

AMERICAN UNIVERSITY OF BEIRUT

SOURCES, DISPERSION AND TOXICITY OF PAHs AND
DIOXINS AT AUB, ZOUK AND DORA

by
JULIE ISSAM NASSAR

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submitted in partial fulfillment of the requirements
for the degree of Master of Science
to the Department of Chemistry
of the Faculty of Arts and Sciences
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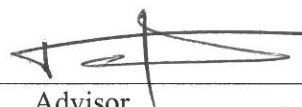
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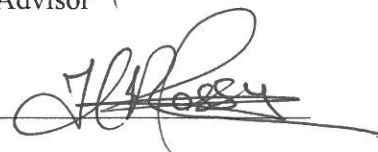
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AN ABSTRACT OF THE THESIS OF

Julie Issam Nassar for Master of Science
Major: Chemistry

Title: Sources, Dispersion and Toxicity of PAHs and Dioxins at AUB, Zouk and Dora

There are two families of toxic air pollutants; polycyclic aromatic hydrocarbons (PAHs) and polychlorinated dibenzo-p-dioxins and dibenzofurans PCDD/Fs, for which assessment and characterization in the atmosphere need to be considered. Polycyclic aromatic hydrocarbons (PAHs) in the atmosphere originate from biogenic sources, such as forest fires and volcanic eruption. However, their presence in populated urban areas is influenced by anthropogenic emissions, such as domestic and industrial activities as well as gasoline and diesel combustion. Persistent organic pollutants (POPs) are semivolatile compounds associated to particulate matter and include polychlorinated dibenzo-p-dioxins and dibenzofurans PCDD/Fs, so called "Dioxins". PCDD/Fs have been reported to be carcinogenic and mutagenic possessing toxicities towards human health. They are released from the incomplete combustion of chlorinated species and incinerators.

The chaotic unregulated emission from the aforementioned sources has led us to conduct a systematic measurement and assessment of PAHs and PCDD/Fs in three representative sites (AUB, Zouk and Dora) of Beirut and its suburbans. Particulate and gaseous phase PAHs and Dioxins were collected using a high volume sampler (HVS) equipped with both quartz fiber filter and polyurethane foam (PUF). Following, thorough and careful extraction and quantification approaches were followed according to international and locally developed standard operation procedures (SOPs).

Results showed spatial variations in the levels of PAHs and dioxins at AUB, Zouk and Dora. The lowest concentrations of these chemicals were registered at AUB. Higher amounts were found in Zouk, but the most toxic levels were in Dora. Strong seasonal variations were observed among PAH levels. Light PAH concentrations were always higher during the winter, whereas heavy congeners amounts were relatively higher in the summer. These sources were apportioned using PMF. Investigations showed that diesel, gasoline and heavy fuel oil burning as well as incinerations are the predominant emission sources in Lebanon. Collected data helped in assessing the incremental lifetime cancer risks (ILCRs) based on a scenario evaluation and suggesting policy recommendations.

CONTENTS

ACKNOWLEDGEMENTS.....	v
ABSTRACT.....	vii
LIST OF ILLUSTRATIONS.....	xii
LIST OF TABLES.....	xiv

Chapter

I. INTRODUCTION.....	1
A. Particulate Matter.....	1
B. Polycyclic Aromatic Hydrocarbons (PAHs).....	2
C. Persistent Organic Pollutants (POPs).....	8
D. Dioxins and Furans.....	9
E. Objective of This Study.....	11
F. Thesis Layout.....	11
II. COLLECTION AND ANALYSIS.....	13
A. Introduction.....	13
B. Sampling Method for The Ambient Measurements of PAHs and Dioxins Using The High Volume Sampler.....	13
C. Sampling Method for The Ambient Measurements of PAHs Using The Low Volume Sampler.....	14

D. The Gravimetric Analysis.....	15
E. Extraction Procedure of Samples Collected with High Volume Sampler (HVS).....	15
F. Extraction Procedure of Samples Collected with Low Volume Sampler (LVS).....	16
G. Chromatography Analysis.....	16
1. Gas Chromatography.....	16
2. Ion Chromatography.....	17
H. Quantification.....	17
I. Quality Control/ Quality Assurance (QC/QA).....	18
III. SPATIAL AND TEMPORAL ASSESSMENTS OF PAHs.....	20
A. Introduction.....	20
B. Study Area.....	21
C. Results and Discussion.....	23
1. Inter-sites Spatial and Temporal Comparisons.....	23
2. Intra-site Temporal Comparison.....	24
D. Conclusion.....	27
IV. SPATIAL ASSESSMENT OF DIOXINS.....	28
A. Introduction.....	28
B. Study Area.....	28
C. Results and Discussion.....	29
D. Conclusion.....	30

V. INFLUENCE OF THE ZOUK POWER PLANT EMISSION ON TOXIN AMBIENT LEVELS IN THE ZOUK AREA.....	33
A. Introduction.....	33
B. Study Area.....	34
C. Results and Discussion.....	35
1. Levels of PM ₁₀	35
2. Levels of PAHs.....	36
3. Levels of BaP.....	37
4. Levels of SO ₄ ²⁻	38
D. Conclusion.....	39
VI. PAHs SOURCE APPORTIONMENT.....	40
A. Introduction.....	40
B. Sources and Markers.....	41
C. PMF Factor Profile.....	44
1. Winter Campaign.....	44
2. Summer Campaign.....	49
D. Conclusion.....	50
VII. PAHs AND DIOXINS CANCER RISK ESTIMATION.....	53
A. Introduction.....	53
B. ILCRs Calculation.....	55
C. Scenario Evaluation.....	58

VIII. CONCLUSIONS.....64

BIBLIOGRAPHY.....66

ILLUSTRATIONS

Figure 1.1: Pyrosynthesis of PAHs	3
Figure 1.2: Structures of the 16 EPA listed PAHs	5
Figure 1.3: Highlighted and named countries are the ones that were reviewed for their PAH levels and reported in Table 1.2.....	7
Figure 1.4: Basic structure of dioxins and furans chlorinated at the 2,3,7,8-positions..	10
Figure 2.1: from left to right: the high volume sampler, the sampling probe, and the filter and PUF compartments constituting it.....	14
Figure 2.2: From left to right: the low volume sampler parts and setup.....	15
Figure 3.1: Labeled are the sampling sites of our study.....	22
Figure 3.3: Light and heavy PAH seasonal profile at AUB.....	25
Figure 3.4: Light and heavy PAH concentrations in Dora during the winter and the summer	26
Figure 3.5: Light and heavy PAH seasonal profile in Zouk	27
Figure 4.1: Dioxin Concentration at AUB, Zouk and Dora during summer 2014.....	31
Figure 5.2: Box-and-whisker plot of the concentration of PM in the ambient air of three representative sites: Z.Mikael, Z.Mosbeh and AUB.....	36
Figure 5.3: Box-and-whisker plot of the concentration values of total PAH ΣPAH measured in Z.Mikael, Z.Mosbeh and AUB.....	37
Figure 5.4: Average BaP concentrations values measured in Z.Mikael, Z.Mosbeh and AUB	38
Figure 5.5: Box-and-whisker plot of the concentration of sulfate (SO ₄ ⁻²) collected on filters at three different sites: Z.Mikael, Z.Mosbeh and AUB.....	39
Figure 6.1: Source contributions at AUB during the winter season (2015)	47
Figure 6.2: Source contributions in Dora during the winter season (2015).....	48
Figure 6.3: Source contributions in Zouk during the winter season (2015)	49

Figure 6.4: Source contributions at AUB during the summer season (2015)	50
Figure 6.5: Source contributions in Dora during the winter season (2015).....	51
Figure 6.6: Source contributions in Zouk during the winter season (2015)	52
Figure 7.1: Weekday Scenario.....	62
Figure 7.2: Saturday Scenario.....	63
Figure 7.3: Sunday Scenario.....	64

TABLE

Table 1.1: ATSDR/US EPA priority PAHs, and their phase distribution at ambient temperature.	4
Table 1.2: The minimum and maximum PAH concentration reported in different cities and countries of the Mediterranean region.....	8
Table 3.1: Reported are the sampling dates at AUB, Zouk and Dora during the winter and the summer of the year 2015.....	22
Table 4.1: The chemical structures of the 17 most toxic congeners of PCDD/Fs.....	31
Table 4.2: WHO TEF for the analyzed PCDD/Fs.....	32
Table 7.1: TEF values of the 16 PAHs as defined by US-EPA.....	56
Table 7.2: inhalation incremental lifetime cancer risk (ILCR) values in the studied sites during winter and summer seasons.....	57

CHAPTER I

INTRODUCTION

A. Particulate matter

Large amounts of particulate matter (PM) are emitted into the atmosphere of populated and industrialized urban areas (Mandalakis, Tsapakis et al. 2002). PM may be solid or liquid particles with diameters between 0.002 and 100 μm . The most important particles with respect to atmospheric chemistry and physics are in the 0.002 to 10 μm range (N.Pitts 2000). Their role in atmospheric processes is defined by a number of their properties, including number, concentration, mass, size and chemical composition. High scientific evidence seems to link particles with less than 10 μm in diameter (PM_{10}) to mortality and morbidity (Lebowitz 1996, Pope III and Dockery 2006, Cakmak, Dales et al. 2007, Ostro, Feng et al. 2007). Particles with diameters between 2.5 and 10 μm are identified as *coarse particles* and those with diameters <2.5 μm are called *fine particles* (Whitby, Husar et al. 1972). These particles consist of many organic and inorganic components out of which the semivolatiles. These latter have been shown to exist in equilibrium between particles and gas phases. Predominant classes of these semivolatile compounds are polycyclic aromatic hydrocarbons (PAHs) and persistent organic pollutants (POPs) that include polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/PCDF). The association of fine particles with mutagenic and carcinogenic chemicals – such as PAHs and POPs – may contribute to acute health effects.

B. Polycyclic Aromatic Hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons are constituted of carbon and hydrogen with two or more fused aromatic rings structure (Ravindra, Sokhi et al. 2008). They have a relatively low solubility in water, a low vapor pressure in the air and are highly lipophilic (N.Pitts 2000). Having low vapor pressure, some PAHs are present at ambient temperature in air in both gaseous and particulate phases. PAHs with 2-3 aromatic rings exist almost in the gaseous phase whereas components with 4 rings and above are particles-associated (Ré-Poppi and Santiago-Silva 2005). Their semi-volatile property makes them highly mobile throughout the environment via deposition and re-volatilization between various matrices making them a widespread environmental problem. When adsorbed on particulate matter, PAHs can undergo photodecomposition when exposed to Ultra-Violet (UV) light.

PAHs may be formed from saturated hydrocarbons under oxygen-deficient conditions (Ravindra, Sokhi et al. 2008). They are the result of pyrolytic processes, especially the incomplete combustion of organic materials. When the temperature exceeds 500 °C, carbon-hydrogen and carbon-carbon bonds are broken to form free radicals (Manahan 1999). These radicals attach to acetylene, which further condenses with aromatic ring structures resistant to thermal degradation. Figure 1.1 illustrates the pyrosynthesis of PAHs, starting with ethane.

