to be attributed to gasoline emissions[29, 33-36]. In contrast to gasoline emissions, diesel emissions has a high factor loading of low molecular weight PAHs including flouranthene, phenanthrene, anthracene and pyrene [32, 37-43]. Power plant emissions are the major source of mainly heavy PAHs like benzo[k] fluoranthene, benzo[a]anthracene, benzo[a]pyrene and chrysene [40, 44].

D-Physical properties of PAHs

PAHs are semi-volatile organic compounds. The ring systems can be present in multiple configurations and several substitution structures[27] [Figure 3]. They have a relatively low solubility in water and are highly lipophilic. At ambient temperature, PAHs can be present in both particulate and vapor phases, depending upon their volatility. Compounds with 2-3 aromatic rings exist almost in the vapor phase, whereas compounds with 4 rings and above are particle-associated[27]. Atmospheric partitioning of PAHs is a form of particle/vapor physical transformation that is affected by many atmospheric conditions among which meteorological parameters such as temperature and relative humidity are of high importance. On one hand, Yamasaki and coworkers[45] demonstrated the effect of temperature on the partitioning of PAHs using Flouranthene, a 3-member aromatic ring PAH, as an example. They showed that lower temperatures cause a greater fraction of Flouranthene to exist in the particle phase. This phenomenon can be explained by the enthalpy of adsorption on particles which is negative in this case. At low temperatures, the equilibrium of partitioning between the particle and the vapor phase shifts toward PAH adsorption on aerosols in the atmosphere. On another hand, Thibodeaux et al[46] investigated the effect of relative humidity on the partitioning of several PAHs. As the relative humidity is decreased down to 0%, sorption of PAHs increases. This increase is due to desorption of water where surface sites are opening up for sorption of the organic compounds. In short, temperature and relative humidity are two parameters with significant impact on the distribution of PAHs in the vapor and particulate phases.

E-Tropospheric transformation and degradation of PAHs

PAH transformation and their fate in the environment is strongly influenced by whether the PAH is present in the vapor phase or is particle bound [47]. Vapor phase PAHs (V-PAHs) (2-3 aromatic rings) are highly susceptible to tropospheric photochemical reactions where they react with hydroxyl (OH) and nitrate (NO_3) radicals leading to either their degradation or transformation[48]. In contrast, particle bound PAHs (P-PAHs) are less susceptible to tropospheric photochemical reactions due to the shielding effects of atmospheric organic compounds which can hinder their oxidation and promote their persistence in the troposphere[49, 50]. In fact, Atkinson, Arey, and their coworkers[51] investigated the kinetics behind the chemical degradation of V-PAHs and P-PAHs. They reported that the reaction rate constants of V-PAHs by OH radicals are higher than those of P-PAHs by three orders of magnitude. For example, they have shown experimentally that tropospheric naphthalene, a compound highly present in the vapor phase, has a rate constant (K_{OH}) of 2.4×10^{-11} , which is higher than that of Benzo(a)pyrene (K_{OH} of 1.1×10^{-14}), a compound highly present in the particle phase. In short, since P-PAHs are less prone to degradation and are more persistent in ambient air than V-PAHs, special attention is given to P-PAHs in atmospheric PAH studies.

Among many factors that affect the fate of V-PAHs in the environment, atmospheric photochemistry appears to be one of the most important parameters in the degradation of V-PAHs. These atmospheric chemical reactions can be classified into two categories based upon the presence and absence of sunlight. During the day, OH radicals are dominantly present in the troposphere as a result of the increased rate of ozone (O_3)'s photolysis (Figure3)

$$O_3 + h\nu \rightarrow O_2 + O\left({}^{1}D\right)$$
$$O\left({}^{1}D\right) + H_2O \rightarrow 2OH$$

Figure 3. Photolysis of tropospheric ozone to produce hydroxyl radicals[52]

These tropospheric OH radicals interact with V-PAHs and trigger either their degradation or transformation into carboxylic acids, aldehydes, ketones, and quinones within a loss lifetime of V-PAHs ranging between minutes to days. Above 40% of these products are degradation products (Figure 4).

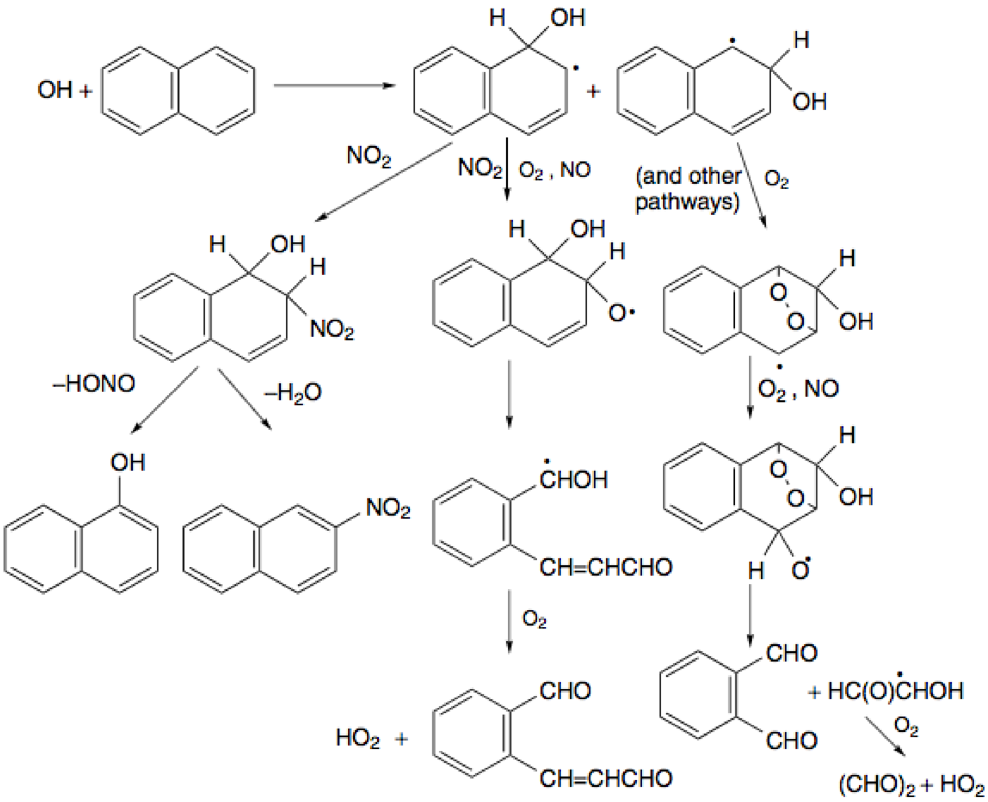

Figure 4. Mechanisms of decomposition and transformation of Naphtalene in the troposphere during day time[53, 54]

In contrast, at night, as a result of the decreased photolysis, tropospheric O_3 are highly available to interact with NO_2 and form NO_3 radicals. In turn, NO_3 radicals interact with V-PAHs to highly produce transformation products mainly Nitro-PAH derivatives within a V-PAH loss lifetime similar to that seen during day time (Figure 5). It is important to note here that these transformation products are highly mutagenic as well as stable and persistent (lifetime = years) which may have strong impact on health and environment.[47]

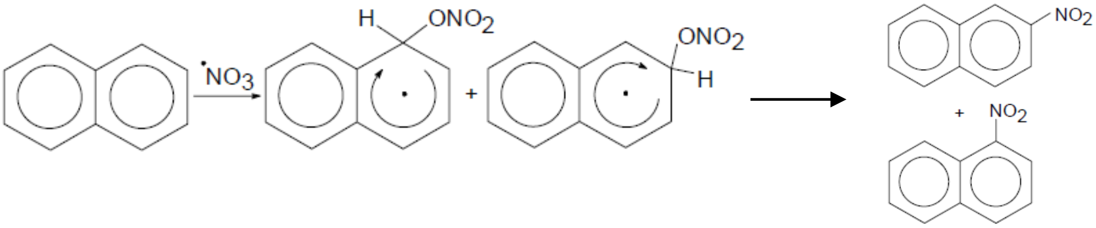

Figure 5. Formation of nitro-naphthalene during night time[51]

F-PAHs associated with particles in the atmosphere

It has been shown that in ambient air semi volatile PAHs have a high affinity to small size particulate matter (PM2.5) known as fine PM. These fine PM include diesel exhaust particles or particles generated from incomplete combustion processes. Fine PMs are mainly composed of a major core of amorphous allotrope of carbon (EC) to which organic compounds, predominantly PAHs, are adhered[55-57]. Through their direct interaction with PAHs, these carbonaceous particles exhibit a potential inhibiting factor on the reactivity of PAHs. This inhibitory effect is due to the slow diffusion of tropospheric oxidants (OH, NO_3 , O_3) as well as to the slow diffusion of atmospheric oxidants into the bulk particle unlike the case of V-PAHs as previously mentioned. In addition, oxidation of volatile organic compounds in the atmosphere releases secondary organic aerosols (SOA) which in turn can shield fine PMs and trap the PAHs inside a highly viscous and hydrophobic medium. Once trapped, these PAHs can no longer evaporate and shield from atmospheric oxidation. This synergy between PAHs and SOA particles does indeed have important impact on increasing their residence time as in the atmosphere, thus leading to longer-range transport[58, 59]. However, direct photolysis of P-PAHs with ultraviolet (UV) sun light radiation is a potentially important process. The major degradation products due to their photolysis are epoxides and quinones[51].

G- PAHs Toxicity

The PAH family includes more than 100 different compounds of various structures and toxicity. Accordingly, the assessment of toxicity for the numerous PAHs in the atmosphere is a complex process. In response, The US Environmental Protection Agency (EPA) has defined 16 unsubstituted PAHs as priority pollutants, based upon their toxicological profile as reported by the Agency for Toxic Substances and Diseases Registry (ATSDR) (Figure6)[60]. These 16 congeners were included in the priority list being suspected to be more harmful than others and exhibiting the highest concentrations in air of all the analyzed PAHs [29].Among those congeners, benzo[a]pyrene (B[a]P), a five member aromatic ring almost found in the particulate phase, has been extensively studied and has been classified by the international Agency for research on cancer (IARC) as a human carcinogen (Group 1)[61]. In response to its carcinogenic property, the European Union (EU) has set an air quality standard for B[a]P in the air of 1 ng/m^3 [62]. However, in the United Kingdom B[a]P annual average concentration was recommended by the Expert Panel on Air Quality Standards (EPAQS) not to exceed 0.25 ng/m^3 [63]. Moreover, other PAHs have been classified as probable human carcinogen (Group 2A) and possible human carcinogen (Group 2B) which are mostly found in the particulate phase [61, 64, 65]. Table 1 shows IARC classification for the 16 priority PAHs and their corresponding Toxic equivalency factor (TEF). TEF expresses the toxicity of individual chemicals within a family of compounds. A TEF of 1 is given to the most toxic chemical in the family (in this case B[a]p); less toxic chemicals are given TEFs of 0.1, 0.01 or 0.001 based on their relative toxicity to B[a]p (Table1).

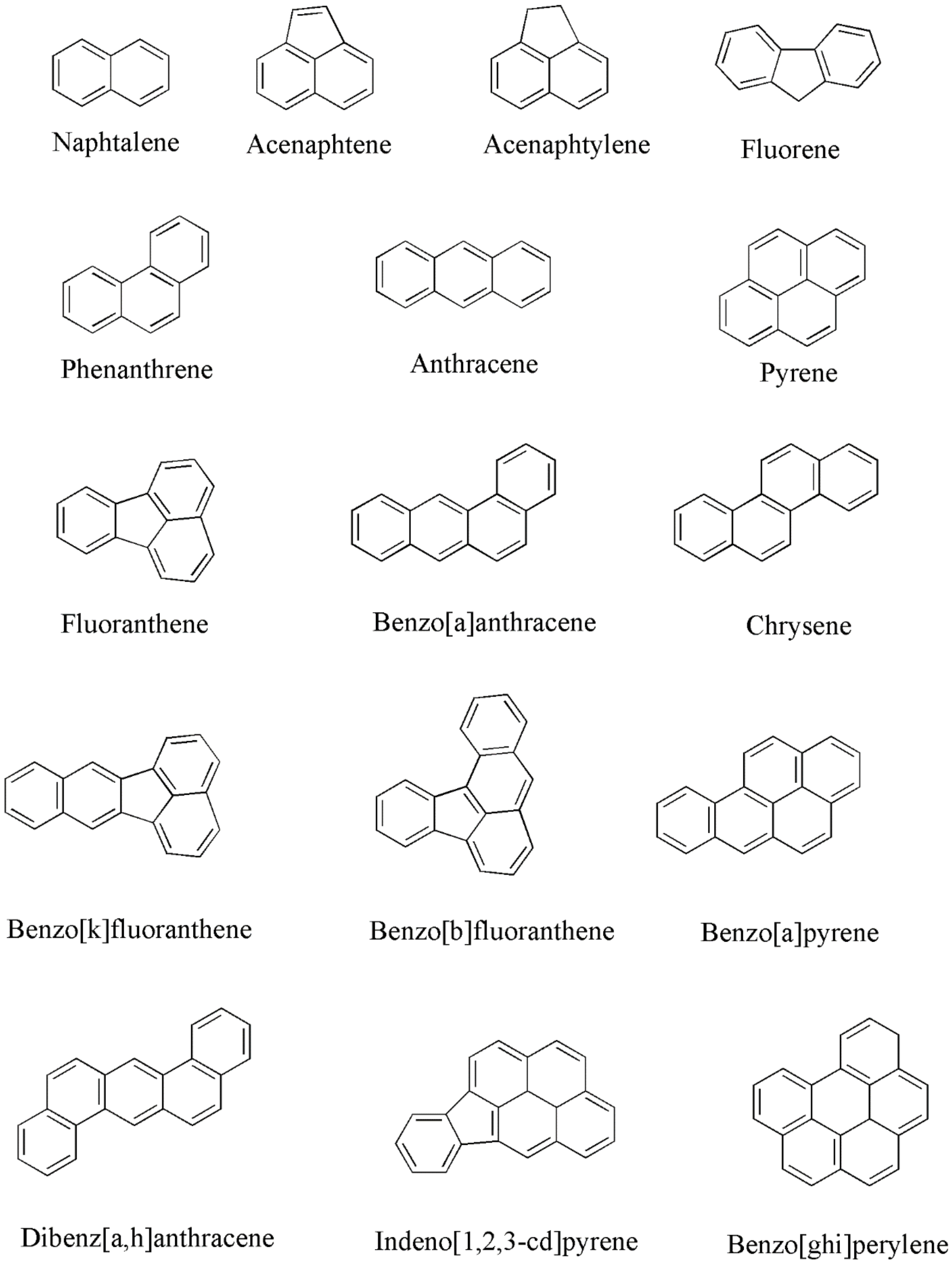

Figure 6. The 16 PAHs identified by the environmental protection agency (EPA)

Table 1. ATSDR / US-EPA priority PAHs, their phase distribution at ambient temperature, IARC Classification and TEF values

PAH	Gas/Particle Distribution	IARC Classification	TEF
Naphthalene	Gas phase	Group 2B	0.0001
Acenaphtylene	Gas phase		0.001
Acenaphtene	Gas phase	Group 3	0.001
Flourene	Gas phase	Group 3	0.001
Phenanthrene	Particle and Gas phase	Group 3	0.001
Anthracene	Particle and Gas phase	Group 3	0.01
Flouranthene	Particle and Gas phase	Group 3	0.001
Pyrene	Particle and Gas phase	Group 3	0.001
Benzo[a]anthracene	Particle phase	Group 2B	0.1
Chrysene	Particle phase	Group 2B	0.01
Benzo[k]flouranthene	Particle phase	Group 2B	0.1
Benzo[a]pyrene	Particle phase	Group 1	1
Benzo[g.h.i]perylene	Particle phase	Group 3	0.01
Dibenzo[a,h]anthracene	Particle phase	Group 2A	1
Indeno[1,2,3-cd]pyrene	Particle phase	Group 2B	0.1

PAHs can affect the human health through various toxicity mechanisms, including genotoxicity, immunotoxicity, developmental toxicity, and carcinogenesis. Long-term exposure to PAHs can induce epigenetic modifications. PAHs contribute to epigenetic remodeling through DNA methylation, histone modification, and microRNA silencing. Through series of reactions catalyzed enzymatically, reactive PAH metabolites attach to cellular proteins and DNA. The formed PAH-DNA adducts of different structural conformations can lead to induced mutations or inactivation of the tumor suppressor genes; which ultimately lead to DNA damage and carcinogenesis (Figure 7) [26, 66-68]. Studies also show that PAHs are potent immunotoxic agents that can lead to immunosuppression through different pathways[69, 70]. Evidence is supporting that PAHs can cause developmental toxicity through prenatal and postnatal exposure to PAHs [71-73].

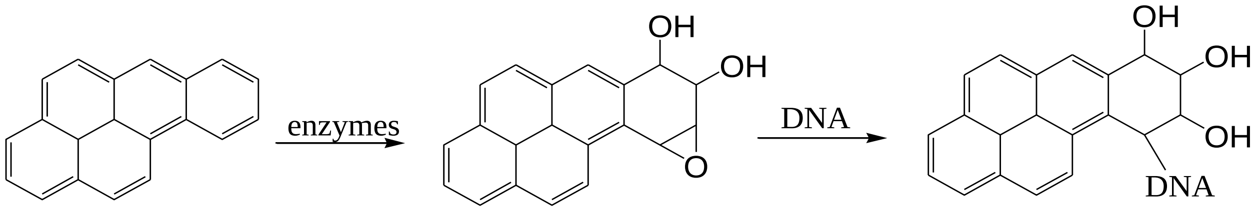

Figure 7. Metabolic oxidation of B[a]P followed by formation of B[a]P-DNA adduct leading to DNA mutation and inducing carcinogenesis[74]

H-Pollution in Lebanon: introducing the rational of studying P-PAHs

The Mediterranean region is known for high pollution episodes due to its enclosed geography. It is situated between the Saharan desert of Africa and the very heavily populated and highly industrialized European continent, which makes it prone to aerosol accumulation. In addition, its proximity to the three continents (Africa, Asia, and Europe) makes out of it an intersection of the air masses that meet in this region. Thus, this Mediterranean basin is characterized by a high humidity, long summers and stagnant winds that originate from eastern Europe. Furthermore, the intense solar radiation present in this area contributes to the high photochemical reactions that leads to pollutants’ formation and/or transformation. These photochemical reactions and pollutants accumulation are much higher in the eastern side of the Mediterranean basin than the western side due to its dry summers and very low precipitation. Not only that, but also the eastern side is characterized by particulate matter dust outbreaks originating from Saharan and Arabian desserts during the fall and spring seasons which thus makes it a controversial region at the pollution level[75-80]. Among the east Mediterranean cities, Beirut (7800 persons/km^2), the capital of Lebanon, a city geographically located between the Mediterranean coast from the west and mount Lebanon from the east (35°28’790”E, 33°54’139’’N) is the city where 88% of the 6 million population are present . In its densely populated city, the roads are often congested with high levels of traffic throughout the day, which can cause delays of up to 30 minutes at some intersections[81]. Moreover, construction operations are a normal part of city activity; with an urban population growth rate of 3.2%, as opposed to the global average of 2.1%[82]. New residence buildings are constructed to accommodate the increasing city population. Construction activities also occur for the maintenance of the country’s outdated infrastructure[83]. Furthermore, due to inadequate power production capacity, the national electric company Electricité du Liban (EDL) has instigated a rotating power outage regime across the country[84]. In turn, citizens have resorted to privately-owned diesel generator to compensate for the needed electric power. It is worth noting, however, that Lebanon lacks heavy industrial facilities, with the exception of a number of thermal power plants and low-duty industrial factories situated away from the main cities of the country[85].

Over the past decade, several instantaneous and long-term studies were conducted in Beirut to investigate the levels, seasonal variation, and composition of atmospheric particulate matter and have reported that ambient PM levels in the greater Beirut area of Lebanon consistently exceed the WHO guidelines by up to 273% for PM10 and around 100% for PM2.5[75, 76, 78, 79, 86]. Furthermore, the daily PM10 and PM2.5 concentrations have been associated with increased respiratory and cardiovascular emergency hospital admissions[87].

Moreover, Reactive oxygen species assay conducted in Beirut have shown that when compared gram by gram, the intrinsic toxicity of roadside $PM_{2.5}$ are relatively greater than the roadside $PM_{2.5}$ studied in Los Angeles[88]. All these studies show the levels of PMs however, the track of the ambient carcinogenic composition i.e P-PAHs over a significant period affected by various emissions is still unclear. In fact, Shihadeh et al. studied P-PAHs emissions from private diesel generators after a 3-hr electricity power outage in Beirut-Hamra between January 2010 and January 2012. They reported an increase over the local background level of approximately 40% of airborne P-PAH in the Hamra area of Beirut [89] . Another study, which was conducted by Daher et al. in 2012 over a period of two months in the summer, reported P-PAHs levels near a major road in beirut to be 11.5 ng/m^3 compared to levels below the detection limits at American university of Beirut (AUB) [86]. In this study, low volume sampling (LVS) technique was used for collection and analysis. Baalbaki et al. studied Gas and particle PAHs for winter and summer in 2015 at three different urban sites and reported that PAH values vary between 13.15 and 91.88 ng/m^3[90]. In this study, the high-volume sampling (HVS) technique was used to collect air samples. Although these studies clearly show that PAH levels in different sites are ubiquitous, up to our knowledge, no baseline of PAH sources and concentrations has been determined yet. In fact, a baseline study is of prime importance. It provides a reference point to monitor and compare PAH levels released by local anthropogenic sources at different urban locations. To be used as a point of reference, it is necessary to respect two criteria: conduct the study at an urban background site and over a long period of time. unlike the cross-sectional study conducted by Daher et al who performed their study at a specific location near the freeway, shihadeh et al. performed a longitudinal study at a specific location. Although these studies have succeeded into evaluating PAH levels released by certain specific sources in specific areas of Lebanon, they have not determined a P-PAH ambient concentration baseline affected by combined emission sources such as gasoline, diesel, heavy fuel oil and incineration at a representative site. In addition, there is a lack of a long-term study that investigates the impact of meteorological factors on P-PAHs' seasonal variation. Therefore, our study has shifted the attention towards defining such a baseline in Beirut. Once such a baseline is established, it is then important to explore the different sources of P-PAHs and to investigate their portion of contribution into the overall P-PAH level in the ambient air. Therefore, a receptor model known as positive matrix factorization (PMF) is used to further look into PAH source apportionment in the urban background site. In order for this model to be highly efficient, it is important to input a high number of samples; a criterion met by our study (n=55). In addition, in order to assess the efficiency of different sampling and analysis techniques used by the aforementioned studies, our study evaluates the efficiency in collecting and quantifying PAHs using LVS and HVS as methods of collection and establishes an optimized analytical extraction method.

I-Study objectives

To establish a baseline level of P-PAHs at an urban representative site, determine P-PAHs seasonal and intermonth variation over a period of a year, explore the main factors affecting their ambient levels, investigate and evaluate the sources of P-PAHs in the ambient air of Beirut.

J-Sampling site:

The sampling site is boarded 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 park and mostly pedestrian small roads (Figure8). All these criteria made our sampling site a wide site relevant for the study of the seasonal variation and for the evaluation of several sources into the ambient PAHs.

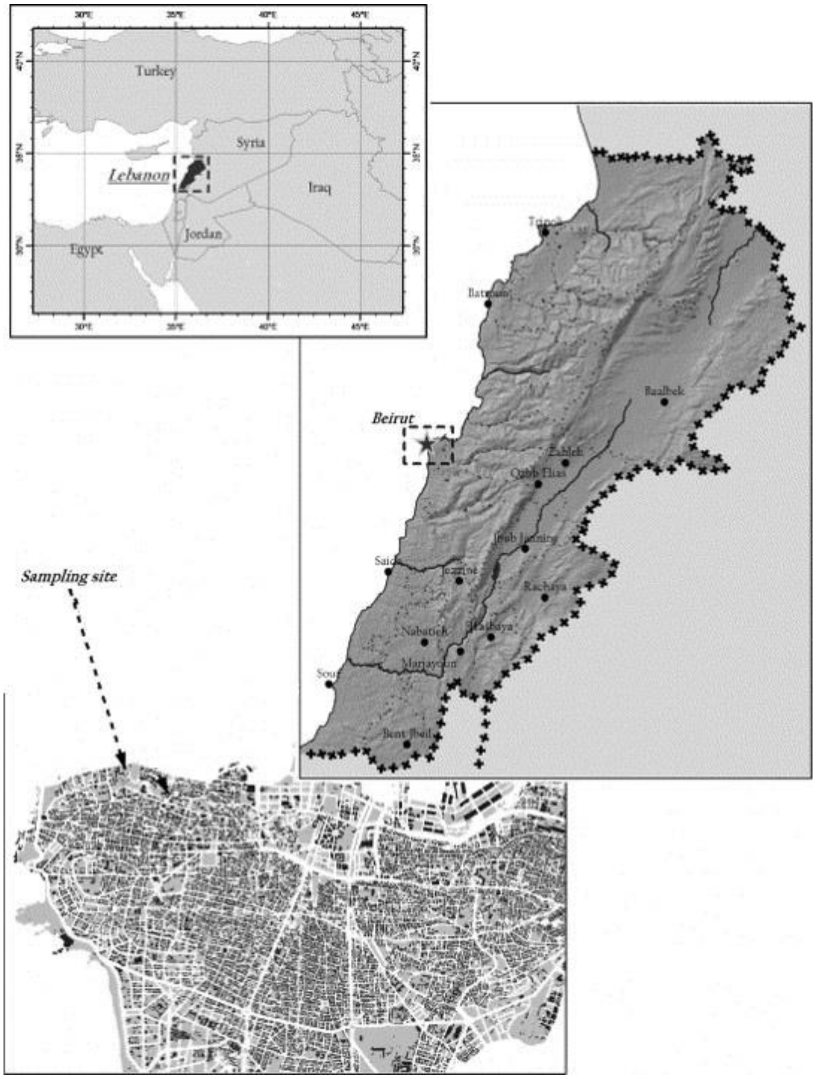

Figure 8. Location of the sampling site

Chapter II

P-PAH SAMPLING, ANALYTICAL METHOD OPTIMIZATION AND VALIDATION

In this chapter, a full description of the adopted sampling method as well as the optimized extraction and quantification procedure for the assessment of PPAHs is presented. Analysis of P-PAHs levels undergo three crucial stages: collection, sample preparation, and instrumental analysis. Samples of ambient air are collected using either a LVS or a HVS for comparison. Sample preparation include filter extraction, sample clean up, and sample concentration. The final stage is quantification of PPAHs, which is carried out using Gas chromatography-Mass spectrometry (GC-MS).

A-PPAHs collection techniques: High and Low Volume Sampling Comparison

EPA developed a compendium method TO-13 for the determination of PAH in ambient air using the high-volume sampling technique (Figure 9). In brief, the gas and particle phase fraction are trapped in series on a Polyurethane foam (PUF) (sorbent) and a 147mm quartz fiber filter, respectively, at a flow rate of 500 L/min. Both PUF and the filter are extracted using Soxhlet extractor and the analytes of interest are then isolated from the matrix using solid phase extraction (SPE), concentrated and finally analysed by GC/MS. The extraction method lasts for 16 hours and consumes up to 500 mL of hexane/diethylether as an extraction solvent for a single extraction at a time. However, some studies reported the use of low volume sampling (LVS) technique (Figure10). It is a collection method that uses lower flow rates (such as 10L/min) to collect PAHs on a 47mm quartz fiber filter. The LVS technique uses Ultra sonication to extract PAHs, which last for 2 hours and requires much lower extraction solvent amount than the HVS extraction technique.

In order to test whether an LVS technique works with a background site like AUB, a low volume sampler (chemcomb Model 3500 Speciation Sampling Cartridge, Thermo electron Corp., Ohio, μUSA) operating at 10 L/min was run side by side for 24-hr with a high-volume sampler (DIGITEL enviro-sense DH77) operating at 500L/min. Both sampler's impactors are designed with a cut point to collect particles of an aerodynamic size of 10 µm in diameter. Prior to sampling, quartz-fiber filters were usually baked in a furnace oven at 500 °C for 5 hours to removed adsorbed organic compounds. Post sampling, the two filters were subjected to extraction and analysis. PAHs collected by the low-volume sampler at AUB were found to be below our detection limit. Other trials, which were repeated using composites of two and three low volume filters, were also unsuccessful in detecting PAHs. Figure 11 shows the comparison between a composite of three low volume filters and a high volume one. This issue was also encountered with Daher et al, where they were able to determine PAHs at the road site but not at AUB[86]. Hence, for this study, the high-volume sampling technique will be adopted but with an alternative optimized extraction method.