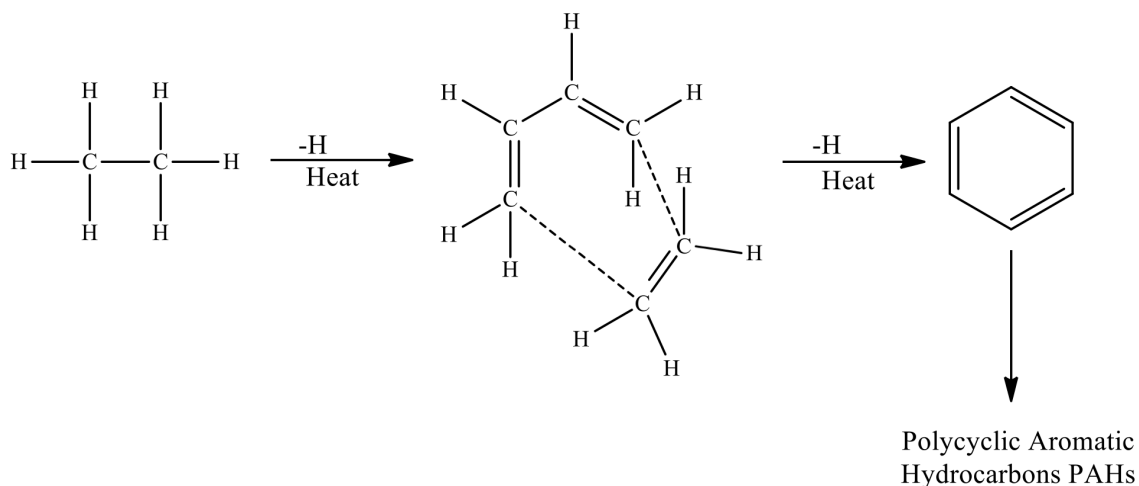


Figure 1.1: Pyrosynthesis of PAHs

About 500 different PAHs have been detected in air. They are able to damage genetically the cells and initiate the development of cancer (NAEI 1970 to 2001). Furthermore, in their health effect, PAHs may initiate gene mutation by developing DNA adducts leading to birth defects and genetic changes (Lawley 1989). Thus, there is considerable concern about the relationship between PAH exposure in the ambient air and the potential to contribute to human cancer incidence and mutagenicity. Out of many congeners, the Environmental Protection Agency (US EPA) has listed 16 priority PAHs (Table 1) based on their toxicological profile according to the Agency for toxic substances and diseases registry (ATSDR) (ATSDR 1995). 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 (Ravindra, Sokhi et al. 2008). Being classified as a Group 1 known human carcinogen (IARC 2010), Benzo[a]pyrene (BaP) is the most potent congener among PAHs (WHO 1998, Boström, Gerde et al. 2002). It is constituted of five aromatic rings and commonly found in the atmosphere in the particulate phase.

Table 1.1: ATSDR/US EPA priority PAHs, and their phase distribution at ambient temperature.

PAHs	Particle /Phase Distribution
Naphtalene	Gas Phase
Acenaphtylene	Gas Phase
Acenaphtene	Gas Phase
Fluorene	Gas Phase
Phenanthrene	Particle gas phase
Anthracene	Particle gas phase
Fluoranthene	Particle gas phase
Pyrene	Particle gas phase
benzo[a]anthracene	Particle Phase
Chrysene	Particle Phase
Benzo[k]fluoranthene	Particle Phase
Benzo[a]pyrene	Particle Phase
Benzo[g,h,i]perylene	Particle Phase
Dibenz[a,h]anthracene	Particle Phase
Indeno[1,2,3-cd]pyrene	Particle Phase

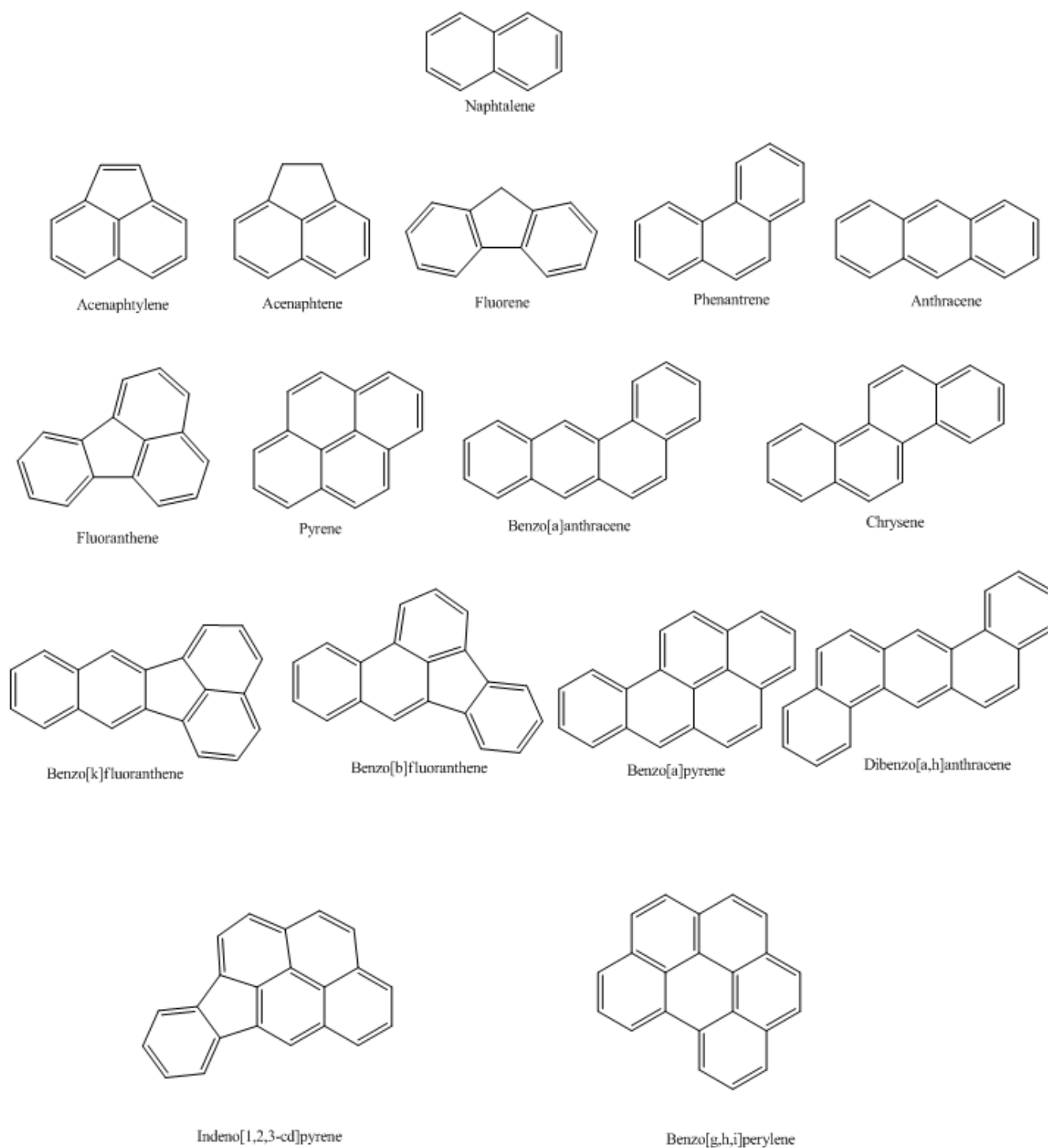


Figure 1.2: Structures of the 16 EPA listed PAHs

Polycyclic aromatic hydrocarbons are emitted by various anthropogenic combustion sources. Fuel combustion (van Drooge and Ballesta 2009), waste incineration, wood and coal combustion, power generation plants, domestic and industrial processes are known to be the main sources of PAHs in the atmosphere (Ravindra, Sokhi et al. 2008). Biogenic emissions (carbonization and volcano) constitute a secondary source of PAHs in the air but their contribution is considered negligible when compared to anthropogenic sources. Domestic emissions are associated with the burning of coal, oil, gas, garbage and organic substances including tobacco and char meat. PAH emissions from these sources are of major concern because they are prevalent in most indoor environments. Mobile sources include the emission from gasoline and diesel vehicles, whereas industrial sources include waste incineration and power production. The assessment of the emission inventories of PAHs showed that gasoline vehicles contributed with 23, and up to 49%, of the total PAH emissions in the United States (US) and the United Kingdom (UK), respectively, and therefore they have been considered as a primary source of PAHs releases (NAEI 1970 to 2001, Zhang and Tao 2009). Moreover other studies show that diesel combustion (in generators or vehicles) can be considered as a major determinant for high PAH levels in the air (Barakat 2001), whereas, industrial sources (incineration and power plant) (paper 2001, Dyke, Foan et al. 2003) contributed less than 10% to the total PAH emissions (Zhang and Tao 2009).

Different PAH sources usually produce different congener distribution. Heavy-duty diesel vehicles (diesel trucks) mark the coexistence of 3-benzene rings light PAHs such as phenanthrene, fluoranthene and pyrene, whereas light-duty gasoline vehicles are the dominant sources of 4 to 5-benzene rings heavy PAHs like benzo[a]pyrene and

benzo[k]fluoranthene (Miguel, Kirchstetter et al. 1998). In addition, waste incinerators may be a significant source of some high molecular weight PAHs such as chrysene, dibenz[a,h]anthracene and benzo[g,h,i]perylene (ROY J. IRWIN 1997, addo 1999, Ravindra, Bencs et al. 2006) and power plant emissions are the major source of mainly heavy PAHs like benzo[k]fluoranthene, benzo[a]anthracene, benzo[a]pyrene and chrysene (Yang, Lee et al. 1998, Chmielewski, Ostapczuk et al. 2010).

Being ubiquitous in the atmosphere and of potent hazard to health, PAH concentrations are one of the pollutants that have been regularly analyzed in many countries around the globe. In this study, levels that have been reported in the Mediterranean Basin (Figure 1.3) are compiled in (Table 1.2).



Figure 1.3: Highlighted and named countries are the ones that were reviewed for their PAH levels and reported in Table 1.2

PAH concentrations are found to be low in Portugal, Italy and Spain. They range between 0.4-14.76 ng/m³. Higher levels of PAHs are observed in Tunisia, Greece and Algeria with an average of around 60 ng/m³. The highest levels of PAHs are reported in Egypt and Turkey reaching up to 1770 and 1672 ng/m³ respectively.

Out of this review, we can see that PAH levels are not the same all over the Mediterranean region because they highly depend on the local emission sources, population and geography characterizing each country. Furthermore, these reported data are mainly elaborated by the countries located in the western European region, which reflects the poor assessment of these chemicals in the Middle East and North Africa (MENA).

Table 1.2: The minimum and maximum PAH concentration reported in different cities and countries of the Mediterranean region

Cities/Countries	Date	ΣPAHs ng/m³	Reference
Alexandria (Egypt)	2013	170-1770	(Khairy and Lohmann 2013)
Algeria (Algeria)	2010	8.00-87.00	(Khedidji, Ladjji et al. 2013)
Bursa (Turkey)	2004-2005	28.6-1672	(Esen, Tasdemir et al. 2008)
Athens (Greece)	2001-2002	0.191-52.16	(Mantis, Chaloulakou et al. 2005)
Urban areas of Italy	2000-2006	0.52-14.76	(Amodio, Caselli et al. 2009)
Bizerti (Tunisia)	2009-2010	9.38-44.81	(Hassine, Hammami et al. 2014)
Barecelona (Spain)	2008-2009	0.4-4.3	(Mesquita, van Drooge et al. 2014)
Potugal	2001	3.00-10.00	(Alves, Pio et al. 2001)

C. Persistent Organic Pollutants (POPs)

Persistent organic pollutants (POPs) are a family of chemicals present in the atmosphere in gaseous and aerosol phases. They are persistent in the environment, because of their long half-lives in soils, sediments and air (Jones and De Voogt

1999). Consequently, atmospheric transport constitutes an important pathway for their wide distribution. In addition to their levels in air, water and soil, concerns center on POPs' impact on human health and wildlife because they can bioaccumulate in the foodchain.

Amongst the important classes of POPs are many chemical families (Stockholm Convention 2004): pesticides including Aldrin and mirex, industrial mainly polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/PCDF). Only PCDD/Fs will be addressed in this study.

D. Dioxins and Furans

A potent class of POPs is "dioxins". This term refers to two categories of differently chlorinated compounds of 75 PCDDs and 135 PCDFs. While all dioxins (PCDD/Fs) are considered persistent organic pollutants, seventeen specific congeners are the most toxic, all of which are 2,3,7,8 chlorine substituted (Figure 1.4). They exist in environmental and biological samples as complex mixtures of various congeners and are transported on a global scale, often through a succession of gas partitioning, air-water and air-soil exchanges (Barrie, Macdonald et al. 1997). Depending on their physical and chemical properties and on the meteorological factors (addo 1999), these components travel in the atmosphere distances ranging between few meters to several kilometers. During their transport, PCDD/Fs can be removed by reactions or by deposition. Dioxins are produced from anthropogenic activities that include thermal processes, incineration and industrial treatment using chlorine (Rappe 1993).

PCDD/Fs' hydrophobicity and resistance towards metabolism permit their diffusion to fatty tissues of animals and humans. Several PCDDs and PCDFs have been shown to cause toxic responses involving dermal toxicity, immunotoxicity, and carcinogenicity. They were recognized also to have adverse effects on reproduction, development and endocrine functions (Van den Berg, Birnbaum et al. 1998). According to WHO, 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) is most potent congener among PCDDs (WHO 1998).

PCDD/Fs ambient monitoring has been carried out in several countries in order to quantitate these pollutants as well as to help sanitary authorities to take actions (Martínez, Abad et al. 2006) because they were recognized by several health organizations to have potential effects on human health (Vallack, Bakker et al. 1998). Based on our literature review, there is a lack of adequate monitoring data and assessment tools in our country and the Middle East and North Africa (MENA) region. So this work tends to fill the gap of knowledge regarding the levels of such species.

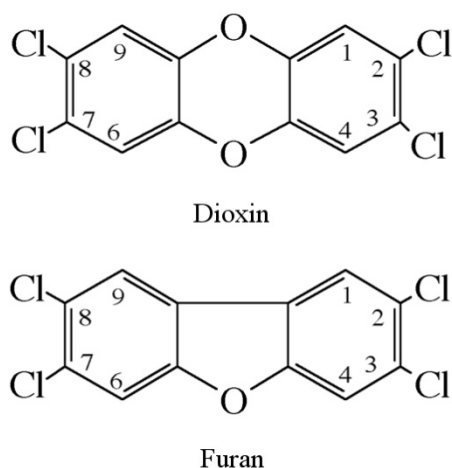


Figure 1.4: Basic structure of dioxins and furans chlorinated at the 2,3,7,8-positions

E. Objective of this Study

This study aims to determine the levels of PAHs and one of the POPs family; particularly dioxins, in the capital Beirut and in two of the coastal and industrial suburban areas (Dora and Zouk). The study will also assess the PCDD/Fs and PAHs spatial variation between the sampling sites. It will also investigate the temporal variation of PAHs within the same site in the three sites. Based on the different congener distribution in each site, this work will present a source apportionment analysis using Positive Matrix Factorization (USEPA PMF) and determine the exposure risk associated with PAH levels in the different sites.

F. Thesis Layout

This presented work consists of eight chapters. Starting in Chapter 1 with an overview of pollutants sources, fates and concentrations in the region. Chapter 2 describes the experimental procedures used to collect, extract and quantify the analytes in question. In Chapters 3 and 4, the spatial variations of PAH and dioxin levels in three representative sites (AUB, Dora and Zouk) are presented. Results provide an accurate and deep understanding of the distribution pattern of these congeners. The temporal variation of PAH is also included and gives a good interpretation of the weather impacts on PAH sources and fates. Chapter 5 elucidates the influence of the Zouk power plant emissions on the residential area surrounding it. In this chapter, a scientific deep study was adopted in order to track the emitted toxins and deploy samplers in the representative sites. The source apportionment of PAHs using the USEPA-PMF model

is detailed in Chapter 6. The computation helps to attribute each source to the corresponding PAH marker and therefore assign contribution of different sources in each site. In order to link the results to health risk assessment, Chapter 7 compiles the estimation of the cancer risk after exposure to PAHs and dioxins in order to report the Incremental Lifetime Cancer Risks (ILCRs). An evaluation of the collected data including a summary of the results is shown in Chapter 8.

CHAPTER II

COLLECTION AND ANALYSIS

A. Introduction

The field measurement studies rely on several analytical steps starting with the collection of a representative sample and followed by extraction, analysis and quality evaluation. These mechanisms are crucial and are, when available, based on standard operating procedures (SOPs) that are internationally recognized. In this study, two collection techniques (high volume and low volume sampling) were adopted each with its appropriate extraction procedure. The high volume sampler was used in the spatial and temporal assessment of PAHs and PCDD/Fs whereas the low volume sampling was more feasible in the power plant study (Chapter 5) because six sampling instruments were used simultaneously.

B. Sampling Method for the Ambient Measurements of PAHs and Dioxins Using the High Volume Sampler (HVS)

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 10 µm diameter. Particles larger than 10 µm in diameter are removed through impaction in the buffer chamber as shown in figure 2.1. A quartz fiber filter (Whatman, 150 mm) collects particle-bound compounds and a polyurethane foam (PUF) 6.0-cm diameter cylindrical

plug with 3-inch thick retains compounds in the gaseous phase. Prior to sampling, PUFs were cleaned using soxhlet extraction for 16 hours at approximately 4 cycles/hour with acetone. Quartz-fiber filters were baked in a furnace oven at 400 °C for 5 hours to remove adsorbed organic compounds. Post-sampling, both the PUF and the filter are wrapped in baked aluminum foils and stored at -20 °C before analysis.



Figure 2.1: from left to right: the high volume sampler, the sampling probe, and the filter and PUF compartments constituting it

C. Sampling Method for the Ambient Measurements of PAHs Using the Low Volume Sampler (LVS)

Particles with aerodynamic diameter equal or less than 10 μm were sampled using a PM₁₀ inlet (chemcomb Model 3500 Speciation Sampling Cartridge, Thermo electron Corp., Ohio, USA) low volume sampler (LVS) at a flow rate of 10 L/min (Figure 2.2). Samples are collected on Teflon (STERLITECH, 47 mm) and glass fiber filters (STERLITECH, Grade B, 47 mm) of 47 mm diameter. Prior to sample collection, glass fiber filters were baked in the furnace oven at 400 °C for 5 hours. In each site, six 24-hr replicate samples were taken during six consecutive days. Post-sampling all filters were stored at -20 °C for no more than one week before being analyzed.



Figure 2.2: From left to right: the low volume sampler parts and setup

D. The Gravimetric Analysis

The mass of collected particles was determined by gravimetric analysis of the Teflon filters using UMX2 microbalance (Mettler Toledo GmbH, CH-8606 Greifensee, Switzerland). Filters are conditioned under controlled temperature and relative humidity for 24 hours before the pre-weighing and post-weighing process. Glass fiber filters were used for the PAH analysis while the teflon filters were used for the ion analysis.

E. Extraction Procedure of Samples Collected with High Volume Sampler (HVS)

Collected samples on filters and PUFs are spiked with internal standards and extracted using a mixture of 300 mL of diethyl ether and hexane by soxhlet extraction adjusted at an evaporation-condensation rate of 2 drops/s for 18 hours. The extract is then rotary evaporated down to 10 mL and reduced further under nitrogen flow to 1 mL. The 1 mL extract is cleaned and concentrated using solid phase extraction (SPE) column followed by nitrogen evaporation, respectively, prior to Gas Chromatography (GC) analysis.

F. Extraction Procedure of Samples Collected with Low Volume Sampler (LVS)

For the determination of PAH concentration, the adopted extraction method is based on the standard operating procedure (SOP TC AA100-1) developed in the Atmospheric and Analytical Laboratory (AAL) at AUB. In brief, the sampled glass fibre filter was spiked with a known amount of the internal standard solution, placed in a 10 mL glass vial to which 8 mL of toluene was added. The vial was then sonicated at 40 °C for 2 hours and then shaken for 30 minutes at medium rate. The volume of the extracted solution was reduced under a nitrogen flow to 1 mL, loaded on a pre-conditioned SPE silica cartridge and eluted with 6 mL of hexane. The eluted solution was concentrated further and the volume was reduced over a gentle nitrogen flow to 200 µl and then transferred to GC vials for analysis.

For the ionic analysis, teflon filters were cut into two equal portions. To one portion, 20 mL fresh double distilled water were added and the filter and solution were sonicated for 40 minutes. The extract was then filtered through a 0.2 µm nylon syringe filter into a glass vial and subjected to Ion Chromatography (IC) analysis to account for sulfates.

G. Chromatography Analysis

1. Gas Chromatography

All prepared samples were analyzed using gas chromatography-mass spectrometry (GC-MS) (Thermo Scientific). The analysis method was adopted from the USEPA compendium TO-13A method. The chromatographic separations were carried

out on a 5MS column (60m × 0.25 mm, 0.25 μm film thickness) using helium (1mL/min) as the carrier gas. The injector was operated in split-less mode 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 source temperature was 250 °C in electron impact mode (70 eV). The mass spectrometer was operated under selected ion monitoring (SIM) mode.

2. Ion Chromatography (IC)

Ion chromatography (IC) was used to determine sulfate concentration in the extracts from teflon filters. Chromatographic analysis were done using Dionex ICS-1100 machine. The eluent (4.5 mM Na₂CO₃/ 1.4 mM NaHCO₃) was introduced at a flow rate of 1.2 ml/min with a sample injection volume of 10 μl. Separations were performed using the Dionex anion exchange analytical column IonPacTM AS22 (250 × 4 mm). For data acquisition, the instrument is linked to Thermo Scientific Dionex Chromeleon program. Chromeleon 7, released by Dionex, is a chromatography data system (CDS) software that combines ionic chromatography and mass spectrometry. It controls, process and manage data from chromatography. Also, it identifies and visualizes all chromatographic data into peaks.

H. Quantification

Using PAH reference standards at concentrations ranging between 0.05 and 10 ppm and an internal standard of 2 ppm, a seven-points calibration curve was prepared. Correlation factor (R^2) ranged between 0.995 and 0.999. The unknown concentration

(x) was computed as follows: $x = \frac{y' - b}{a}$ where a, b and y' are the slope, the intercept and $y' = \frac{Area[unknown]}{Area[IS]}$, respectively.

A five-points calibration curve, ranging from 0.01 to 0.5, was prepared for the IC with a correlation factor greater than 0.995. The areas for standards constituted the y-axis and the standards concentrations constituted the x-axis. Thus, the unknown concentration (x) is equal to $x = \frac{y'' - b}{a}$ where a, b and y'' are the slope, the intercept and $y'' = y' = \frac{Area[unknown]}{Area[IS]}$.

I. Quality Control/Quality Assurance (QC/QA)

All extracted and laboratory analyzed data were subject to strict quality control procedures. Only certified reagent grade solvents and standards were used for analysis. Recovery was calculated for the solid-phase extraction, rotary evaporation and soxhlet extraction steps. The filter and PUF combined were spiked with 2-ppm concentration of standard and internal standard solutions. The recovery of the whole extraction method determined by comparing theoretical to experimental results ranged between 65 up to 128%. Repeatability was determined by running four consecutive samples of 2 ppm each during the same day. Results showed that the relative standard deviation ranged between 1.4 and 8.2 %. The limit of detection (LOD) of this method was defined as the lowest quantity of a substance that can give a detected signal on the chromatogram. LOD was calculated based on the standard deviation (s) of seven replicates and the slope (m) of a seven-points calibration curve ($LOD = 3s/m$). LOD values ranged between 8 to 38 pg/m^3 . The limit of quantification (LOQ) for this method was defined as the lowest amount of a substance that can be quantitatively determined with suitable

accuracy and precision. LOQ is expressed as: (LOQ = 10s/m), and its values ranged between 38 and 125 $\mu\text{g}/\text{m}^3$.