Figure 9. From left to right: the high-volume sampler, the PM_{10} sampler impactor, and the HVS compartments constituting it

Figure 10. From left to right: the low volume sampler with a PM_{10} impactor, and the setup

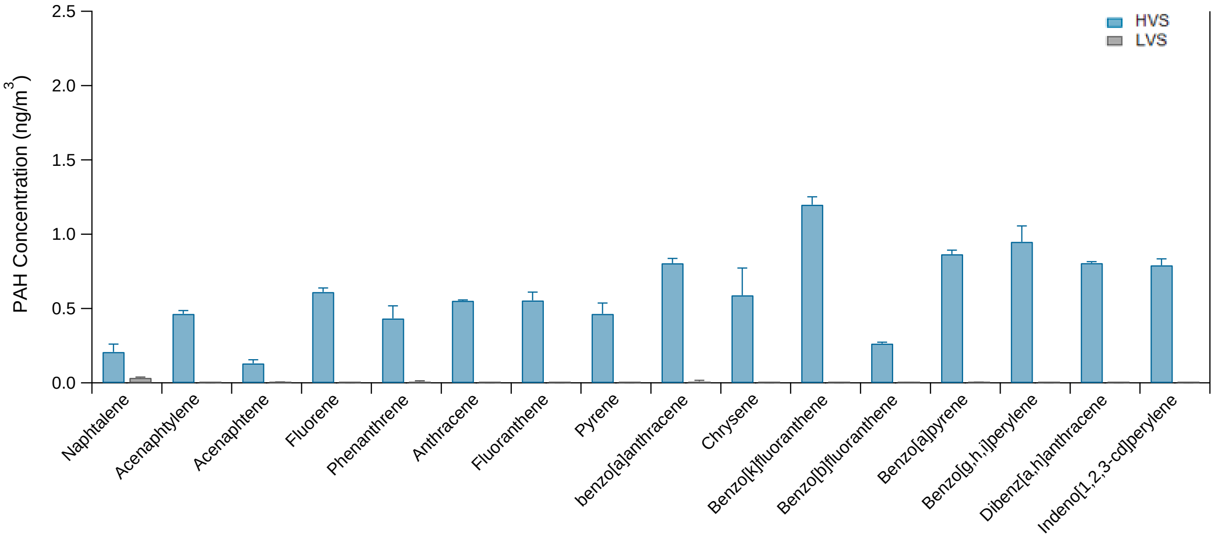

Figure 11. Comparison of PPAH concentrations between high and low volume sampling

B-Sample preparation of HVS filters

1. Materials

PAH standards and deuterated internal standards containing 17 and 4 PAH compounds respectively, and dissolved in methylene chloride were obtained from Absolute standards. HPLC-grade toluene and hexane solvents were procured from sigma Aldrich. SPE cartridges (1000 mg/6 mL HyperSep SI) and quartz filters (Advantec, QR-100, 150 mm) were obtained from Thermo Scientific and Whatman International, respectively.

2. Filter extraction

In recent years, there has been a growing effort to reduce or to eliminate solvent use when extracting analytes of interest from various matrices and hence limit the impact of waste solvent on the environment. An extraction procedure was developed by optimizing four parameters: choice of solvent, extraction volume, extraction time and extraction temperature. PAHs are known to be non-polar compounds and soluble in many solvents among which benzene, toluene, and dichloromethane have similar polarity to PAHs and are compatible with GC-MS. In the ideal case, benzene is the most suitable extraction solvent but due to its hazardous properties it was not used. Dichloromethane is more polar and volatile than toluene. Toluene is a nonpolar solvent that have a similar structure and compatible polarity to PAHs and is not a highly volatile organic solvent that cannot evaporate during extraction procedure and decreases the recovery of the analytes, for these reasons toluene was chosen as an extraction solvent for PAHs. To evaluate the extraction parameters, triplets of quartz filters were spiked with PAH standard and internal standard of 2μg/ml. Each three replicate solutions were sonicated at 40°C for either 0.5,1, and 1.5 hours and finally injected into GC-MS. The best recoveries of PAHs were for those sonicated for 1.5 hours which marked a recovery above 80%. A volume of 250 mL was found to be sufficient to extract PAHs without causing an excessive dilution and decreasing the waste solvent in comparison to soxhlet which uses up to 500ml of extraction solvent.

3. *Sample concentration*

Sample concentration is a critical requirement to increase PAH concentrations. Our aim is to concentrate the sample down to 1 mL. Rotary evaporation was employed because the sample of 250 ml would require a fast and an efficient concentration method of evaporation. Nitrogen evaporator was not considered because it is time consuming. Hence, a rotary evaporation was considered and the samples were concentrated at 45°C down to 1ml.

4. *Solid phase extraction*

In order to minimize the matrix interference, a clean-up procedure that purifies the sample from residual compounds other than PAHs is necessary. There are different types of clean-up techniques among which solid-phase extraction is the most applicable. The general procedure starts by conditioning the SPE cartridge, loading the sample and then eluting analytes of interest. The conditioning step was performed by washing the cartridge with 10 mL of hexane. This step is recommended by manufacturer 's instructions to activate the functional groups on silica surfaces. Subsequently the concentrated sample of 1 ml was loaded onto the SPE cartridge and finally elution was performed using 10 ml of hexane as a mobile phase.

5. Final concentration step

After completing SPE procedure, a nitrogen evaporation step is essential to concentrate the sample for better precision in the quantification of the desired analytes. This step is crucial because PAHs are expected to be present in low ppm amounts in ambient air. A concentration volume down to 200 µL was good to quantify PAHs with precision without over killing the final sample. Both the flow rate and the temperature of evaporation were investigated. The vapor pressures at 25 ºC of the 16 PAHs ranges between 2.1×10^{-11} and 8.9×10^{-2}Pa and that for toluene is 3.8 Kpa. Consequently, sample concentration was carried out at atmospheric room temperature where PAHs are relatively less volatile than toluene. To determine the optimal flow rates, standard solutions of 2 µg/mL were concentrated down to 200 µL at 15 and 10 L/min. The recovery at 15 L/min was found to be between 60 to 90% for PAHs compared to greater than 80% for 10 L/min. Consequently, the slowest flow rate of 10 L/min was selected. Having optimized all the sample preparation procedure, the sample is ready for GC-MS analysis.

C-Instrumental analysis using GC-MS

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 Rtx-5MS column (60 m × 0.25 µm film thickness× 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 ˚C. The GC oven was programmed from 80 °C (hold for 3 minute) to 170 °C (10 °C/min, hold for 1 min), to 180 °C (3 °C /min, hold for 0 min), to 270 °C (10 °C/min, hold time 0 min), then ramped to 300 °C (3 °C/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 8-point calibration curve in the range from 0.1 to 10 µg/mL, good linearity was observed with correlation coefficients (R^2)>0.995 for most of the 16 PAHs(see figures 12 and 13).

D- Quantification

Using PAH reference standards containing 16 PAH compounds at concentrations ranging between 0.1 and 10µg/ml and spiked by 2 µg/ml of deuterated PAH internal standard (IS) containing four PAH compounds which are acenaphtylene-d, phenanthrene-d, chrysene-d, perylene-d used to obtain the relative response factor for individual PAHs, an eight-points calibration curve was prepared. Quantification is based on a regression equation $y = ax + b$ where $y= Area\ [\text{standard}] / Area[IS]$, x is the concentration a, b are the slope and intercept respectively. Correlation factor (R^2) ranged between 0.995 and 0.999 for the different PAHs calibration curves. The unknown concentration (x) was computed as follows: $x = y' - b / a$ where a, b and y' are the slope, the intercept and *Area*[*unknown*] / *Area*[*IS*], respectively.

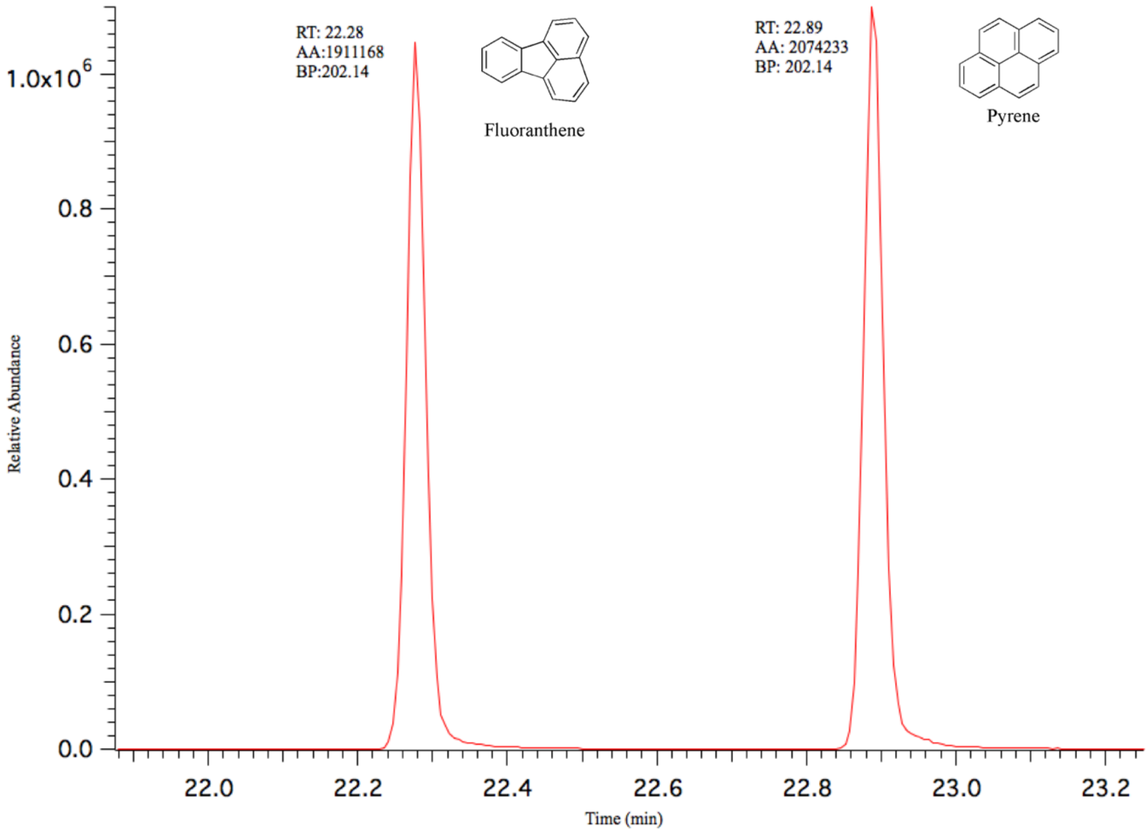

Figure 12: Examples of the elution peaks for fluoranthene and pyrene of same molecular weight

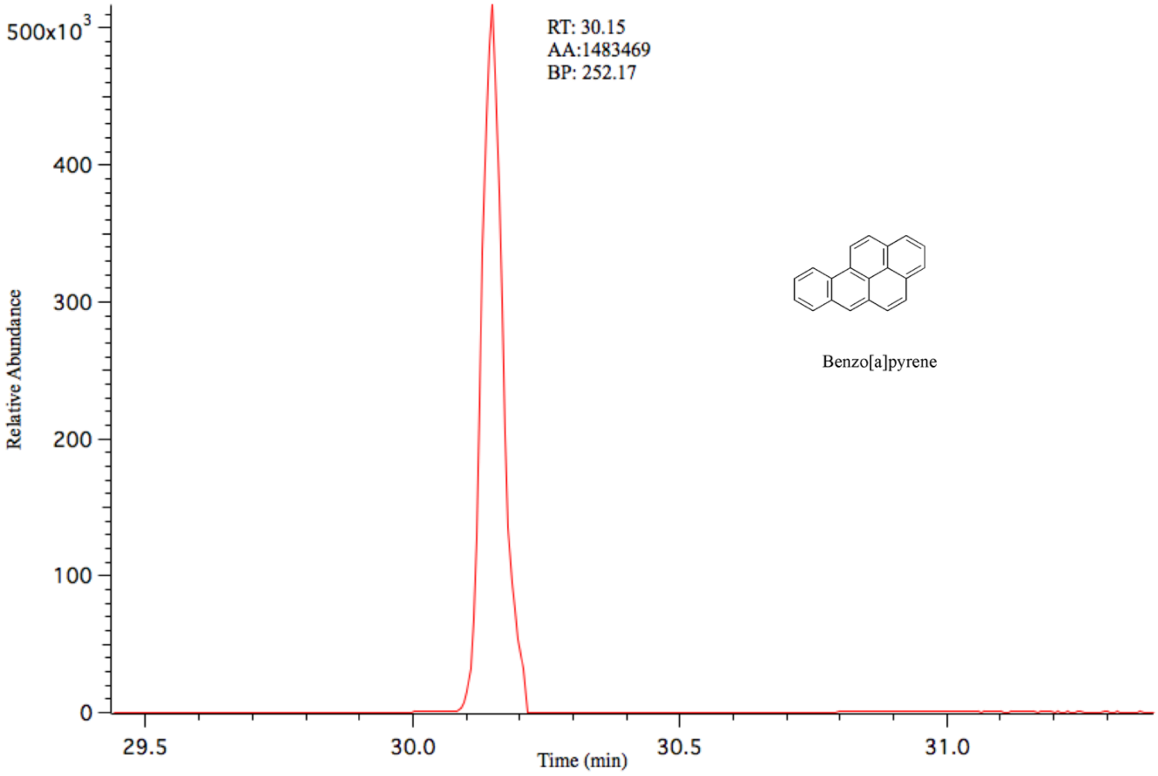

Figure 13. Example of elution peak of benzo(a)pyrene the group one carcinogen among the PAH family.

E-Method validation

Validation is an integral part of quality control (QC) and quality assurance (QA) practices to judge the reliability, consistency and accuracy of the method. The key criteria for this evaluation are: linearity, limit of detection, limit of quantification, recovery and repeatability.

1. Linearity

Linearity evaluation verifies that PAHs are found in a range where their response is linearly proportional to their concentration. It is commonly judged by examining the correlation coefficient of calibration curve. In this study, a direct calibration curve is used. PAH standards ranging between 0.1 and 10 μg/mL are prepared and spiked with a constant amount of deuterated internal standards (2μg/mL)

The relationship between the ratio of the analytes signal to the IS signal and analyte standard concentrations was found to be linear for the whole examined range of the 16 PAHs with correlation coefficient >0.995 (Figure14).