Moreover for the IC, repeatability was as well determined by running 4 consecutive aliquots of 0.5 ppm each. The relative standard deviation was below 10%. The limit of detection and quantification of 7 aliquots of sulfates were 6 and 17 $\mu\text{g}/\text{m}^3$, respectively.

CHAPTER III

SPATIAL AND TEMPORAL ASSESSMENTS OF PAHs

A. Introduction

Polycyclic aromatic hydrocarbons are highly toxic and are considered important organic pollutants in the ambient air. When they are released into the atmosphere, they will partition into three different phases; the gases (e.g., 2-ring volatile congeners), the semivolatile (e.g., 3-ring compounds) and the solids, which are adsorbed to the surfaces of, fine aerosol particles (e.g., 4- to 6-ring congeners). Gases and semivolatile congeners constitute light PAHs whereas solids components form the heavy ones.

In the atmosphere, PAHs can be subject to many processes that induce their depletion (N.Pitts 2000) and affect their levels. These processes include dilution, volatilization, accumulation on sediments or in water and photodegradation. This latter involves the transformation of mainly light PAHs to different intermediate products and is highly influenced by the sunlight intensity (Arey, Zielinska et al. 1967).

Seasonal differences in environmental conditions including rain, temperature and wind speed affect the rate of the aforementioned depletion processes and therefore the distribution pattern of PAHs in the atmosphere. The magnitude of PAH pollution depends as well on the sampling location and the type of the contributing source in each site (Menichini, Monfredini et al. 1999, Mastral, López et al. 2003, Li, Porter et al. 2009).

In order to have an insightful description of PAH behavior in our ambient region, we conducted a spatial and temporal study of PAHs in Beirut and its suburbs. This study is the first comprehensive PAH analysis in Lebanon.

B. Study Area

Ambient measurements were carried out on three different sites (American University of Beirut; AUB, Zouk and Dora) (Figure 3.1) of Beirut and its suburbs in winter (January-March 2015) and summer (June-July 2015) (Table 3.1). Site 1 is considered an urban background site and is situated on the rooftop of the chemistry department at AUB. AUB is surrounded by dense greenery and separated from the sea by a road-way experiencing relatively light traffic. Site 2, so representative of an urban residential site, is located on the balcony of the Zouk Mikael Municipality. The city of Zouk Mikael lies along the Lebanese coast with a population of 350,000. It has an area of 3.1 Km², looks westward over the sea and is surrounded from the north by Sarba village, from the east by Antoura, and from the south by Zouk Mosbeh. Site 3 is the balcony of Audi bank in Dora, one of Beirut's highly polluted suburbs. This sampling site is adjacent to the highway that is continuously experiencing heavy traffic with increased congestion throughout the day. In this campaign, eleven 24-hour samples were collected from each site according to the collection technique previously discussed in Chapter 2.

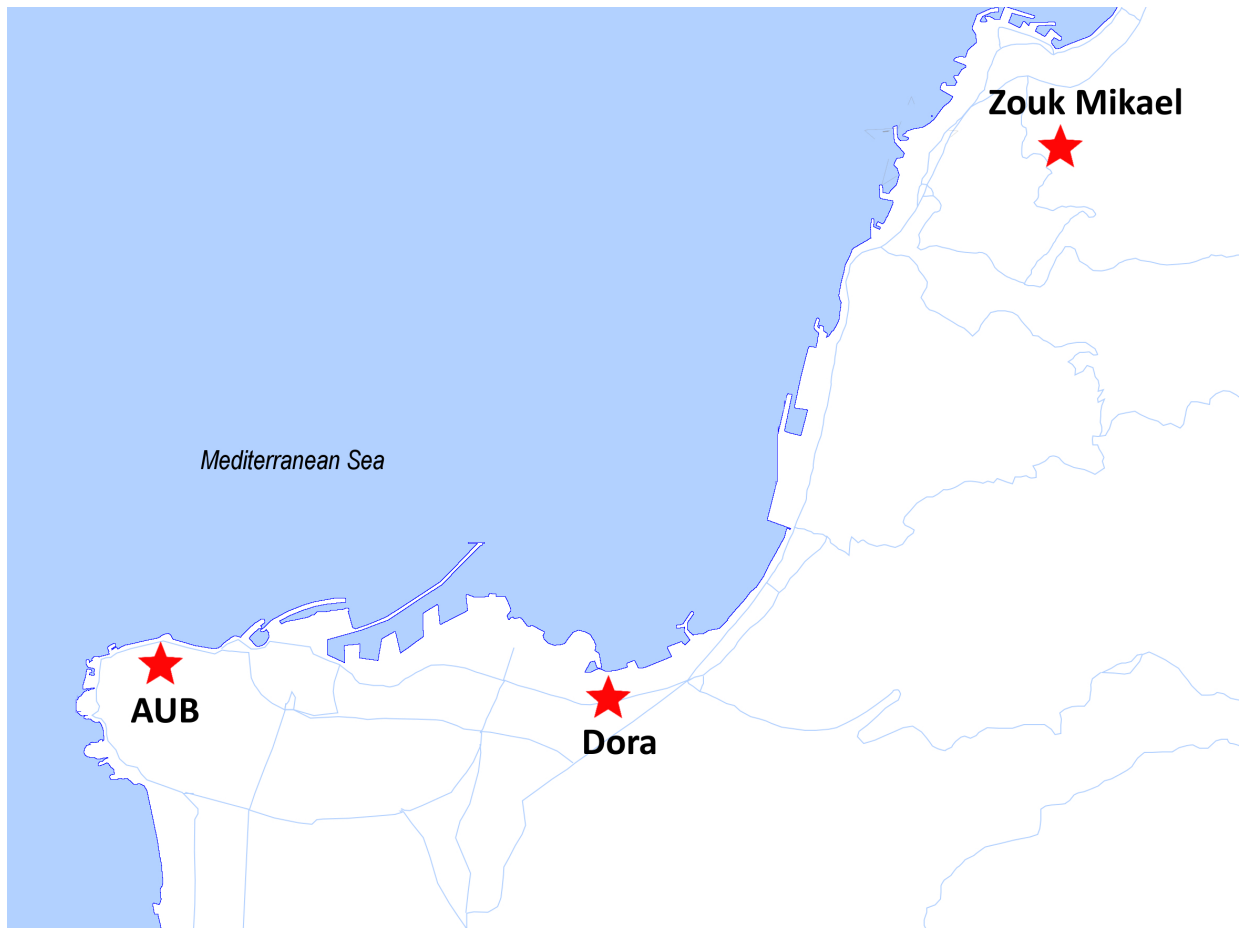


Figure 3.1: Labeled are the sampling sites of our study

Table 3.1: Reported are the sampling dates at AUB, Zouk and Dora during the winter and the summer of the year 2015

	Winter-2015	Summer-2015
AUB	January 19-22 and 27	June 16-18, 22 and 24
Zouk	February 2, 4, 5, 17 and 26	July 6-11
Dora	March 4, 5, 9, 16 and 17	July 15,16 and 20-23

C. Results and Discussions

1. Inter-sites spatial and temporal comparison

The average total PAH concentrations, (Σ PAHs), at the three sampling sites varied from 13 to 69 ng/m³ during summer with the highest concentration recorded in Dora (Figure 3.2). Dora is a highly populated suburb directly affected by various emission sources including heavy traffic and had PAH levels 550% higher than AUB and 160 % than Zouk. However, concentrations were not enough for toxicity assessment the reason why comparisons between sites will be based on toxicity equivalents TEQ where $TEQ = TEF \times C_i$. PAH TEQ were comparable between Dora and Zouk which means that heavy toxic PAH components have high concentrations in Zouk.

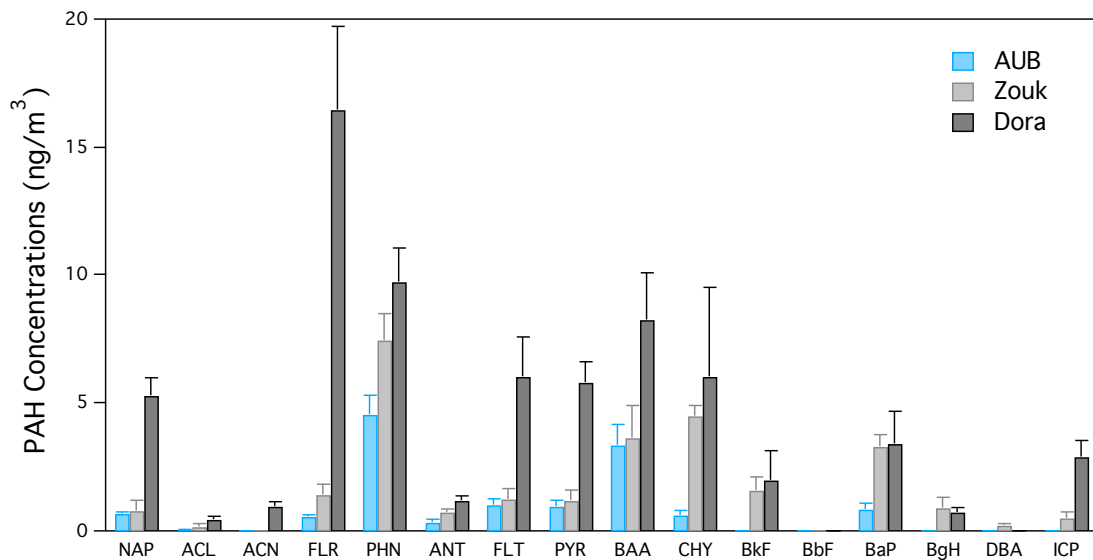


Figure 3.2: Σ PAHs concentrations in AUB, Zouk and Dora during summer 2015

2. Intra-site temporal comparison

A temporal evaluation within the same site is discussed in this part. The seasonal profiles of the light and heavy PAHs are compared separately.

At AUB (Figure 3.3), volatile and semivolatile PAH levels reached around 29 ng/m³ during winter and around 7 ng/m³ during summer. Moreover, particle-associated PAHs were almost the same in both seasons: 7 ng/m³ during winter and 5 ng/m³ during the summer season. These high PAH levels during winter may be attributed to the occurrence of an inversion layer and increase in domestic heating. Results were in accordance with results reported in literature (Greenberg, Darack et al. 1985, Baek, Field et al. 1991, Menichini 1992, Harrison, Smith et al. 1996, Caricchia, Chiavarini et al. 1999). Furthermore, this major difference among light PAHs between winter and summer can be explained on one hand by the increase in PAH emission for the same reasons stated above and on the other hand by the fact that their decay rates increase enormously during summer because of the significance of their photodegradation.

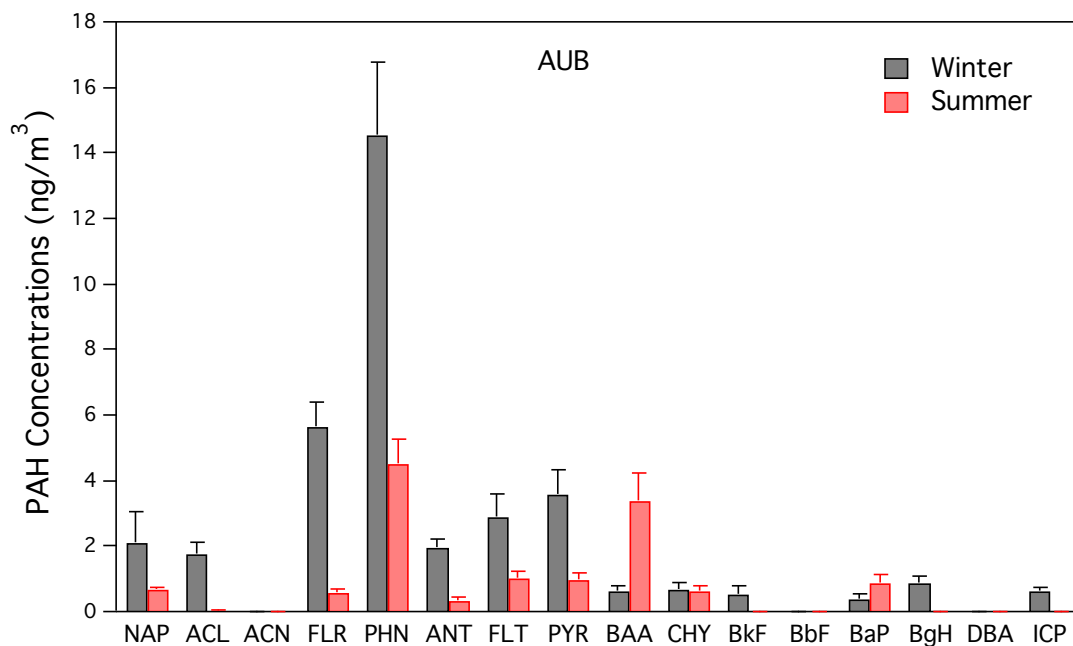


Figure 3.3: Light and heavy PAH seasonal profile at AUB

As shown in figure 3.4, light components in Dora reached up to 65 ng/m³ in winter in comparison with 40 ng/m³ in summer for the same aforementioned arguments. In contrast, heavy PAH concentrations in the summer exceed by 2 ng/m³ those registered in winter because of the higher levels of heavy benzo[a]anthracene and chrysene that are markers of incinerators which might become more frequent during the summer season. This suggestion is confirmed in the source apportionment study presented in Chapter 6.

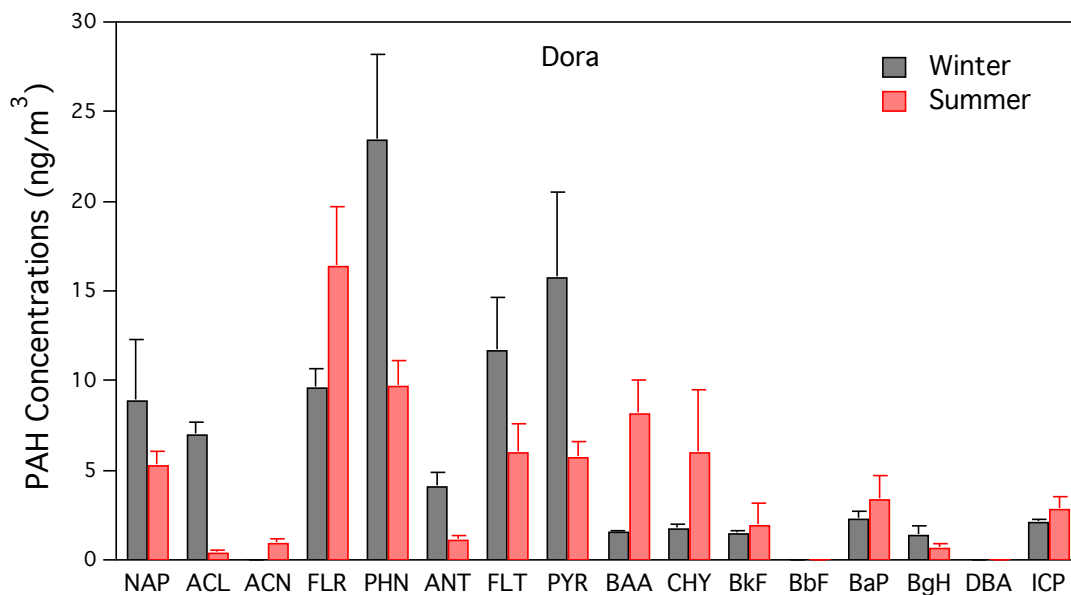


Figure 3.4: Light and heavy PAH concentrations in Dora during the winter and the summer

As shown in Figure 3.5, the same trend of light PAHs was observed in the Zouk for the same previously stated reasons. But, this time the higher levels of the heavy ones is caused by a remarkable increase in benzo[a]pyrene concentrations; from 0.8 ng/m^3 in winter up to 3.3 ng/m^3 in summer as well as in benzo[a]anthracene and chrysene. The elevation of these heavy congeners marks the emission from a heavy fuel oil combustion source, mainly the power plant. Levels are more concentrated in summer due to stagnant weather conditions with minimal dilution contrary to what is expected to happen in winter.

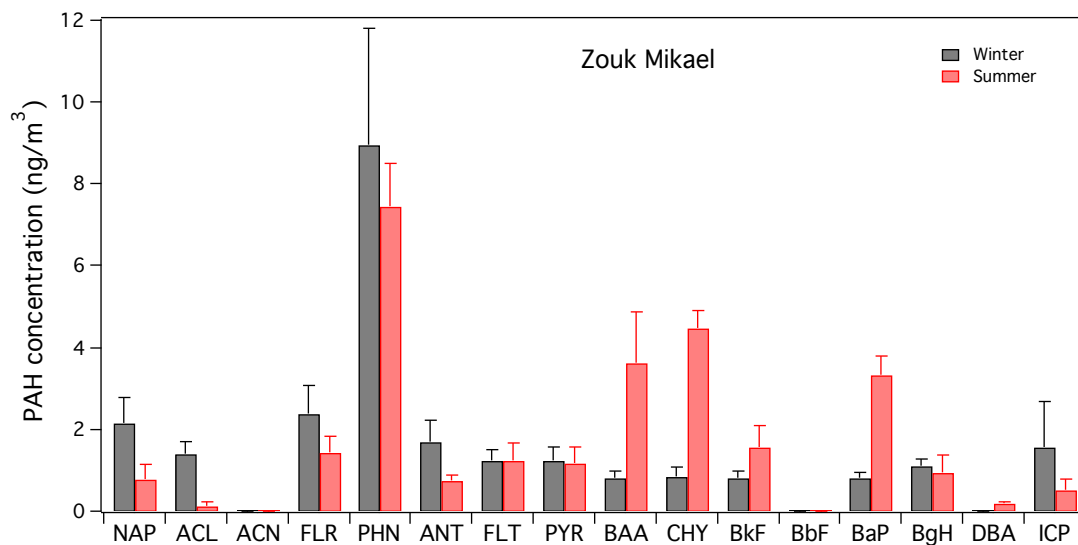


Figure 3.5: Light and heavy PAH seasonal profile in Zouk

D. Conclusion

Based on the data showed above, it can be noted that the effect of the spatial and temporal variation on the PAH distribution pattern. Temperature, wind direction and speed, and the emission sources of each site control the PAH fate and behavior in the atmosphere.

CHAPTER IV

SPATIAL ASSESSMENT OF DIOXINS

A. Introduction

The Stockholm Convention on Persistent Organic Pollutants (POPs) is an international settlement to protect human health and the environment from chemicals of global concern due their persistence in the environment, their long-range transport and their ability to bio-accumulate in ecosystems and mainly in humans (UNEP 2013). The long-term exposure even to low levels of PCDD/Fs can lead to increased cancer risk, alteration of the immune system and reproductive disorders. No one government alone can protect its citizens or its environment from dioxins because of their long range transport. In response to this global problem, the Stockholm Convention on (POPs) calls for elimination of these hazardous components. The lack of experimental data and the reported estimated increase of 114% between 1998 and 2004 of dioxin emissions in Lebanon (Jawdeh 2006) was alarming. We were therefore motivated to conduct a monitoring evaluation of these chemicals that was the first in the Middle East and North Africa (MENA) region.

B. Study Area

Ambient measurements were carried out on three different sites (AUB, Zouk Mikael and Dora) of Beirut and its suburbans in the summer (June-July 2014). Considered an urban background site, site 1 is situated at the roof of the chemistry building at AUB. Site 2 is an urban residential site located on the rooftop of the

Basiliat -Chouerites nunnery in Zouk Mikael. Whereas site 3, which well describes an urban/industrial environment, is situated on the balcony of Audi Bank in Dora. In each site, three 24-hours samples were collected using the high volume sampler. For the analysis method, please refer to Chapter 2 and for site description, kindly refer to Chapter 3.

C. Results and discussion

We attempted to quantify Dioxins and Furans in the air in our lab. Specificity was attained for the quantitative determination of the seventeen most toxic 2,3,7,8-substituted PCDD/Fs congeners (Table 4.1). However, since our GC-MS system is a low-resolution program, we weren't able to differentiate between isomers having such close retention time on the GC spectrum. In order to have a better idea of the distribution and levels in Lebanon, the samples were sent to the ALS Environmental Laboratory in the United States of America (USA) that uses high resolution GC and MS (HRGC-HRMS).

Ambient air average concentrations of the three samples of 2,3,7,8-substituted PCDD and PCDF congeners in the gas and particulate phase are provided in Figure 4.1. The total average concentration determined in the urban background area of Beirut (AUB) was 0.086 pg/m^3 much lower than in the urban residential center (Zouk) that reached 0.125 pg/m^3 and this latter was slightly lower than the one recorded in Dora of about 0.145 pg/m^3 . It is noted that no amounts of the most potent congener 2,3,7,8-TCDD was observed in any of the sampling sites.

The total mean concentration measured in the urban area of Beirut was about 0.135 pg/m^3 . This concentration is lower than the corresponding concentration

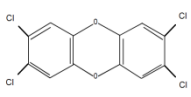
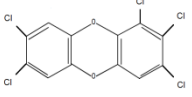
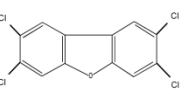
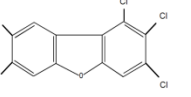
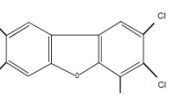
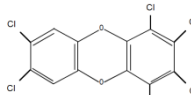
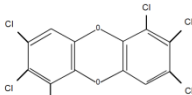
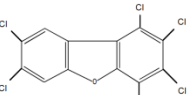
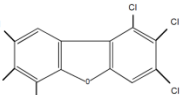
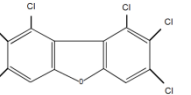
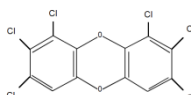
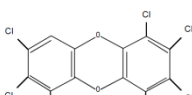
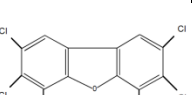
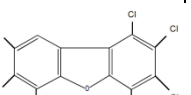
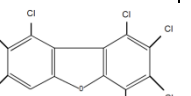
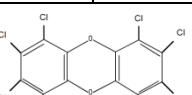
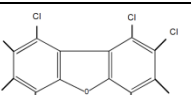
measured in Athens of 0.7 pg/m³ (Mandalakis, Tsapakis et al. 2002) and Manchester of 2.1 to 17 pg/m³ (Lohmann, Harner et al. 2000).

In order to express the toxicological relevance of these PCDD/Fs amounts, total concentrations were also calculated on a Toxicity Equivalence Quotient (TEQ) basis. TEQ expresses the toxicity of specie based on a toxicity equivalence factor (TEF) relative to the most toxic component. TEQ are obtained by multiplying the analyte concentration by its corresponding TEF. The WHO TEF values for humans/mammals are reported in (Table 4.3). The average TEQ-values measured in AUB, Zouk and Dora were 0.3, 4.9 and 2.7 fg/m³ respectively. Consequently, Zouk was the highest toxically influenced site by PCDD/Fs emissions eventhough it has a lower mean concentration than that measured in Dora.