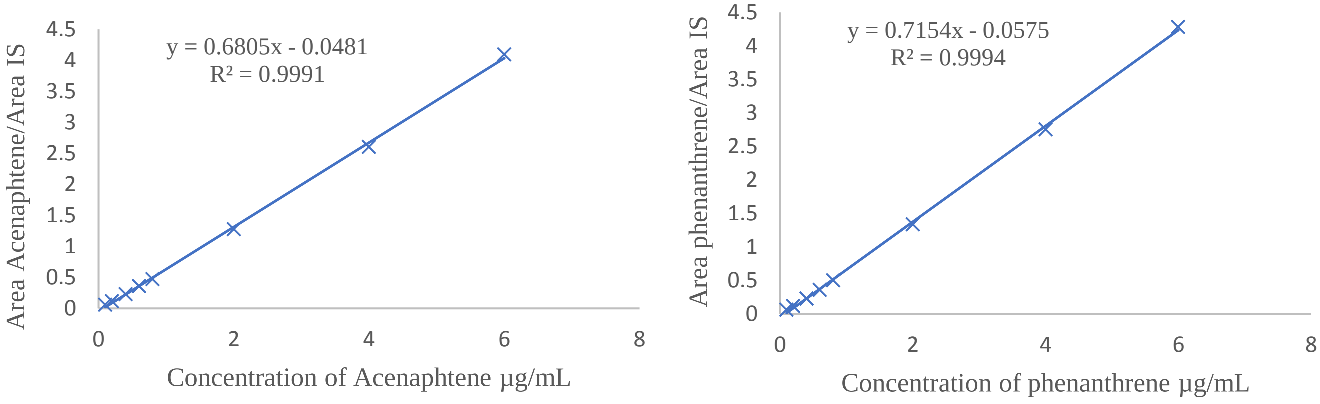

Figure 14. Examples of direct calibration curves of Acenaphtene and phenanthrene

2. *Method Limit of detection*

Limit of detection (LOD) is the lowest concentration of analyte that can be detected but not necessary quantified. Based on the standard deviation response and slope, LOD is expressed as following:

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

Where σ is the standard deviation of the ratio of the analytes signal to the IS signal of seven replicates of analytes prepared at a low concentration and s is the slope of the direct calibration curve. LOD analysis was carried out using seven replicate extractions of 0.1

µg/mL spiked with 2 µg/mL of deuterated internal standard. The results have shown that detection limits of the 16 PAHs ranges between 0.01 and 0.05 µg/ml

3. *Method Limit of Quantification*

Limit of quantification (LOQ) is the lowest concentration of analyte that can be measured with an acceptable level of accuracy and precision. Based on the standard deviation response and slope, LOQ is expressed as following:

$$\text{LOD} = \frac{10\sigma}{S}$$

The quantification limits of the 16 PAHs were analyzed using seven replicate extractions of 0.1 µg/mL. The results have shown that LOQ ranges between 0.03 and 0.16 µg/ml

4. Repeatability

Repeatability describes the closeness of agreement between a series of measurements obtained under the same operating conditions (one operator, same equipment and on the same day). It is expressed by the percent relative standard deviation (%RSD) of analytical results obtained from a minimum of five measurements at three different concentrations (low, medium and high). The acceptance criteria are based on type of analysis, complexity of matrix and the level of tested concentration. The results of six replicate standards for three concentrations (0.1, 4 and 8 µg/mL) revealed %RSD ranges between of 4 and 8%.

5. Recovery

A valid extraction should reveal a high % recovery of the analytes. The recovery is the ratio of extracted concentration obtained from the sample treated according to the whole extraction procedure to that of a sample of same concentration directly analyzed on GC-MS. It is assessed using six extraction measurements over three concentration levels covering the working range: 0.5, 6 and 10 µg/mL. The recovery was found in the acceptable range between 83 and 110%. Consequently, all the QC and QA requirements are fulfilled and the method is ready for measuring PPAHs in ambient air.

6. *Blank repeatability*

Field blanks, which accompanied samples to the sampling sites, were used to determine any background contamination using the same analysis method with samples. Concentrations of PAHs in the blanks were below the method detection limits in all the analysis period.

Chapter III

RESULTS AND DISCUSSION

TEMPORAL AND SEASONAL VARIATION OF P-PAHs AT AUB

In brief, this work developed a method for the quantification of P-PAHs. After the method was validated, every six days P-PAHs were sampled using a high-volume sampler, extracted from filters and finally analyzed using GC/MS. The aims of this work after developing the method is to construct a baseline level of P-PAHs at an urban background site. Moreover, to monitor the seasonal as well as the intermonth variation of P-PAHs and to investigate the factors affecting their levels. Source apportionment was conducted to explore the main sources contributing to P-PAHs in the ambient air of an urban site. Toxicity evaluation is provided and incremental life time cancer risk was computed. Results are shown below.

A- variation of ∑P-PAHs, P-B[a]p and individual P-PAHs

1-Temporal variation of ∑P-PAHs, P-B[a]p:

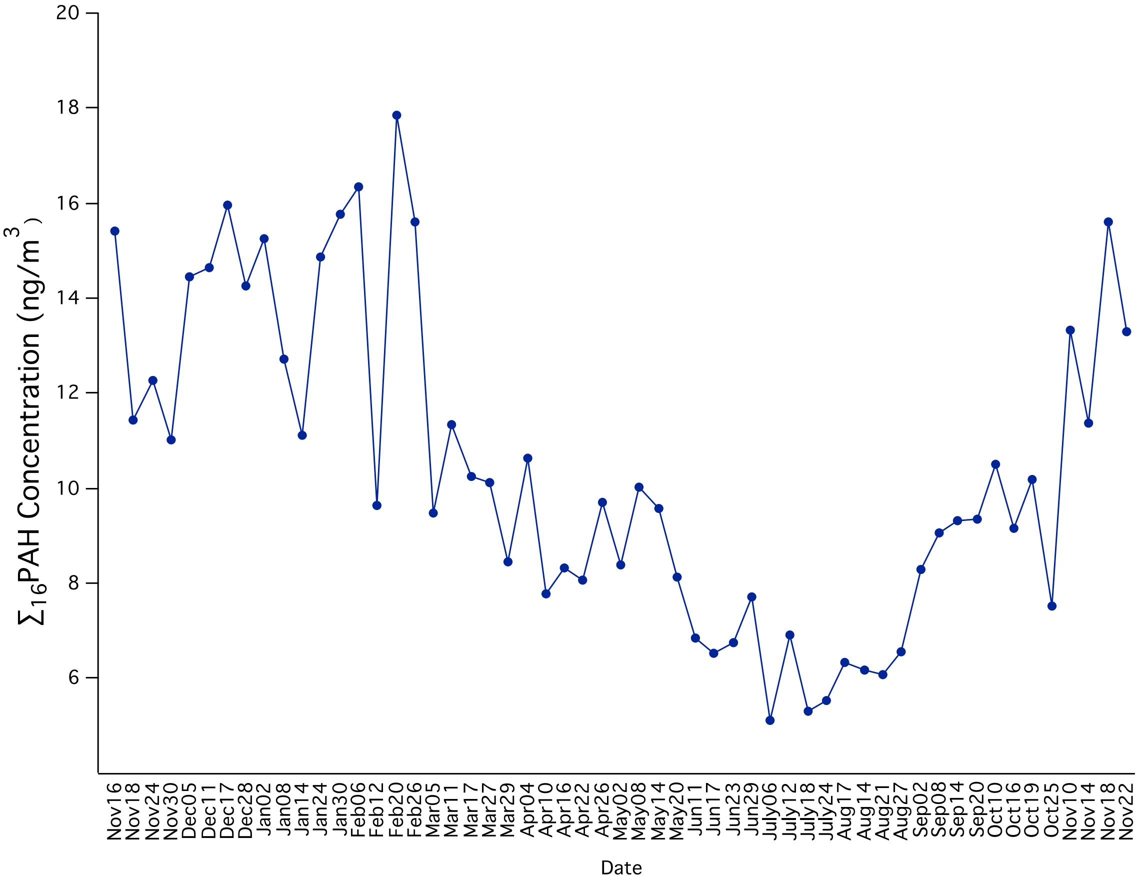

Figure 15. Temporal variation of the sum of P-PAH concentration on the sampled days

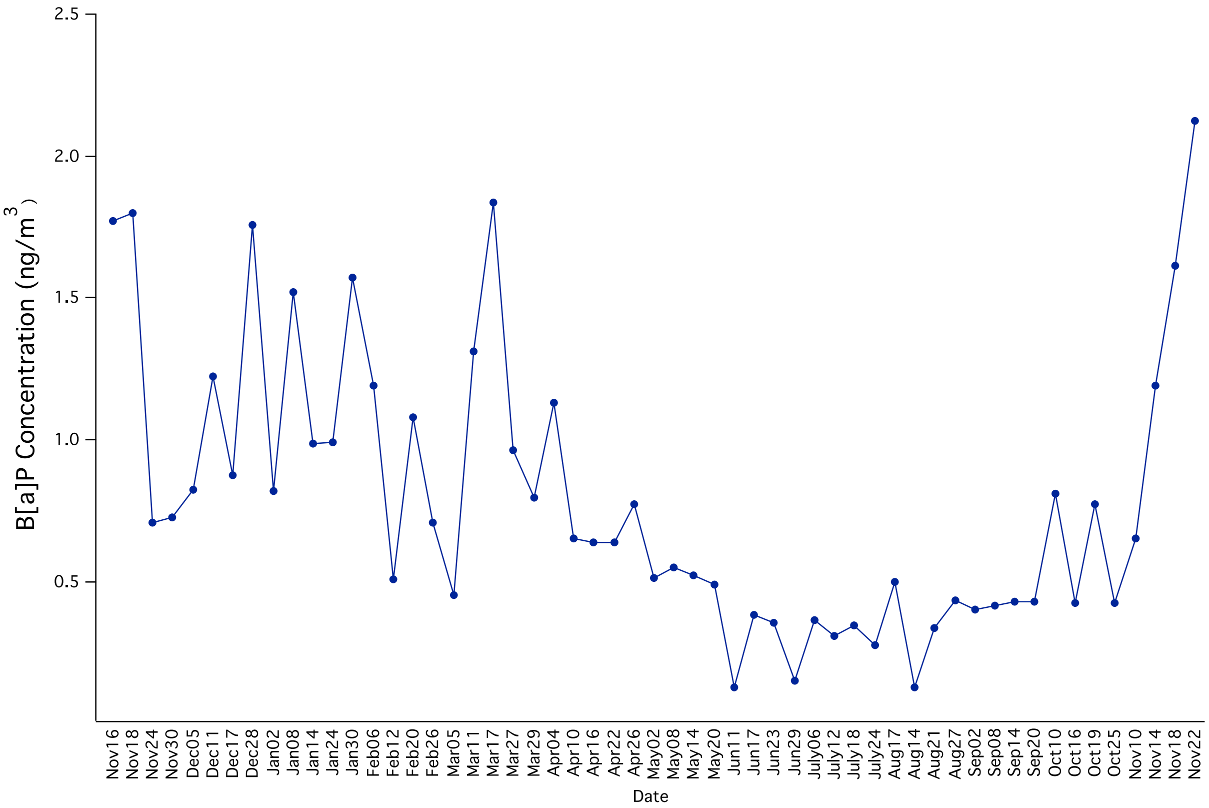

Figure 16. Temporal variation of B[a]P (Group 1 carcinogen) concentration on the sampled days

The data shows a high temporal variation throughout the year with higher concentration during winter and fall(Figure 15 and 16). The maximum sum of P-PAHs of 17.89 ng/m^3 was measured on February 20/2017 and the lowest of 5.1 ng/m^3 measured on July/06/2017. The high difference in concentration can be attributed to high variation in the meteorological conditions. For example, on February 20,2017 parameters such as temperature (14°C), average humidity (38%) and wind speed (1.66mps) favored a concentration of P-PAH higher than what was observed on November 24 under 20°C, 17% RH, and 2.77mps. Variations in meteorological conditions are suspected to have an effect on the days that were sampled throughout the year. Of particular interest is a group 1 carcinogen, BaP, which followed the same trend of temporal variation during the sampled days. The concentration of B[a]P exceeded 1ng/m^3 16 days out of 55 that were sampled. Most of the exceedances were during the winter and fall. The higher concentration detected for B[a]p was on November 18/2017 striking 2.12 ng/m^3, whereas the lower concentration detected of 0.13 ng/m^3 was recorded on August 14, 2017.

2-Seasonal variation of individual P-PAHs

Figures 17-20 show the seasonal variation of the individual P-PAHs during the four seasons. A strong seasonal variation of P-PAHs was observed. During the winter and the fall seasons, the standard deviation of the individual P-PAHs was high. This high deviation is attributed to the unstable wind speed during cold period which can either induce the accumulation or dispersion of P-PAHs. Figure 21 shows the effect of wind speed during the cold period on P-PAHs sum. There is a negative correlation between the P-PAHs and wind speed which in turn has an effect on increasing the standard deviation. However, this deviation decreases during spring and summer where the weather and specifically the wind speed is more stagnant and stable.

It is clear that as the molecular weight increase, the PAHs are more prone to partition to the particle phase. In fact, this is the case of Benzo[a]anthracene, Chrysene, Benzo[k]flouranthene, Benzo[b]flouranthene, Benzo[a]pyrene, Benzo[ghi]perylene, Dibenzo[a,h]anthracene, Indeno[1,2,3-cd]pyrene, characterized with a low vapour pressure ($Vp<10^{-6}$ Pa) and almost found in the particle phase. However, Naphthalene, Acenaphtylene, Acenaphtene, Flourene, Phenanthrene, Anthracene, Flouranthene and

Pyrene have a lower concentration due to their partitioning between the particle and the vapor phase, which is more prominent during the warm seasons that increases their vaporization rate (Vp $>10^{-6}$ Pa).

The results of this study are comparable to those of Teixeira et al.[91], which show higher HMW PAHs for the winter time. Thus, the magnitude of HMW PAHs was increased with increasing aerosols found in the winter time due to meteorological variables as well as the increased source emissions in the winter time.

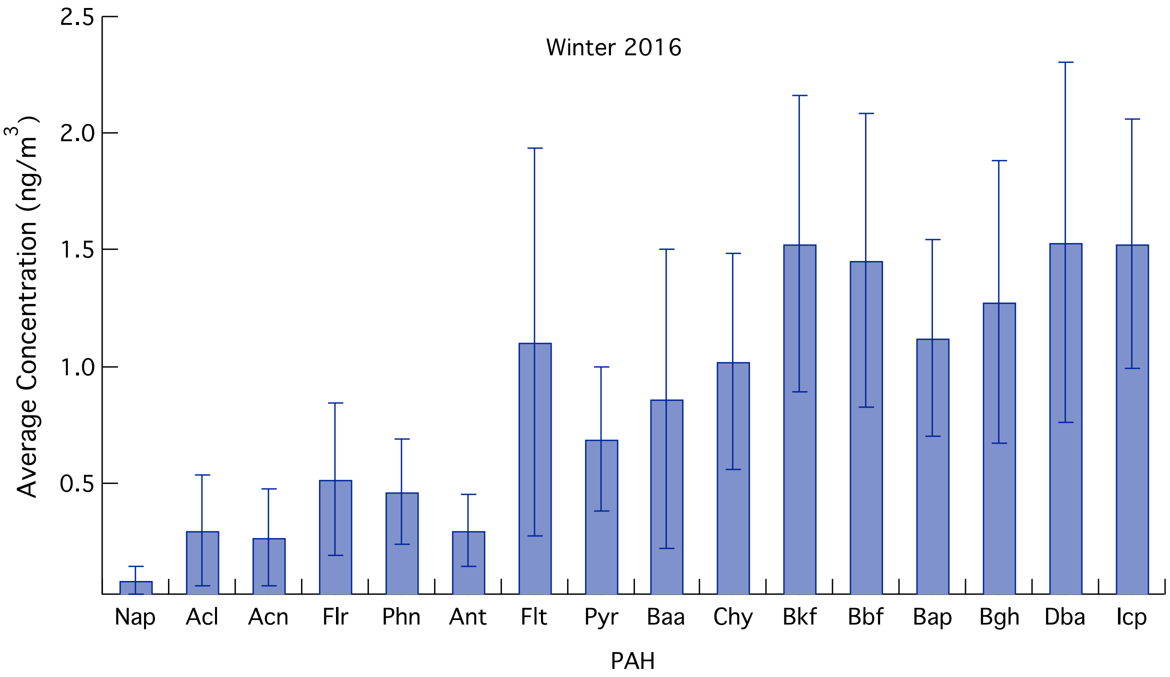

Figure 17. Seasonal variation for the average concentration of the 16 PAHs during the winter season extending between November 16, 2016 to February 26, 2017 (n=17)