D. Conclusion

In light of these findings, the measurable levels of PCDDs and PCDFs observed in the sampling sites were low, still regulations should be taken into account in order to reduce the levels even further because as it was stated by the Stockholm Convention the long exposure to even low levels can induce severe health effects (StockholmConvention 2004).

Table 4.1: The chemical structures of the 17 most toxic congeners of PCDD/Fs

PCDDs			PCDFs		
					
2,3,7,8-TCDD	1,2,3,7,8-PeCDD	2,3,7,8-TCDF	1,2,3,7,8-PeCDF	2,3,4,7,8-PeCDF	
					
1,2,3,4,7,8-HxCDD	1,2,3,6,7,8-HxCDD	1,2,3,4,7,8-HxCDF	1,2,3,6,7,8-HxCDF	1,2,3,7,8,9-HxCDF	
					
1,2,3,7,8,9-HxCDD	1,2,3,4,6,7,8-HpCDD	2,3,4,6,7,8-HxCDF	1,2,3,4,6,7,8-HpCDF	1,2,3,4,7,8,9-HpCDF	
					
1,2,3,4,6,7,8,9-OCDD					1,2,3,4,6,7,8,9-OCDF

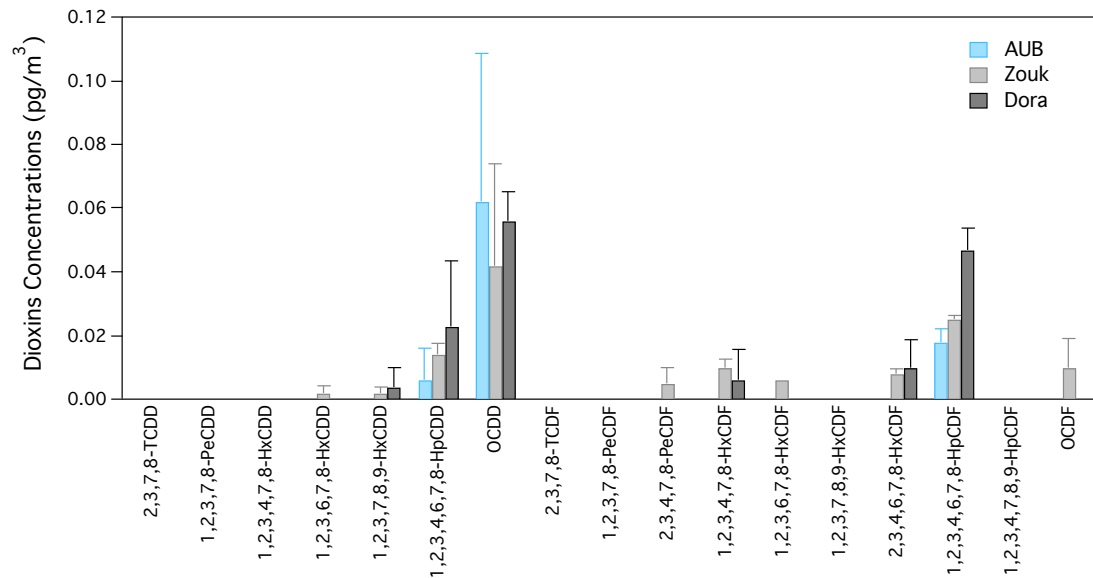


Figure 4.1: Dioxin Concentration at AUB, Zouk and Dora during summer 2014

Table 4.3: WHO TEF for the analyzed PCDD/Fs

Analyte Name	TEF
2,3,7,8-TCDD	1
1,2,3,7,8-PeCDD	1
1,2,3,4,7,8-HxCDD	0.1
1,2,3,6,7,8-HxCDD	0.1
1,2,3,7,8,9-HxCDD	0.1
1,2,3,4,6,7,8-HpCDD	0.01
OCDD	0.0003
2,3,7,8-TCDF	0.1
1,2,3,7,8-PeCDF	0.03
2,3,4,7,8-PeCDF	0.3
1,2,3,4,7,8-HxCDF	0.1
1,2,3,6,7,8-HxCDF	0.1
1,2,3,7,8,9-HxCDF	0.1
2,3,4,6,7,8-HxCDF	0.1
1,2,3,4,6,7,8-HpCDF	0.01
1,2,3,4,7,8,9-HpCDF	0.01
OCDF	0.0003

CHAPTER V

INFLUENCE OF THE ZOUK POWER PLANT EMISSIONS ON TOXIN AMBIENT LEVELS IN THE ZOUK AREA

A. Introduction

The electrical power plant in Zouk Mikael, which was built in 1956, was first operated in 1983. The plant is equipped with four turbines and four stacks running on Heavy Fuel Oil (HFO-6; density of 971 kg/m^3) continuously at an average of 2.5 units per day (Lebanon Electricity Board). Each operating unit burns 40 tons of HFO per hour to produce a calorific value of 42000 mega-joules/ton (Weather Forecast and Pollution Investigation for Lebanon report, FEA, AUB, 2015). Reported emission amount to ~1800 Kg of total suspended particle per day from which expected air pollutants with potentially significant toxicity by the World Health Organization (WHO) are particulate matter (PM), particle bound Polycyclic Aromatic Hydrocarbons (PAHs), a type 1A PAH carcinogen; Benzo[a]pyrene (BaP), and Sulfur dioxide; (SO_2) (Millman, Tang et al. 2008).

Sulfur dioxide is a product of heavy fuel combustion. The heavy fuel oil usually used in power plants contains at least 2000 times more sulfur than road fuel. Upon combustion, sulfur contained in fuel causes emissions of SO_2 and also contributes to PM levels and their content in sulfates (SO_4^{2-}). SO_2 emissions cause environmental problems such as acid rain affecting soil and water and damage to cultural monuments, churches and the Zouk-old souk.

The continuous emissions of black fumes from the power plant stacks and the association of these fumes with increased hospital admission as well as reported 80

cancer cases/year (Degagements Toxiques de la Centrale Thermo-Electrique de Zouk Mikhael report, Dr. Paul Makhoul, 2014) alerted the ~350,000 residents living in the areas surrounding the Zouk Mikhael plant. The growing concerns of local residents from increased toxin levels in the area led to this study where levels and distribution of ambient heavy fuel combustion markers in the air emitted by the Zouk power plant are assessed. In particular, PM₁₀ distribution profile due solely to the power plant is generated using The Air Pollution Model (TAPM) software and ambient concentrations of PM₁₀, PAHs and SO₂ were determined.

B. Study Area

The Air Pollution Model (TAPM) is a software that predicts weather patterns and combines it with atmospheric chemical reactions to show pollutant transport. TAPM was used to model the Zouk power plant contribution to the pollution in the nearby region, using the emissions data that we have collected from Electricite Du Liban (EDL) engineers. After loading the surface information, synoptic data, and pollutant physical parameter and flow rate, TAPM tracked the PM₁₀ concentrations based on a simple tracer method in the selected region and for the year of 2014. Two distinct zones that have the highest concentration of PM₁₀ were identified. Based on this simulation, instruments were deployed on three representative zones (Figure 5.1). Zone 1 and Zone 2 refer to the most and second-most influenced regions by the power plant, respectively. Zone 3 is the least affected area and is considered as an urban background site for reference. Zone 1 is located at the rooftop of Jean Nakhoul Real State Building in Zouk Mikhael and referred to as the Z.Mikhael site and Zone 2 at the rooftop of Yassou' al-Malak building in Zouk Mosbeh and designated as the Z.Mosbeh site. Zone

3 is located at the rooftop of the chemistry department at AUB and is denoted as AUB site.

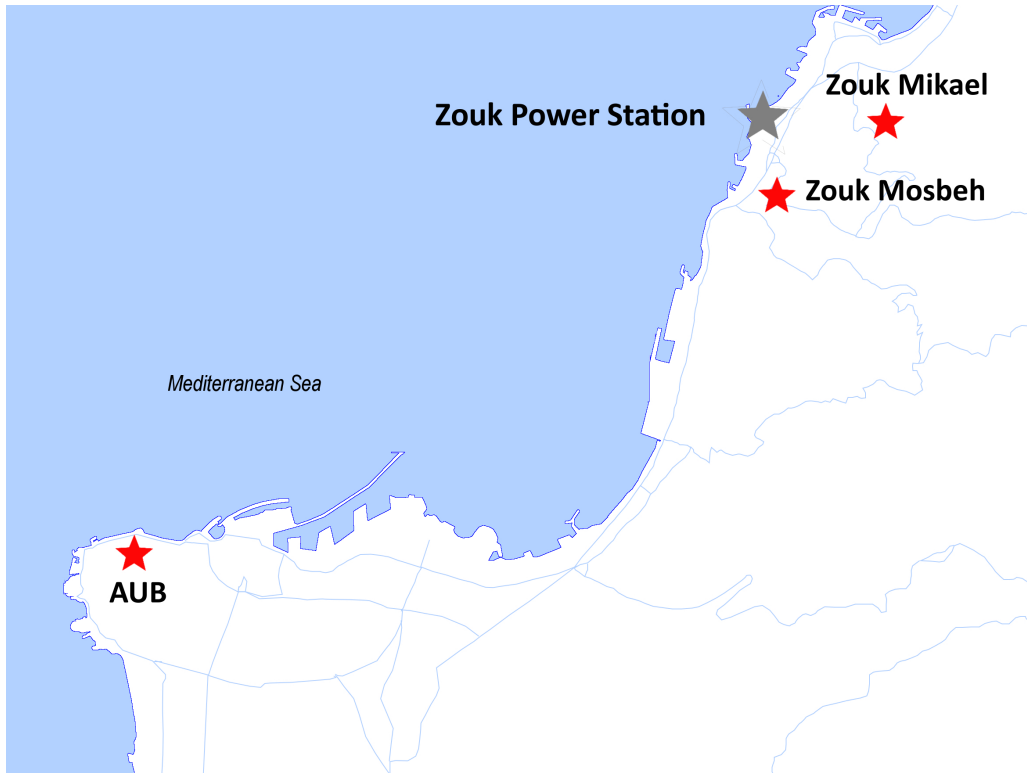


Figure 5.5: The site locations in Zone 1; Z.Mikael, Zone 2; Z.Mosbeh and Zone 3; AUB

C. Results and Discussion

1. Levels of PM_{10}

Figure 5.2 shows the box and whisker plot of PM_{10} concentrations measured at the three sites; Z.Mikael, Z.Mosbeh and AUB. In this plot, the bottom and top of the box represent the 25th and 75th percentiles, respectively. The band near the middle of the box represents the median or 50th percentile, while the whiskers represent the minimum and the maximum concentration. From this graph, it is deduced that a slightly higher

PM₁₀ levels of 53 µg/m³ is calculated for the Z.Mikael region. Both Z.Mosbeh and AUB exhibited similar concentrations within the experimental margin of error.