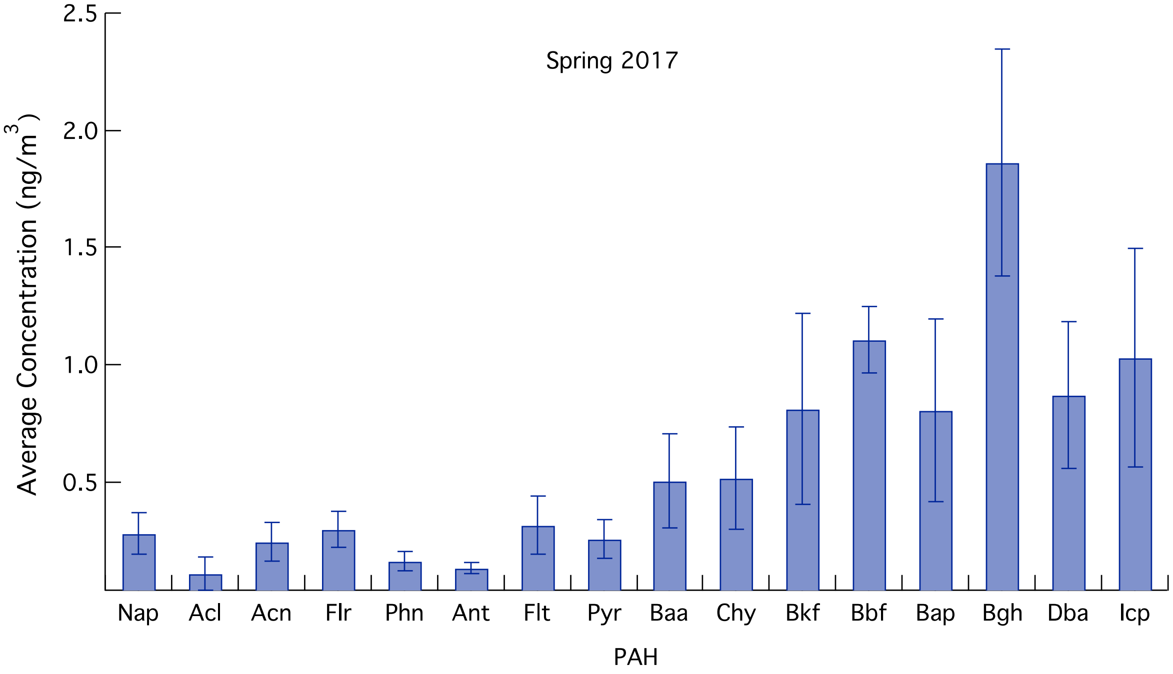

Figure 18. Seasonal variation for the average concentration of the 16 PAHs during the spring season extending between March 5, 2017 to may 20, 2017 n=14

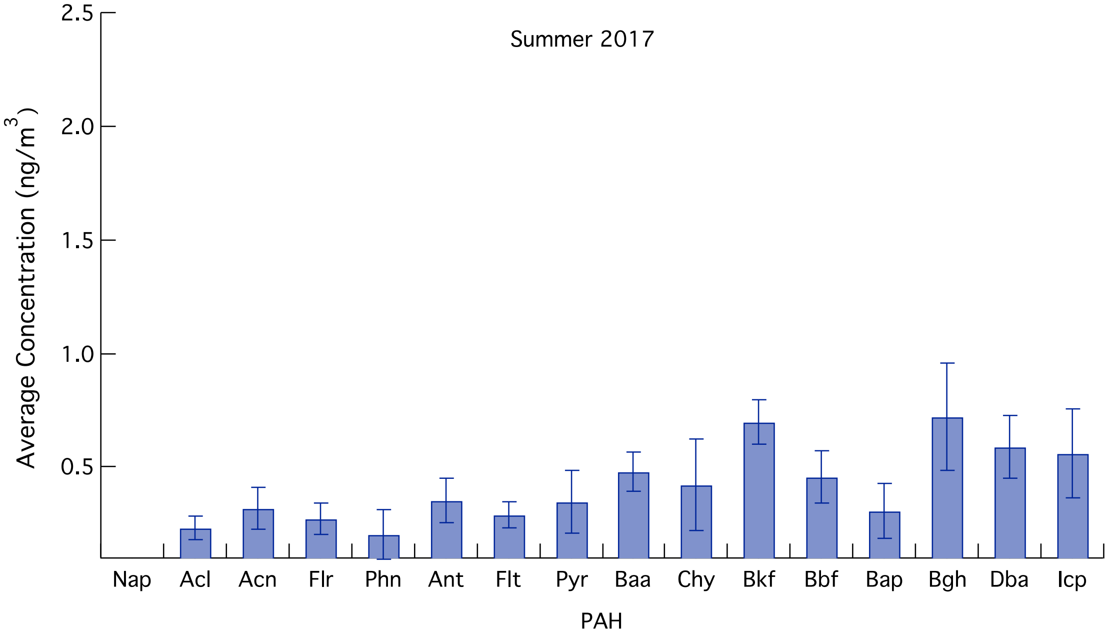

Figure 19. Seasonal variation for the average concentration of the 16 PAHs during the summer season extending between June 11, 2017 to august 27, 2017 (n=12)

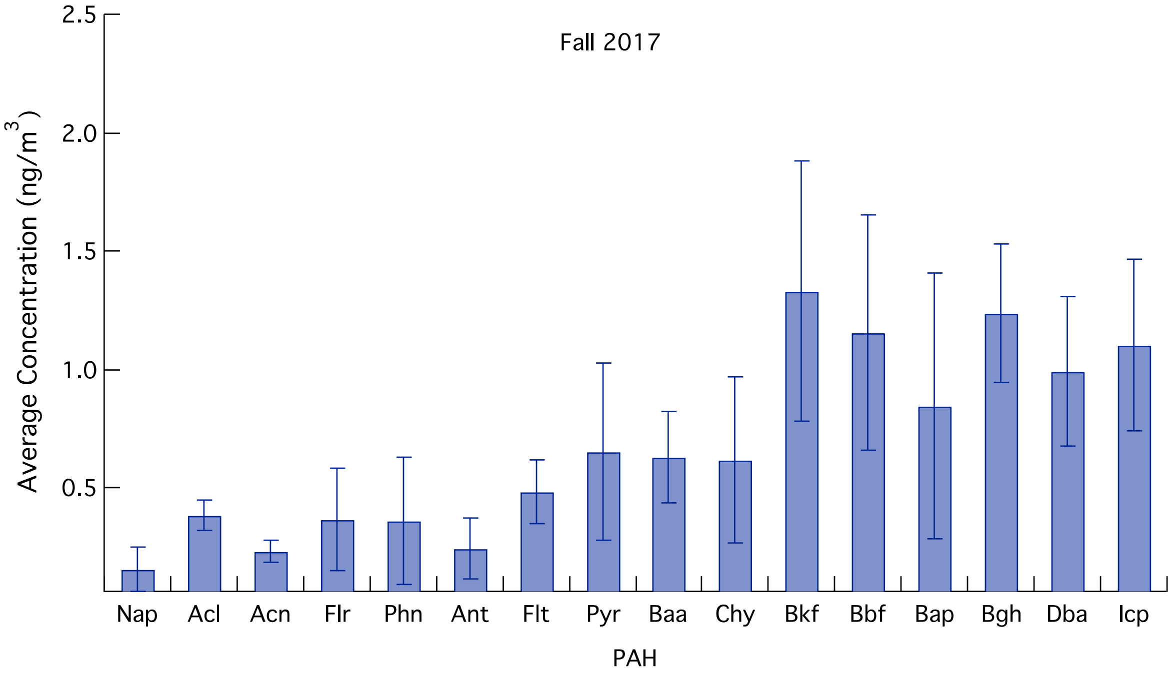

Figure 20. Seasonal variation for the average concentration of the 16 PAHs during the Fall season extending between September 9, 2017 to November 22 2017 (n=12)

Abbreviations: Nap(Naphthalene), Acl(Acenaphtylene), Acn(Acenaphtene), Flr(Flourene), Phn(Phenanthrene), Ant(Anthracene), Flt(Flouranthene), Pyr(Pyrene), Baa(Benzo[a]anthracene), Chy(Chrysene), Bkf(Benzo[k]flouranthene), Bbf(Benzo[b]flouranthene), Bap(Benzo[a]pyrene), Bgh(Benzo[ghi]perylene), Dba(Dibenzo[a,h]anthracene), Icp(Indeno[1,2,3-cd]pyrene)

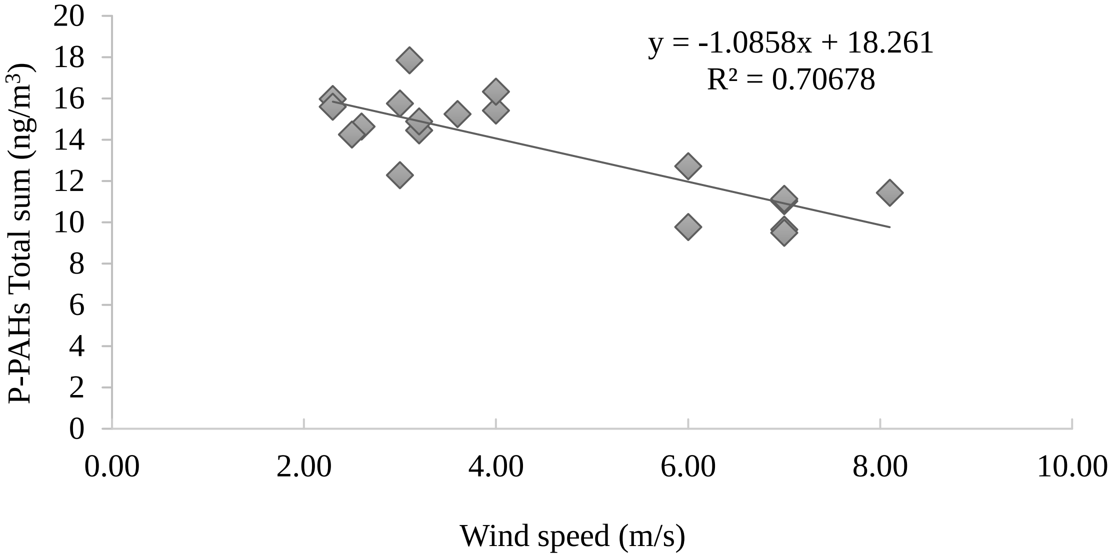

Figure 21. Correlation between sum of P-PAHs concentration and wind speed during the cold seasons

3-Intermonth and Seasonal variation of $\sum_{16}$P-PAH and P-B[a]P

Whisker and box plots are shown in figures 22-25 for the P-PAH sum and P-B[a]p during the 12 months campaign and the four seasons. The whisker plots indicate how the points vary from each other during the month or the season. The small squares and the line inside the box represent the mean and the median respectively.