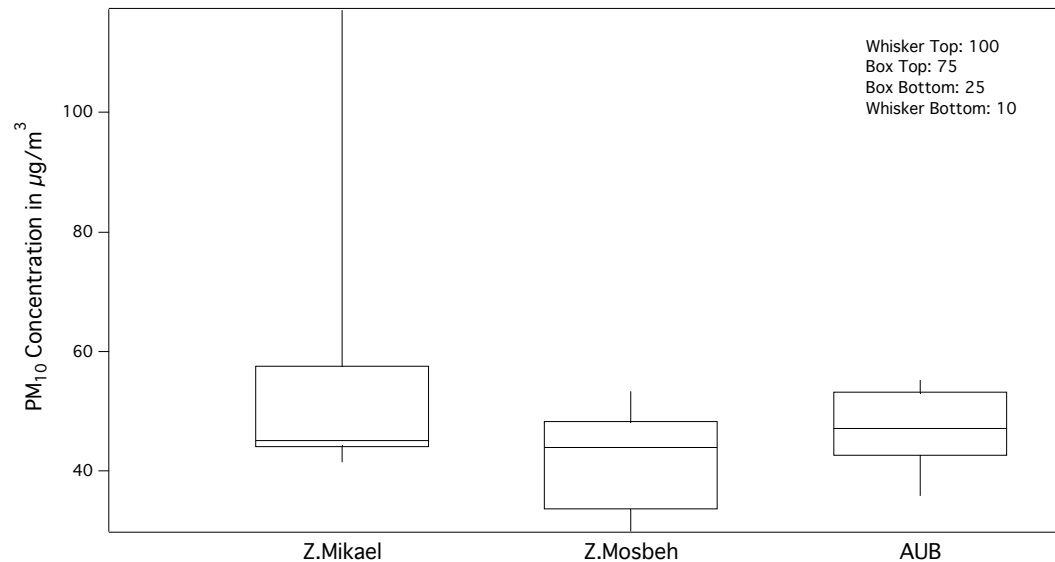


Figure 5.2: Box-and-whisker plot of the concentration of PM in the ambient air of three representative sites: Z.Mikael, Z.Mosbeh and AUB

2. Levels of PAHs

The variation of the sum of the 16 PAH priority pollutants (Σ PAHs) among the three sites are shown in Figure 5.3. A clear difference in the mean Σ PAH concentration is shown between Z.Mikael and Z. Mosbeh from one side and AUB from the other. It is also evident that AUB site exhibits the lowest mean Σ PAH concentration; values consistent with its location and hence its choice as a background site.

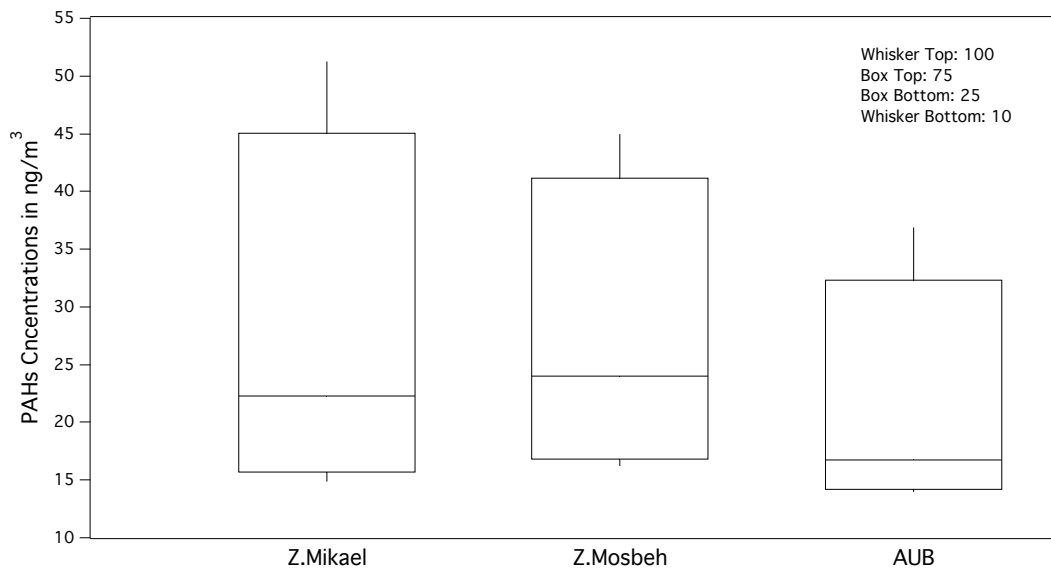


Figure 5.3: Box-and-whisker plot of the concentration values of total PAH Σ PAH measured in Z.Mikael, Z.Mosbeh and AUB

3. Levels of BaP

Benzo[a]pyrene (BaP) is considered one of the most toxic PAH congeners. It is classified by the U.S.EPA as a probable human carcinogen based on numerous studies that demonstrated the association of BaP with the increase in tumor incidences (U.S. EPA, Toxicity and Exposure Assessment for Children's Health). As shown by the bar graph in (Figure 5.4), the concentration of BaP in Z.Mikael exceeds by 68% the level in Z.Mosbeh and is absent at AUB.

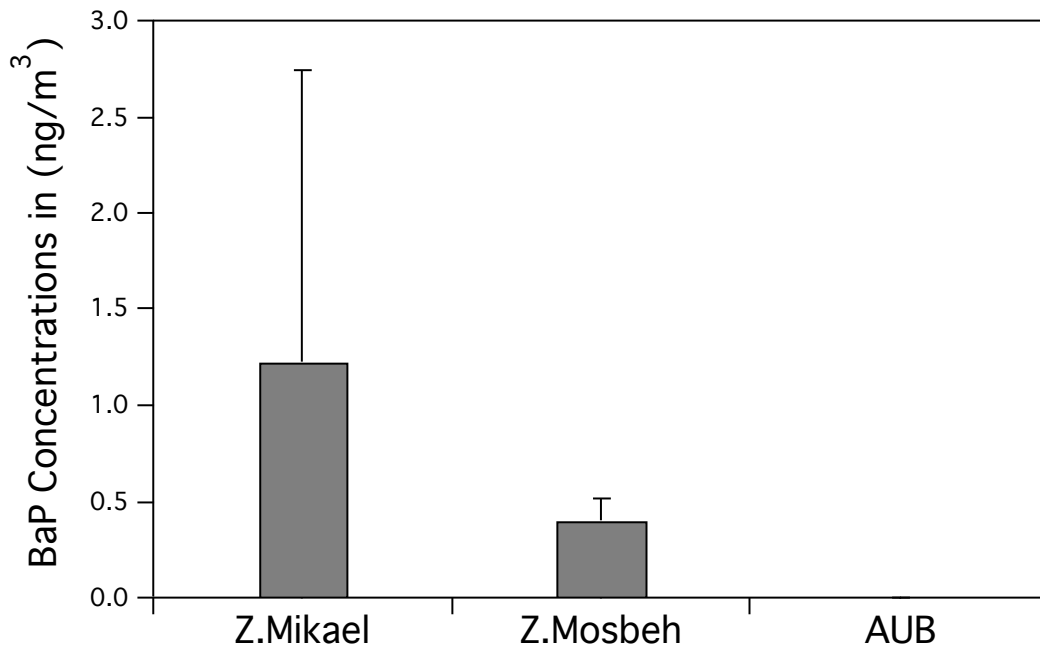


Figure 5.4: Average BaP concentrations values measured in Z.Mikael, Z.Mosbeh and AUB

4. Levels of SO_4^{2-}

It is reported that the high sulfur content in HFO produce upon burning a notable amount of gaseous SO_2 in the air (Sippula, Hokkinen et al. 2009). $SO_2(g)$ undergoes several transformations in the atmosphere and leads to the increase in the concentration of SO_4^{2-} in airborne particles (Equations 1-3).



The quantification of sulfate (SO_4^{2-}) in the three sites clearly shows the highest concentration of particle sulfate in Z.Mikael (Figure 5.5).

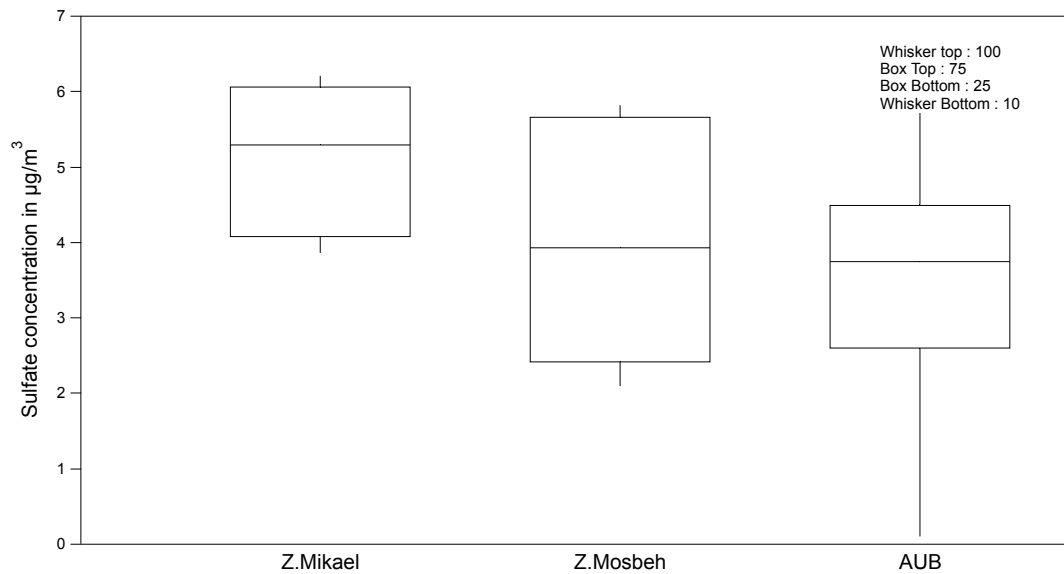


Figure 5.5: Box-and-whisker plot of the concentration of sulfate (SO_4^{-2}) collected on filters at three different sites: Z.Mikael, Z.Mosbeh and AUB

D. Conclusion

Experimental evaluation of pollution markers (PM_{10} , PAHs, BaP and SO_2) of heavy fuel oil burning in the three sites showed that the Zouk region exhibits the highest concentrations of these toxins. Thus, both theoretical and experimental methods confirm that the Zouk power plant is a large source of atmospheric pollution.

In fact, emissions from fuel oil combustion depend on (i) the grade and composition of the fuel (ash and sulphur content), (ii) the type and size of the boiler, (iii) the firing and loading practices used, (iv) the level of equipment maintenance and (v) the completeness of combustion. It is suspected from the levels of ΣPAH , and combustion markers like BaP and SO_4^{2-} that the Zouk power plant is not well maintained and the fuel combustion process is not controlled. Consequently, particulate emissions and its associated toxins will increase significantly.

Chapter VI

SOURCE APPORTIONMENT OF PAHs

A. Introduction

Polycyclic aromatic hydrocarbons are ubiquitous as they are formed by the incomplete combustion of many processes. Having multiple and diffuse sources, PAH control strategies were hard to be determined; the reason why assessors came up with source apportionment as a key aspect of such a requirement. Source apportionment is a crucial exercise to identify PAH various sources and therefore reduce the pollution of the urban atmosphere.