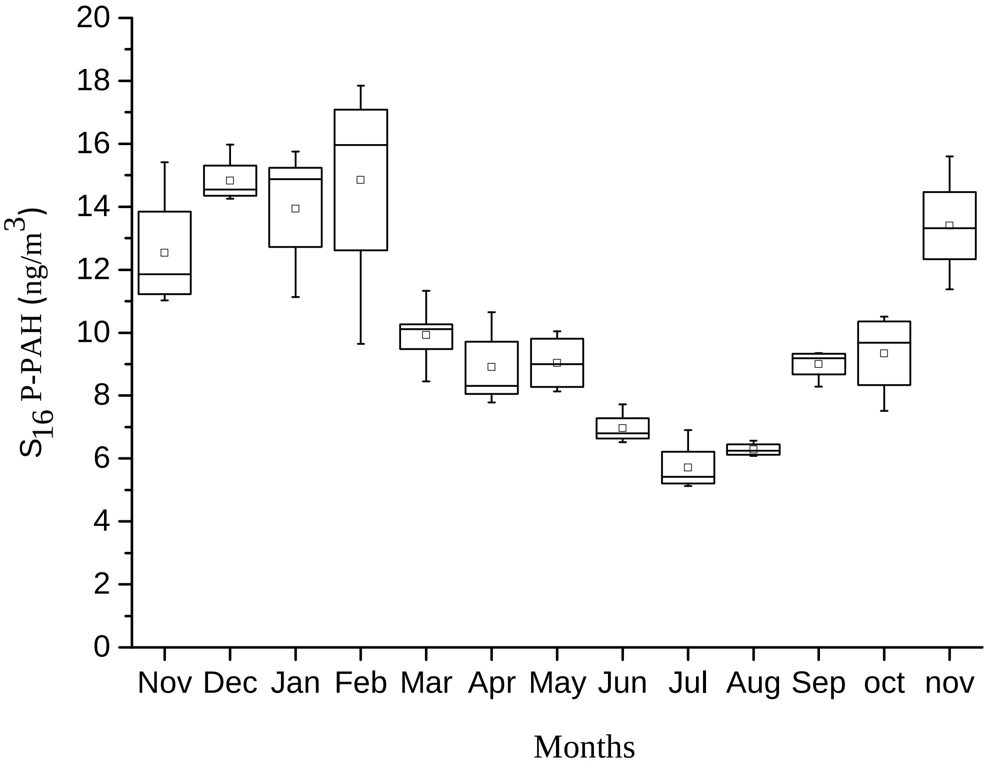

Figure 22. Whisker and box plot of ∑P-PAH during the twelve months campaign

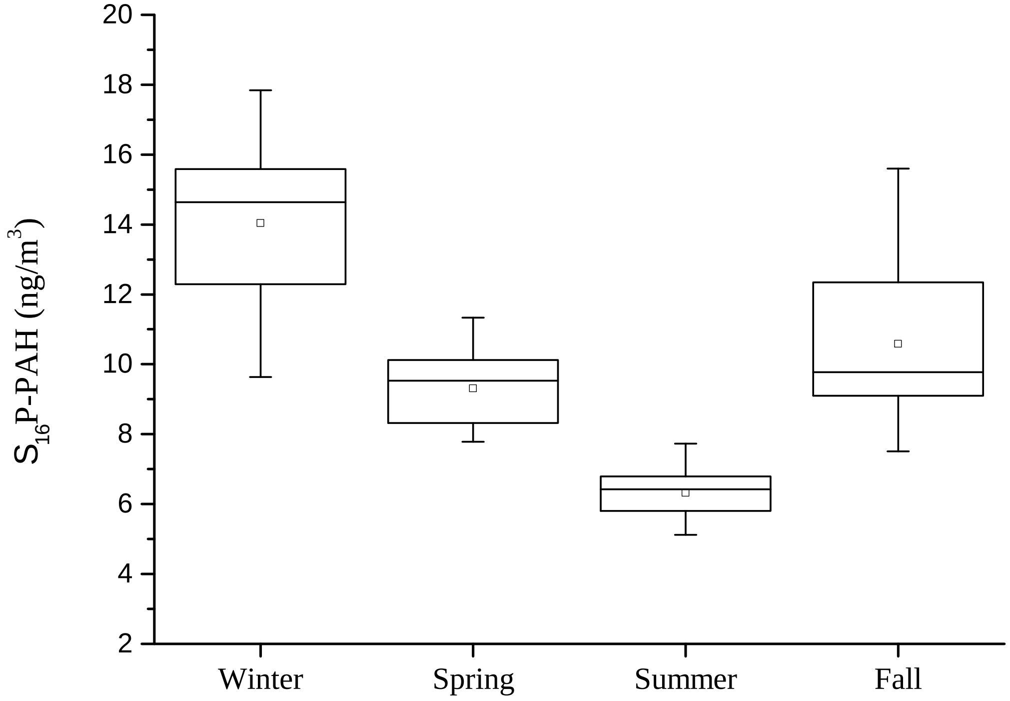

Figure 23. whisker and box plot of ∑PPAH during the four seasons

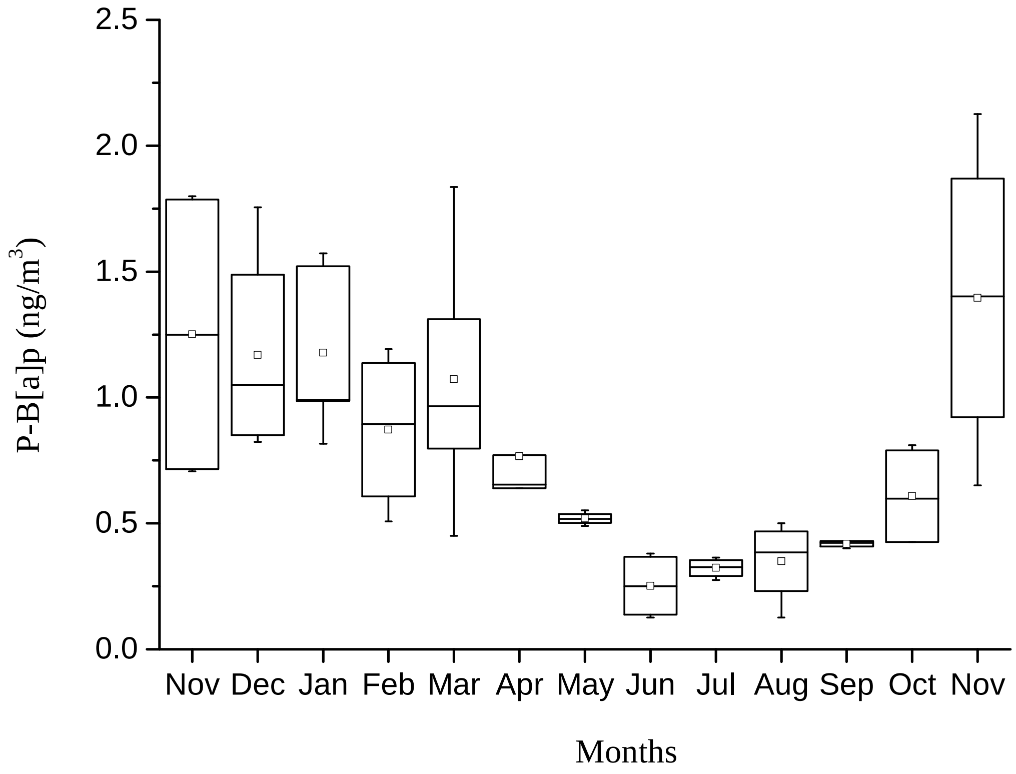

Figure 24. whisker and box plot of P-B[a]p during the twelve months campaign

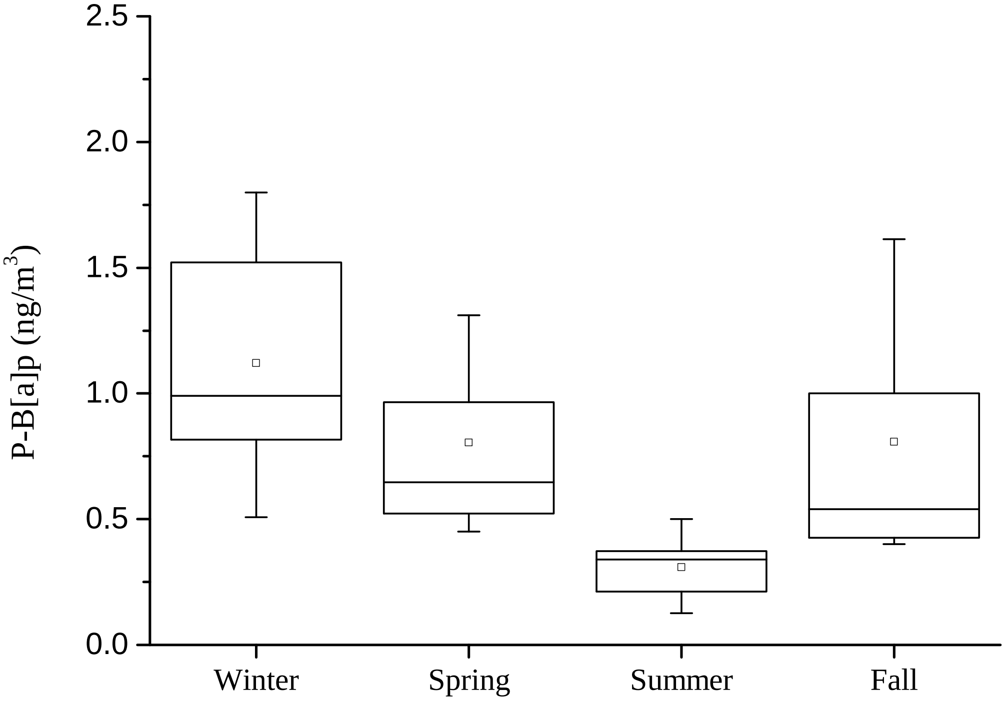

Figure 25. whisker and box plot of P-B[a]p during the twelve the four seasons

The P-PAHs mean increased from 12.9± 2.0 in November 2016 to 14.9±3.0 in February 2017. Then it started decreasing until reaching the lowest value of 6.3± 0.2 in July 2016. Finally, P-PAHs started increasing gradually to reach 13.4±1.7 in November 2017. The mean of P-PAHs during the seasons was 14.0±2.3, 9.3±1.1, 6.3± 0.7, 10.8±2.4 for winter, spring, summer, and fall respectively. The annual mean for the P-PAH sum was 10.4±1.3.

P-B[a]p concentration fluctuated between 1.3±0.6 and 1.1±0.52 between November 2016 and March 2017, then the concentration decreased to 0.3± 0.2 in August 2017. Finally, it increased again to reach 1.4±0.6 in November 2017. The mean B[a]p of the seasons was

1.1±0.4,0.8±0.4, 0.3±0.1, 0.8±0.6 for winter, spring, summer and fall respectively. The annual mean for B[a]p was 0.8±0.3. Although the annual guideline value of B[a]P is 1.0 ng/m^3 according to Directive 2004/107/EC was not exceeded during this campaign, the UK Air Quality guideline value of 0.25 ng/m^3 was exceeded.

B-Discussion of Results:

The variation of P-PAHs in air depends on the time of the year where both the seasonal emission sources and meteorology are different. The increase of P-PAHs in the winter and fall have been reported in many studies[92-97]. In the cold seasons, the increase in PAH concentrations can be related to the emission from domestic heating that are absent during the warm seasons[32, 98]. Furthermore, the low ambient temperature during this period has an effect on reducing the efficiency of fossil fuel combustion in the vehicular engines. According to Devos et al, PAH emissions from gasoline vehicles are 10 times higher than that of diesel vehicles because of the cold starts of the engines during winter[29, 99-101].

The meteorology too has a great impact. One main aspect is the inversion layer which frequently occurs during the long cold winter nights where there is an excessive nocturnal cooling of the ground surface due to rapid rate of loss of heat from the ground that exceeds the amount of radiation received from the sun. This phenomenon restricts the upward vertical mixing and dispersion of PAHs and traps them below the inversion layer near a ground level [102-107]. The cold period is characterized with low ambient temperature, reduced solar radiation and high relative humidity which all limit the physical and chemical decomposition of P-PAHs, which in turn increases their persistence in the atmosphere[36, 105, 108-110]. Also, enhanced PAH condensation/adsorption to suspended particles often occurs at lower temperatures [29, 32]. Moreover, the size distribution of particles varied by season could also alter PAH concentrations. Duan et al.[111] have indicated that the accumulation mode of PAHs is slightly shifted to larger particles in cooler seasons as comparing with that in a warm season. The magnitude of aged particles with PAHs is decreased during warm seasons due to the presence of good dispersion conditions. It is likely that larger particles tend to be correlated with aged particles by Kelvin effect[112].

On the other hand, the high temperatures in the summer as well as the high solar radiation and low humidity favors the thermo-, photo- and chemical- oxidation for decomposing atmospheric P-PAHs. Furthermore, PAHs are known as semi volatile organic compounds and their distribution in the atmosphere between the gas and particle phases is highly influenced by the ambient temperature. Higher temperatures during the warm seasons yield a relatively larger portion of PAHs partitioned to the gas phase especially those of the low molecular weight. Figure 26 shows the correlation between temperature and P-PAHs sum. It is evident that as the temperature increase P-PAHs decrease.

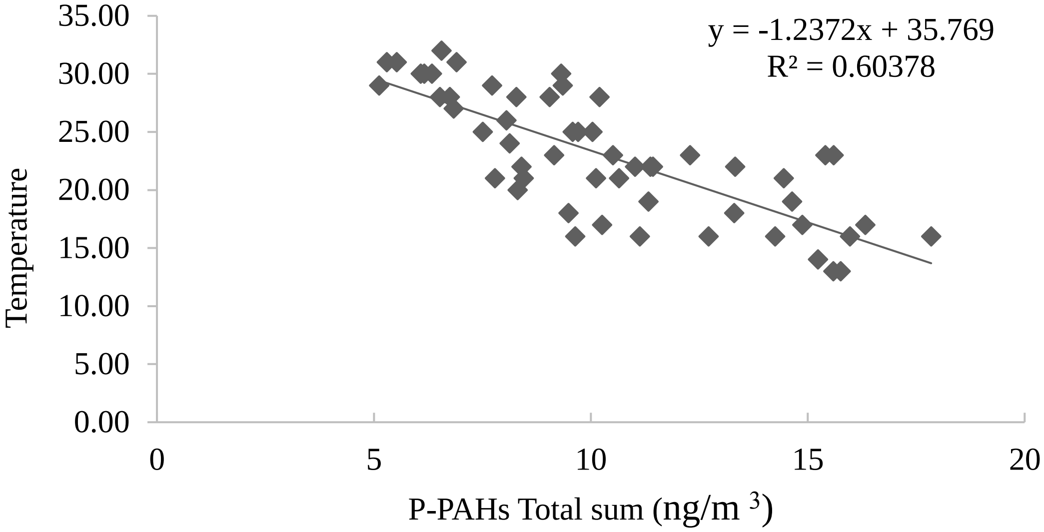

Figure 26. Correlation between sum of P-PAHs and temperature during the cold and warm seasons

C- Classification of P-PAHs

Classification of P-PAHs can be done based on the number of their aromatic rings, and this was used to construct the distribution pattern of the P-PAHs (Figure 27) in each season to better understand their source emissions. The main components of P-PAHs in every season at all sites were those of the four to five aromatic ring that constitute Baa, Chy, Bkf, Bbf, Bap, Bgh, Dba, Icp. These eight dominant components covered 55%–66% of the total 16 PAHs and exhibited a variation throughout the seasons of the year in contrast to the three or six member rings which didn't show a significant variation during the seasons. This indicates the effect of the increase in the emission sources for the four and five-member ring PAHs during the cold period as described before. These results suggest that the emission sources and/or meteorological conditions in winter are quite different from those of the other seasons.

The combustion-derived PAHs (COMPAHs) have been classified by some authors [113-122], and include Fluo, Py, Chry, BbF, BkF, BaA, BeP, BaP, Indeo and BghiP. This criterion was applied to our data. The sum of the main combustion-derived PAHs concentrations (COMPAHs) covered 67%–77% of the total PAHs in PM_{10}. In all seasons, the combustion-derived PAHs represented more than half of the total PAHs. Several studies determined that the ratio of ∑COMPAH/ΣPAHs is an indicator of the PAH origin whether they are of petrogenic or of pyrolytic origin. ∑COMPAH/ΣPAHs ≤ 0.3 indicates petrogenic origin while ∑COMPAH/ΣPAHs ≥ 0.7 indicates a pyrolytic origin[106, 123-127]. In this study, at AUB the value of COMPAH/ΣPAHs at AUB was in the range of 0.67-0.77 throughout the seasons which highly indicates the effect of combustion sources (pyrogenic) such as diesel and gasoline combustion on the PAHs at AUB. Another ratio is considered to understand the fate of LMW PAHs which is the ratio of LPAH/HPAH. Several studies pointed out that the concentrations of LMW PAHs in ambient air might not reflect their origin because they are more susceptible to atmospheric degradation. A ratio 0.2<LPAH/HPAH<0.4 indicates that degradation of LPAH is likely to have occurred[128-130]. At AUB, the ratio was between 0.2 and 0.3 which indicates that high degradation of LMW PAHs have occurred.

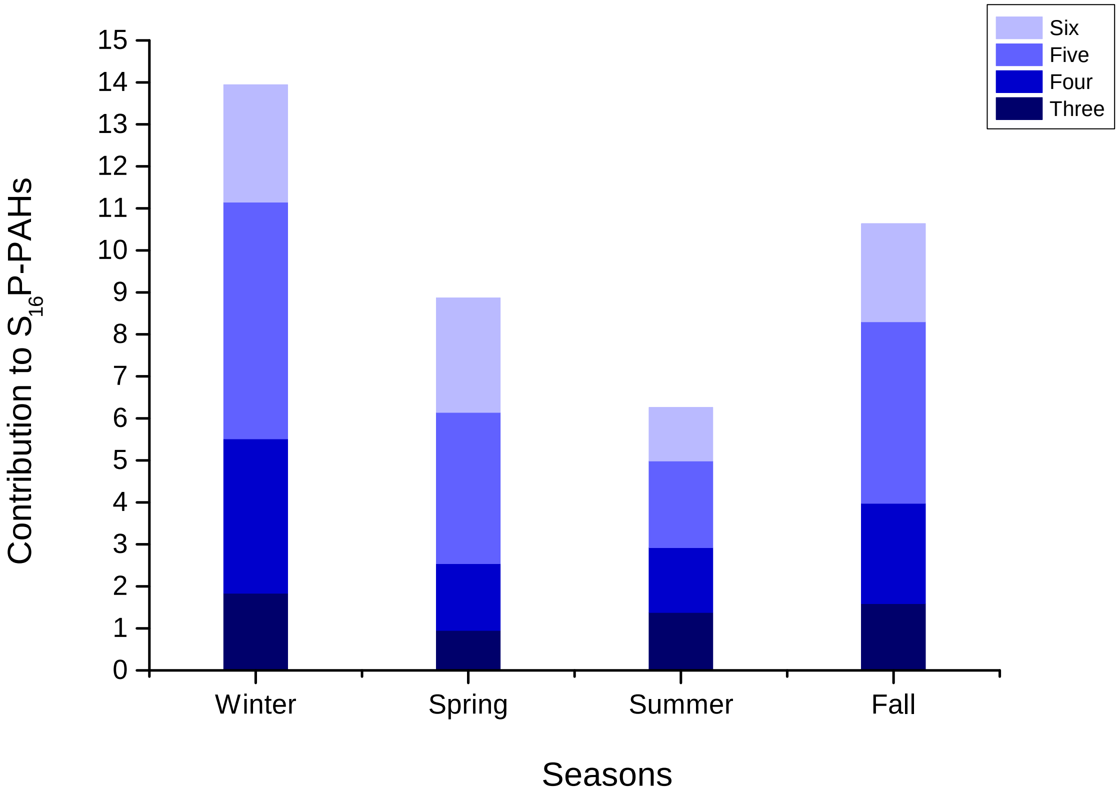

Figure 27. Contribution of the three, four, five and six member rings to the total P-PAH sum.

D- Bap Toxicity Equivalent concentration

B[a]p is the most PAH known for its carcinogenic and mutagenic character. Nevertheless, tracking this PAH alone would underestimate the carcinogenic effects of the other PAHs. Accordingly, B[a]p toxicity equivalent concentration has emerged to focus on the total toxicity associated with the exposure to a mixture of PAHs. The individual carcinogenic potencies of PAH in relation to B[a]P can be expressed through the B[a]P equivalent concentrations (BaP_{eq}), by multiplying the concentration of each PAH by the respective TEF value, using the following equation:

$$BaP_{eq} = \sum_{i}^{n=1} C_i \times TEF_i$$

Where C_i is the concentration of PAH congener *i* and TEF is the toxicity equivalency factor of the PAH congener *i* relative to B[a]P.

In this work, the TEF concept was applied and values of TEF reported by IARC were used to calculate the TEF-adjusted concentrations (based on BaP) of carcinogenic PAHs. The total toxic equivalent represents the result of the sum of the BaP_{eq} values ($\sum BaP_{eq}$). The mean value obtained for the carcinogenic potential estimated through the sum of BaP_{eq} in the four seasons was 3.2±0.9, 2.1±, 1.2 ± and 2.3± for winter, spring, summer and fall respectively. The annual mean for BaP_{eq} was 2.1 ng TEF m^{-3}. The results show that higher potential risk for human health upon exposure to the PAHs mixture is expected during the winter season(Figure 28).

The fraction between each BaP_{eq} and the total toxic equivalents ($\sum BaP_{eq}$) provides the percentage contribution of each PAH to $\sum BaP_{eq}$. Dba, which was the specie found in high concentrations and due to its corresponding TEF (TEF of 1), was the highest contributor to $\sum BaP_{eq}$, with an average of 47.0 % for the period of 2017, followed by BaP with a 35.0 % contribution.

Of all the 16 PAHs considered priority pollutants by the US-EPA, only BaA, Chry, BaP, BbkjF, Ind and Dba were considered potential carcinogens [131] and, in this study, these compounds have been the species with the higher contribution in relation to $\sum BaP_{eq}$.

Figure 29 shows the equivalent toxicity concentration contribution for these six species in the four seasons. The contribution of carcinogenic potential of B[a]P ranged from ~ 27.6 (summer) to ~ 39.8% (spring) and Dba ranged from ~ 43.1% (spring) to ~ 52.8% (summer). The remaining species showed contributions below 10% to ∑ BaP_{eq}. The high value obtained was related to a higher contribution from the Dba with an average toxicity concentration of 0.996 ng TEF m^{-3} in 2017. The results suggest that focusing only on B[a]P, which is mostly used as a marker of the genotoxic and carcinogenic PAH, would probably underestimate the carcinogenic potential of the other studied PAHs. It should be noted that Dba is listed in the group 2A carcinogen family with a TEF equals to 1 in that family.

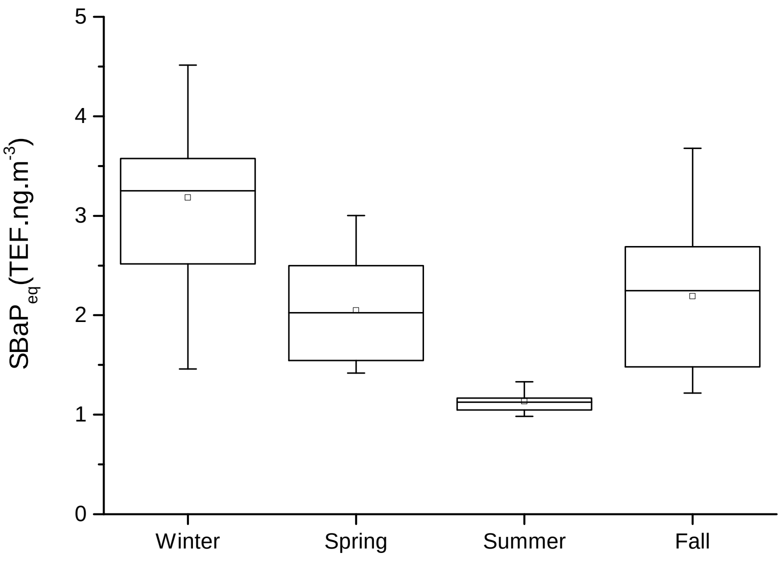

Figure 28. Seasonal variation of B[a]p equivalent toxicity concentration

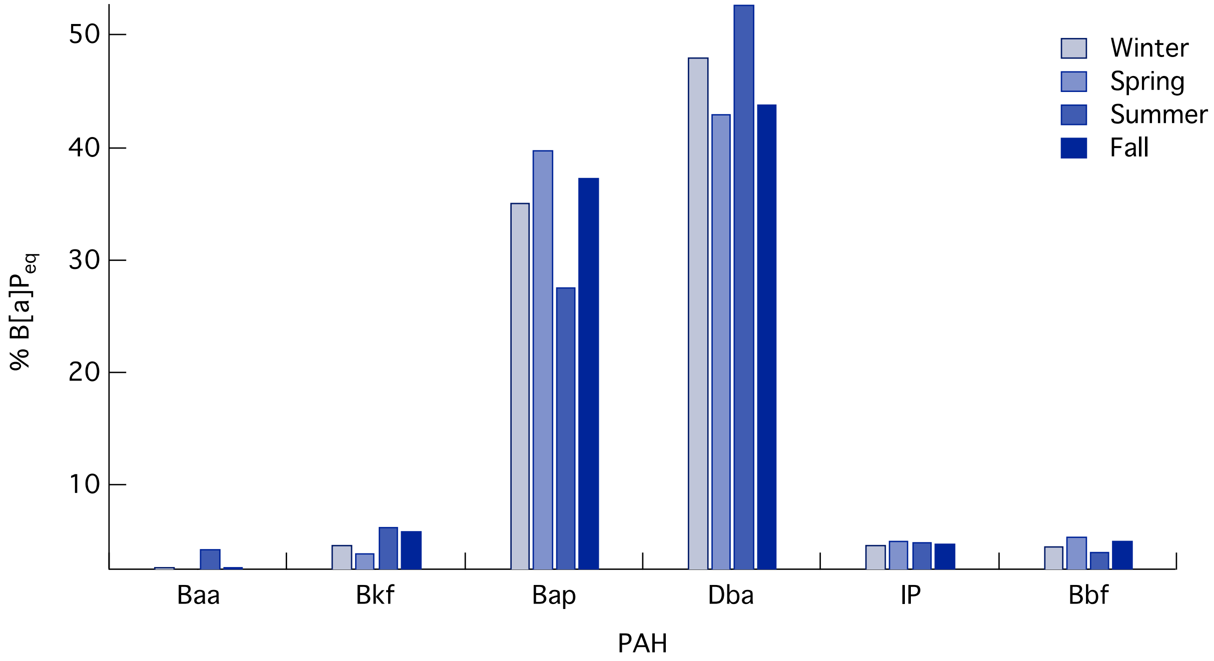

Figure 29. Percent contribution of the most carcinogenic PAHs to the B[a]P toxicity equivalence

E-Incremental lifetime cancer risk assessment

A growing number of studies have highlighted the health risks of atmospheric PAHs, especially those on fine particle [132-135]. The metric method used for estimating cancer risk is the inhalation incremental lifetime cancer risk (ILCR), which is associated with specific inhalation and exposure parameters, and calculated from the following equation:

$$ILCR = \frac{E \times SF \times EF \times ED \times CF}{BW \times AT}$$

in which E is the daily exposure level by inhalation (ng.day^{-1}) for a specific age which is calculated using the toxic equivalent concentration sum and the inhalation rate (IR) for a specific age group (21.4 m^3/day for adults) and the time of exposure which was taken as 23 hours using the following equation: $E = \sum BaP_{eq} \times IR \times Time\ of\ exposure$

The ILCR can then be calculated. *SF* is the inhalation carcinogenic slope factor for BaP, which has a geometric mean of 3.14 kg.day/mg, and a geometric standard deviation of 1.8 [136], E_D means the exposure duration (50 years for adults), EF is the exposure frequency (252 day. year^{-1}), BW is the body weight (70 kg for adults) and AT is the lifespan of carcinogens (25,550 days); and CF (mg/ng) is a unit conversion factor (10 $^{-6}$)[137].

In our study, ILCRs for adult's population at the urban site, were estimated. This age was selected because it has the highest inhalation rate and exposure duration. A scenario of an adult individual living all time at the same level of the rooftop at AUB and exposed to this ambient level was simulated. It is worth noting here that the values obtained represent a lower limit exposure risk since only the inhalation route was assessed and other exposure routes (ingestion and dermal contact) were not considered.

The computed ILCRs from exposure to airborne PAHs were estimated assuming that adult lives in the urban site of the sampled area for 24 hours and for 365 days/year. Computed ILCR averaged at 1.4×10^{-6} in winter period which was the only significant value that exceeded the commonly acceptable threshold determined by IARC of 10^{-6} . To sum up, these results show that out of a 10^{6} population one adult individual would have the chance to develop cancer upon exposure to the PAH baseline mixture in the urban site. However, in daily life and at the exposure levels and not at rooftops ambient levels individuals are more exposed to PAHs and ultimately this value of cancer risk estimation would be higher.

CHAPTER IV

SOURCE APPORTIONMENT OF P-PAHs USING POSITIVE MATRIX FACTORIZATION

This chapter presents the major receptor models available for source apportionment. Among these models, we highlight the features of Positive matrix factorization (PMF), the model that is widely used to partition sources that contribute into air quality assessment. For this model to be valid, certain parameters should be first optimized. Therefore, these parameters are further detailed. Upon optimization, an interpretation of this model's output data can finally be generated.

A-Introduction to receptor modeling:

source apportionment using receptor modeling has been developed in order to elicit information about the sources that might be affecting a certain receptor site for a particular contaminant. The most widely used models are: chemical mass balance (CMB), principal component analysis (PCA), and positive matrix factorization (PMF)[138]. In brief, CMB is a regression based mass balance methodology proved by various studies to be efficient in modeling [139]. It assesses the percent contribution of a single source to the contaminant in a receptor site. The application of CMB is appropriate only when the source and its profile is known, so in this case the contribution of the source for a given data set is calculated. When the number and the profile of sources is unknown PCA can be employed to the large data sets[138]. It is based on the analysis of the correlation between measured concentrations of chemical species in a number of samples, assuming that highly correlated compounds come from the same source[140]. However, such factor analysis model is limited due to the fact that it can generate negative profiles of species in a source as well as it does not account for the uncertainties in measurements. In addition, PCA can give qualitative information about the nature of the source profiles, but it does not provide a quantitative apportionment[138]. To solve all the limitations by the aforementioned receptor models, a useful tool in source apportionment called PMF was developed by EPA in 1994. This multivariate factor analysis model accounts for all the drawbacks of the previously mentioned models. Therefore, PMF has now become the most widely used source resolution model with more than 1000 papers stating its application[138, 141-144].

B-Principle of PMF: theoretical overview

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 goal of solving this equation is to find values of g_{ik} , f_{kj} , and p that best reproduce X_{ij}. This is accomplished by adjusting g_{ik} , f_{kj} until a minimum value of Q_{robust} for a given p is found. Q_{robust} is the goodness of fit parameter calculated excluding outliers. However, Q_{true} is the goodness of fit parameter calculated including all collected data. For a stable and reliable solution Q_{robust} and Q_{true} should be more or less comparable to each other. Q_{robust} is expressed as:

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

Thus the function Qrobust is basically the residues divided by uncertainties or is the weighted sum of sqaures 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[144].

C-PMF model optimization and validation

A critical step in PMF modeling is the determination of the correct number of factors/sources. In the optimization step, it is important to examine and respect five parameters in order to correctly estimate the number of factors. Thus, an optimal estimation leads to a more stable, robust, and reliable solution that best reproduce the set of data originally provided by the user. The aforementioned five parameters are: signal to noise ratio, closenes of Qrobust to Qtrue, residual analysis, correlation coefficients between observed and estimated concentrations and bootstrap mapping. In this study, a 65 × 16 (65 samples with 16 PAHs each) was introduced into the EPA PMF 5.0. The number of factors from 3 to 6 was examined and the proximal number of factors was decided. According to the aforementioned parameters a 3-factor solution gave the lowest Q_{robust} 1450 close to Q_{true} 1459 (Qrobust/Qtrue= 0.993), a good scaled residuals range, best correlation coefficients and a good bootstrap mapping . The output results were easily interpretable and comparable to source profiles apportioned and reported in literature.

1-Signal to noise ratio (S/N):

It indicates whether the variability in the measurements are real or within the noise of the data. If the data are within the noise, this indicates that our measurements are either near or below our detection limits. This is done by comparing our data to the calculated uncertainties which were provided by the user. The uncertainties can be calculated using multiple ways. One of the most common ways to calculate uncertainties is based on the limit of detection of the analytical method[145, 146] such that:

- When $X_{ij}>LOD$, $U_{ij}=0.1X_{ij}+ LOD/3$ Equation 1
- when $X_{ij}<LOD$, $U_{ij}=0.2X_{ij}+LOD/3)$ Equation 2

Because our measurements for the 16 PAHs were above the detection limit in all the samples Equation 1 was used for the calculation of the uncertainties. The strength of the species is examined by calculating their signal to the noise (S/N) ratio. Species are considered strong if their S/N ratio is above 1, weak when S/N ratio is between 0.5 and 1, and bad when S/N ratio is below 0.5. According to our input data, all the species' strength were ≥ 5.8, which are considered strong and thus, none of the 16 PAHs were excluded from the model.

2- Observed/ predicted scatter plots:

Scatter plots compare observed (input data) values and predicted (modeled) values for each species to determine if the model fits the individual species well. In PMF, the minimum accepted correlation coefficient (R^2) of one specie is 0.6[144]. for the 16 PAHs inputted to the model, the range of R^2 was between 0.86 and 0.98 suggesting that the measured concentrations were well explained by three factor/source analysis.

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[144].

4-Bootstrap mapping

Is an indication whether the number of factors is approximate or has to be optimized[147-150]. A bootstrap model consists of running at least 100 bootstraps. The mapping percentage of each one of the assigned bootstrap factor to the base factor, indicates how unique are the different factor profiles. When a high number of a given bootstrapped factor highly overlap with more than one base factor, it may suggest that the factor profiles are not unique and the number of factors may have to be optimized. In this study, the mapping percentage of the three base factors with the three bootstrap factors was over 80%, which indicates that the number of factor is appropriate.

Once most of the PMF validation parameters were met, it is concluded that the appropriate number of factors affecting our study's receptor site is three. Thus, interpretation of the output follows.

D-PMF output Results

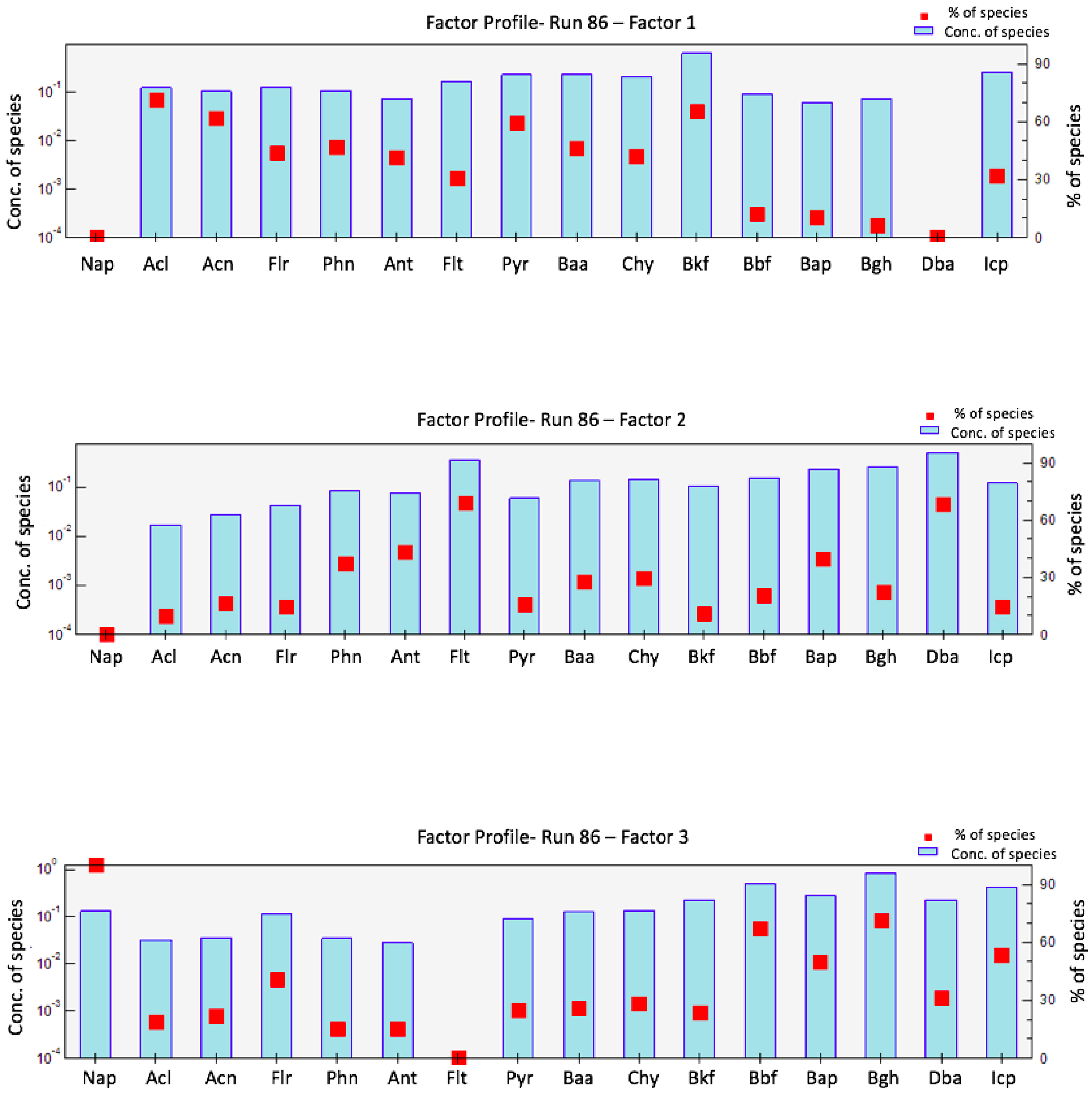

Figure 30. The three factor profiles for factors 1,2 and 3 determined by PMF and the fraction of the species in each. Nap(Naphthalene), Acl(Acenaphtylene), Acn(Acenaphtene), Flr(Flourene), Phn(Phenanthrene), Ant(Anthracene),

Flt(Flouranthene), Pyr(Pyrene), Baa(Benzo[a]anthracene), Chy(Chrysene), Bkf(Benzo[k]flouranthene), Bbf(Benzo[b]flouranthene), Bap(Benzo[a]pyrene), Bgh(Benzo[ghi]perylene), Dba(Dibenzo[a,h]anthracene), Icp(Indeno[1,2,3-cd]pyrene)

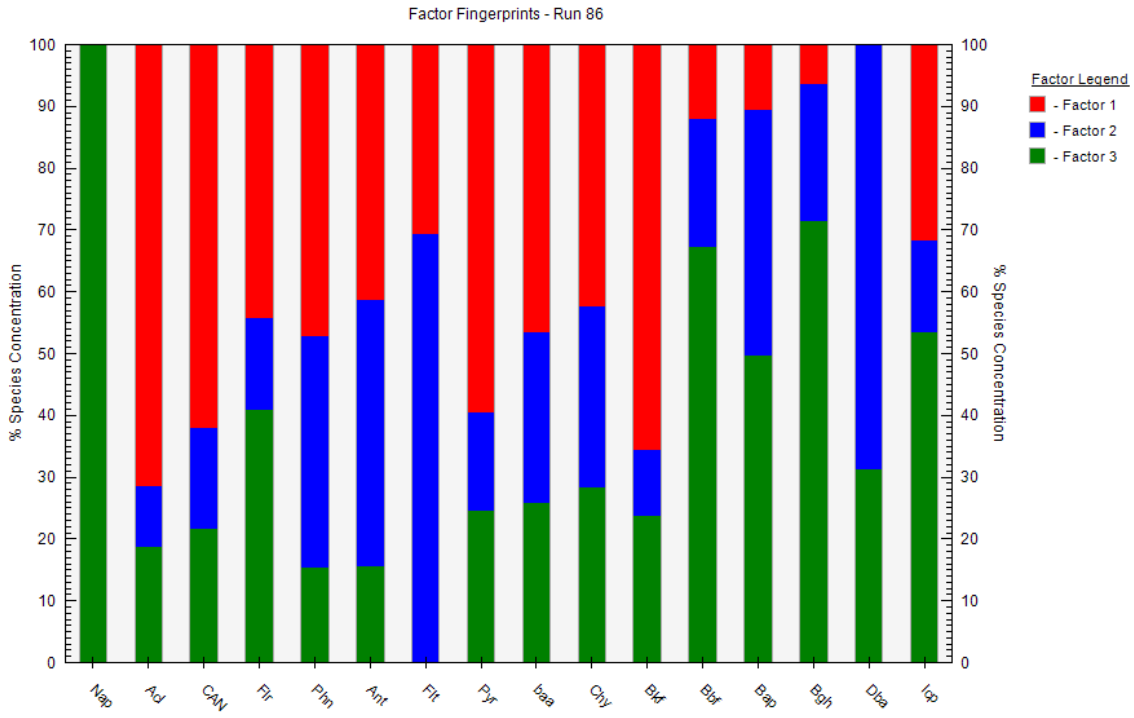

Figure 31. Fingerprints (PAH markers) of the three factor profiles according to PMF results

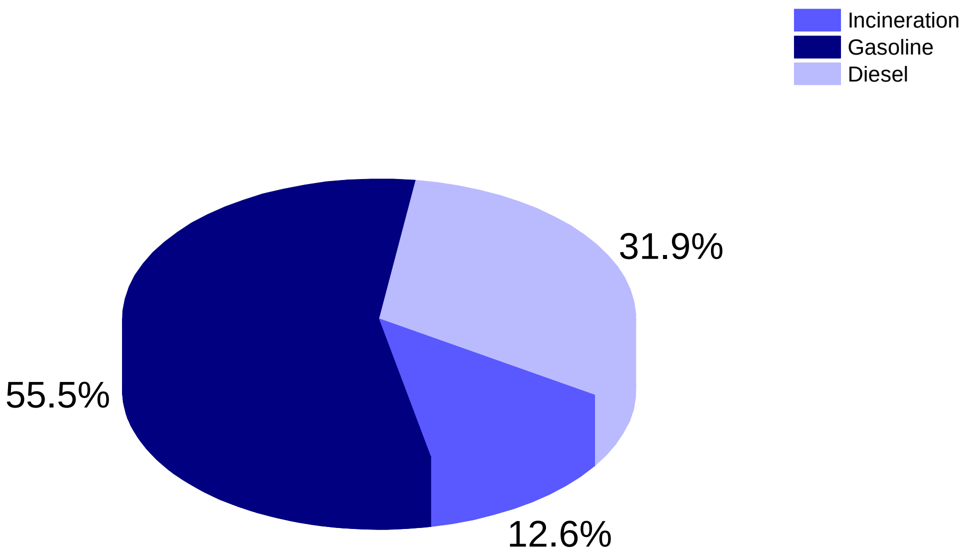

Figure 32. The portion contribution of the three factors to the total ambient P-PAH

E-Results and Discussion:

A three-factor model associated to P-PAHs gave the best fit in the PMF analysis. Mass contributions ($\sum_{total}$PAH) were 31.9%,12.6%,55.5% for factors 1,2 and 3 respectively. Factor 1 (shown in Figure 30) accounted for 31.9% of the sum of the measured 16 PAHs. It has a high loading of 3-4 ring PAH characteristics which means that it is highly influenced by low molecular weight PAHs. The major PAHs contributing to factor 1 were pyrene 68%, acenaphtylene 70%, acenaphtene 80%, benzo[k]flouranthene 70% and moderate contributions of flourene, phenanthrene, anthracene, chrysene, and benzo[a]anthracene. It is important to note that 5-6 member ring PAH contributions are negligible in this profile. It has been revealed that diesel emissions are enriched in flouranthene, pyrene and benzo[k]flouranthene, chrysene relative to gasoline emissions[32, 39-42, 151]. Accordingly, factor one is attributed to diesel engine emissions. Diesel emissions are known to produce low molecular weight PAHs due to high temperature-induced cracking of hydrocarbons and formation of lower weight PAHs. In fact, in Beirut especially in hamra area, there is a continuous use of diesel generators as a quick fix to Lebanon's electricity problem. Electricite du Liban (EDL), the national electricity provider, has established a black-out rotating schedule of three hours per day for the area surrounding the sampling site. In fact, Shihadeh et al, have revealed that diesel generators contribute up to 40% of the total atmospheric P-PAH in Hamra area. The World Bank has reported that self-generation satisfies 33%–38% of electricity consumption in Lebanon[84]. In addition, the commercial ships that deport from and land in Beirut harbor have a serious impact on the total P-PAHs in the AUB area due to the high consumption of marine diesel oil by these ships.

Next, Factor two represents 12.6% of the sum of the measured 16 P-PAHs. This factor highly consists of dibenzo[ah]anthracene (72%) and flouranthene (71%) with moderate contribution of LMW P-PAHs (phenanthrene 35%, anthracene 50%) and HMW P-PAHs (Benzo(a) pyrene 40%) (see Figure 30). As reported by Zhao et al, Dibenzo[ah]anthracene and flouranthene are highly released by incinerators [152]. 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[153].

Factor three contributes to 55.5% of all the measured 16 P-PAHs. High loadings of benzo[b]flouranthene (70%), benzo[a]pyrene (52%), benzo[ghi]perylene (75%), indeno[cd]pyrene (57%) and naphthalene are observed. By visually comparing factor three to factor one (see Figure 30), we can conclude that factor three exhibits five to six-member ring P-PAHs, which means that factor three is influenced by HMW P-PAHs. Indeed, this kind of profile is usually attributed to gasoline emissions, which in AUB accounts for almost half of the P-PAHs[33, 34, 36-38]. The primary source of PAHs from gasoline is the on-road vehicles. In fact, AUB is surrounded 100 m West by the coastal Mediterranean road, a very busy street during rush hours, and 200 m East by Bliss street, a very busy street all day. Thus, no wonder why gasoline contributes to 55.5% of P-PAHs in the AUB area.

Chapter V

CONCLUSIONS

PM_{10}-bound PAHs were measured during the year of 2017 covering all the seasons at an urban coastal site in Lebanon (AUB). The results show a high day to day variation even throughout the same season which were linked to the meteorological conditions that had a great impact on the dispersion or accumulation of P-PAHs. However, this variation between the samples decreased as we approached the spring and summer seasons, where both the weather and the emission sources are stagnant and stable in contrast to the cold period where the emissions are more ubiquitous due to seasonal emissions such as domestic heating and unstable weather. This variation was also clear in the individual P-PAHs, which showed a higher deviation during the cold period than the warm one. The HMW P-PAHs were the dominant P-PAHs at the site which reflect their low volatility rate and their origin from the most dominant source: gasoline emissions. Classification of P-PAHs showed that the 4-5-member ring P-PAHs were the only P-PAHs that had the highest contribution to the ∑P-PAH and exhibited a significant seasonal variation in contrast to the three and six-member ring, which reflect their seasonal combustion (pyrogenic) origin that is prominent in winter and absent in the other seasons. Source apportionment using PMF succeeded into evaluating the major sources of P-PAHs at the urban coastal site which were identified as gasoline, diesel and incineration with a portion contribution of 55.5%,31.2% and 12.6% respectively. The toxicity equivalent concentration of B[a]p was higher during the cold period.

This work was the first comprehensive study that succeeded into the determination of a P-PAH baseline at a representative site in Lebanon and into the evaluation of day to day and the seasonal variation of P-PAH at an urban coastal site exposed to several emission sources. In addition, this study represents a background dataset of P-PAHs that would be representative when comparing the levels to another urban location affected by an increase on the baseline level from specific emission sources. At the end, the cancer risk estimations showed that at ambient level exposure on a rooftop like AUB an adult individual would have a chance to develop cancer.

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