To apportion sources, several techniques have been developed (Jang, Alam et al. 2013). Diagnostic ratios as a form of source marker have been widely used (Rogge, Hildemann et al. 1993, Venkataraman, Lyons et al. 1994, Khalili, Scheff et al. 1995), but in a situation where multiple sources are considered, this technique is of very limited value (Galarneau, Makar et al. 2007). Principal Component Analysis (PCA) has been used as a statistical factor analysis method capable of separating chemical constituents of the atmosphere according to their source, however the drawbacks of PCA includes the issue of negative results when the scaling of the variables is not appropriate (Hopke 2008, Viana, Kuhlbusch et al. 2008, Mari, Harrison et al. 2010, Jang, Alam et al. 2013). Being proved by several studies to be a useful tool in source apportionment, positive matrix factorization (PMF) was considered as an important receptor model (Larsen and Baker 2003, Song, Shao et al. 2007, Srivastava and Jain 2007, Sofowote, McCarry et al. 2008, Wang, Tian et al. 2009, Ma, Li et al. 2010) and

therefore used in our study. PMF is a statistical factor analysis method and is able to quantify the factor contribution directly without the use of multiple regression analysis. It decomposes the receptors by three matrices-factor contribution (G), factor profile (F) and residual (E) (Jang, Alam et al. 2013). A data set is viewed as a data matrix X of i by j dimensions, in which i number of samples and j chemical species were measured. The solution in PMF is calculated through the weighted least square fit to search for proper e_{ij} by minimizing the sum of the normalized Q (Hopke 2000).

$$Q(E) = \sum_{i=1}^n \sum_{j=1}^m \left(\frac{e_{ij}}{\delta_{ij}} \right)^2 \quad (1)$$

B. Sources and markers

PAHs are mainly emitted by various anthropogenic sources. Biogenic emissions (carbonization and volcano) constitute a secondary source of PAHs in the air and their contribution is considered negligible when compared to anthropogenic sources. PAHs various anthropogenic sources are classified according to the main categories (domestic, mobile and industrial) (Rogge, Hildemann et al. 1993, Westerholm and Li 1994, Yang, Lee et al. 1998, Oros and Simoneit 2000, Pisupati, Wasco et al. 2000, Schauer, Kleeman et al. 2002, Ravindra, Sokhi et al. 2008). Domestic emissions are associated with the burning of coal, oil, gas, garbage and organic substances including tobacco and char meat. PAH emissions from these sources are of major concern because they are prevalent in most indoor environments and outdoor combustion sources.

Mobile sources include the emission from gasoline and diesel vehicles, whereas industrial sources include waste incineration and power production in particular heavy fuel oil (HFO) combustion. Road traffic (gasoline and diesel vehicles) is a major source

of PAH emission in urban areas (Guo, Lee et al. 2003, Motelay-Massei, Ollivon et al. 2007, Vardoulakis, Chalabi et al. 2008, Miller, Lemke et al. 2010). In a study conducted in the United Kingdom (UK) where they assessed the emission inventories of PAHs, it was reported that gasoline vehicles contributed to 49% to PAHs emission and therefore have been considered as a primary source of PAHs releases (NAEI 1970 to 2001). Moreover, vehicle oil combustion in the United States (US) was the major PAH emitter in the atmosphere with a contribution of 23% of the total source emissions (Zhang and Tao 2009). Other studies show that diesel combustion (from generators or vehicles) is considered a major determinant for high PAH levels in the air (Barakat 2001, Duran, De Lucas et al. 2001). Hence, in populated urban areas and less regulated exhausts' emissions, there is some concern that urban levels of PAHs would increase to unacceptable levels (Khalili, Scheff et al. 1995, Miguel, Kirchstetter et al. 1998, Marchand, Besombes et al. 2004). Conversely, industrial sources (incineration and power plant) (paper 2001, Dyke, Foan et al. 2003) contributed less than 10% to the total global emissions of PAHs (Zhang and Tao 2009). In fact, the relative contribution of different PAH sources are variable between countries depending on the energy structure and population density (Zhang and Tao 2009). For example, in India, the country relies heavily on biofuel for energy production, and therefore biofuel accounted for over 90% of the total PAH emissions whereas, coal combustion accounted for 60% of the energy consumption in China (Agency 2006a). To attribute PAH emission to the appropriate source, some PAH congeners have been suggested as fingerprints to indicate the processes that emit PAHs in the atmosphere.

Heavy-duty diesel vehicles (diesel trucks) are the major sources of lighter PAHs coexisting of 3-benzene rings such as phenanthrene, fluoranthene and pyrene, whereas

light-duty gasoline vehicles are the dominant sources of higher molecular weight PAHs of 4 to 5 benzene rings like benzo[a]pyrene, benzo[k]fluoranthene and benzo[a]anthracene (Miguel, Kirchstetter et al. 1998). In addition, waste incinerators may be a significant source of some high molecular weight PAHs such as chrysene, dibenz[a,h]anthracene and benzo[g,h,i]perylene (ROY J. IRWIN 1997, addo 1999, Ravindra, Bencs et al. 2006) and heavy fuel oil emissions are the major source of mainly heavy PAHs like benzo[k]fluoranthene, benzo[a]anthracene, benzo[a]pyrene and chrysene (Yang, Lee et al. 1998, Chmielewski, Ostapczuk et al. 2010) (Table 6.1).

Table 6.1: Attribution of PAH makers to the appropriate emission source

Fingerprints (PAHs Congeners)	Sources
lighter PAHs coexisting of 3-benzene rings such as phenanthrene, fluoranthene and pyrene	Diesel emission
higher molecular weight PAHs of 4 to 5 benzene rings like benzo[a]pyrene, benzo[k]fluoranthene and benzo[a]anthracene.	Gasoline emission
Chrysene, benzo[g,h,i]perylene and dibenz[a,h]anthracene	Waste Incineration
heavy PAHs like benzo[k]fluoranthene, benzo[a]anthracene, benzo[a]pyrene and chrysene	Heavy fuel oil emission

C. PMF factor profile

PAH datasets (concentrations and uncertainties) of urban sites (AUB, Zouk and Dora) for both winter and summer campaign 2015 were inputted for PMF analysis where a four factor model was used. All congener emission profiles for specific source types stated above were used in order to designate each factor.

1. Winter Campaign

In the Base Model Results, the PMF output gives residual analysis, observed/predicted scatter plots, observed/predicted time series for uncertainties purposes and profiles contributions, factor fingerprints, G-space plot and factor contributions for factors assignment and contribution assessment purposes. Out of these outputs, the factor contribution section is presented in a pie-chart that shows the contribution of each factor to the emission of each congener of the 16 studied PAHs. In addition, in the profile contribution section, a graph shows the contribution of each factor in each sampling site. The four factors that were considered in the model were assigned based on the abundances of the different congeners.

Factor 1 which showed the predominance of Fluorene, Phenanthrene, Fluoranthene and Pyrene at 48, 40, 81 and 86%, respectively was assigned to diesel emissions. This was based on several studies that resulted in similar assignment for the predominance of these four congeners (phenanthrene, fluorene, fluoranthene and pyrene) (Rogge, Hildemann et al. 1993, Miguel, Kirchstetter et al. 1998, Marr, Kirchstetter et al. 1999, Gambino, Iannaccone et al. 2000)

Factor 2 showed mainly the presence of 16% fluorene, 19% dibenzo[a,h]anthracene, 16% benzo[g,h,i]perylene and 18% Indeno[1,2,3-cd]pyrene. Chen et al found that dibenzo[a,h]anthracene, benzo[g,h,i]perylene and indeno[1,2,3-cd]pyrene are highly emitted from incinerators (Chen, Su et al. 2007) and loading of benzo[g,h,i]perylene is highly associated with waste emission (Benzo[g,h,i]perylene entry. 1997). Therefore, factor 2 is assigned to incinerations.

Factor 3 was mainly influenced by the abundance of phenantrene, acenaphthene, benzo[a]anthracene, chrysene and indeno[1,2,3,-cd]pyrene that have been associated with heavy fuel oil combustion (Yang, Lee et al. 1998, Li, Mi et al. 1999).

Factor 4 was characterized by around 50% contribution to benzo[a]pyrene with substantial contributions of benzo[a]anthracene (41%), beno[k]fluoranthene (61%), and indeno[1,2,3-cd]pyrene (35%). Miguel et al (1998), reported that gasoline vehicles are dominant sources of benzo[a]pyrene and high molecular weight PAHs (Miguel, Kirchstetter et al. 1998, Marr, Kirchstetter et al. 1999, Schauer, Kleeman et al. 1999). Therefore factor 4 fits the behavior of gasoline burning.

Hence, gasoline, diesel, incinerations as well as HFO combustion are considered the main emission sources of PAHs in our study.

Based on the PMF outputs and the factor identification of the four factors, attribution of sources to each site resulted in the following distributions shown in Figures 6.1, 6.2 and 6.3 for AUB, Dora and Zouk, respectively. At AUB, the highest source contribution was assigned to HFO burning (47%), followed by diesel combustion (14%), and almost equal emissions from incineration (8%), and gasoline burning (9%). The Dora site registered high percentages of diesel combustion (67%),

gasoline burning (76%) and incinerations (40%). HFO combustion sources contributed by only 25%. In Zouk, HFO emission was the predominated source of PAHs (62%). The emission from gasoline recorded 59% of total PAHs, 17% were attributed to incineration and only 1% to diesel combustion.

AUB, an urban background site and therefore not directly affected by PAHs emissions, is supposed to be the least influenced among the studied sites by the various sources. Assignments were in agreement with the assumption except for heavy fuel combustion that had a remarkable contribution at AUB (47%) although AUB is at a distance from all the power plants in the region. This situation can be explained by the presence of the AUB site in proximity of the Beirut harbor hosting a number of ships running on heavy fuel oil (Cooper 2001). Being one of the most populated city in Beirut, ranking high in traffic congestion and hosting the Burj Hammoud waste dumping, Dora is subject to be highly influenced by diesel (power generators and light-duty vehicles) and gasoline emissions as well as waste incinerators releases but poorly affected by heavy fuel combustion existing at certain distances from the power plants in the region. These aforementioned assumptions were in accordance with what was found from the PMF output. The Zouk site looks over the power plant and is at few kilometers away from a road that usually experiences traffic in the morning and the afternoon because of nearby schools. Emission from these local sources can explain the major contribution of gasoline and heavy fuel combustion to the total emission sources. Being away from diesel and incineration sources, the contribution of these latter was in accordance with the results obtained by the PMF.

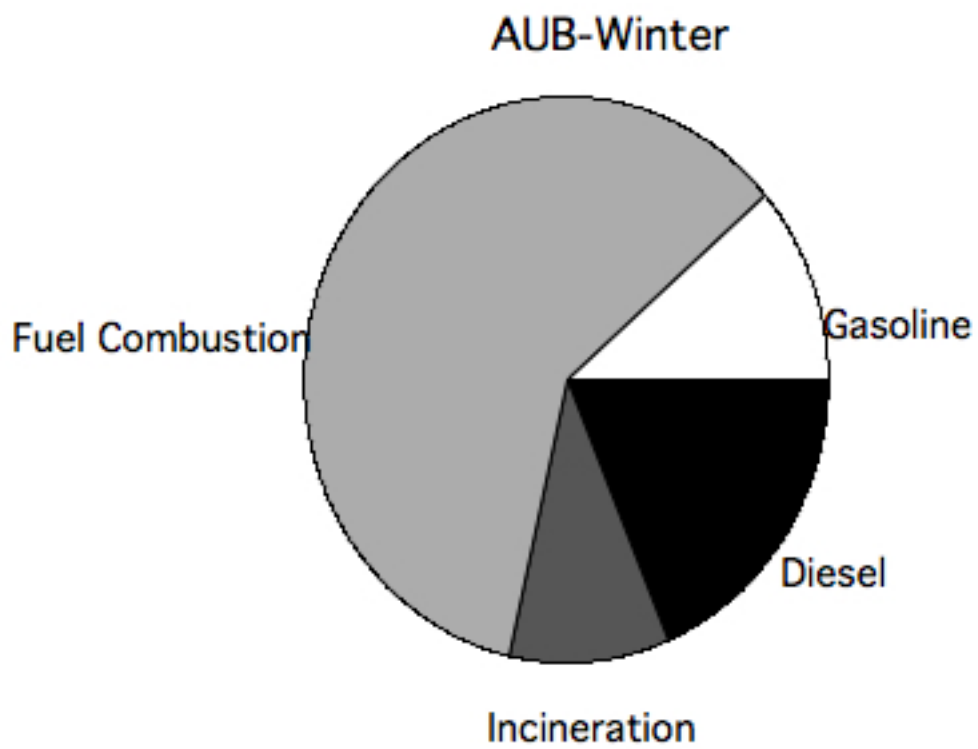


Figure 6.1: Source contributions at AUB during the winter season (2015)

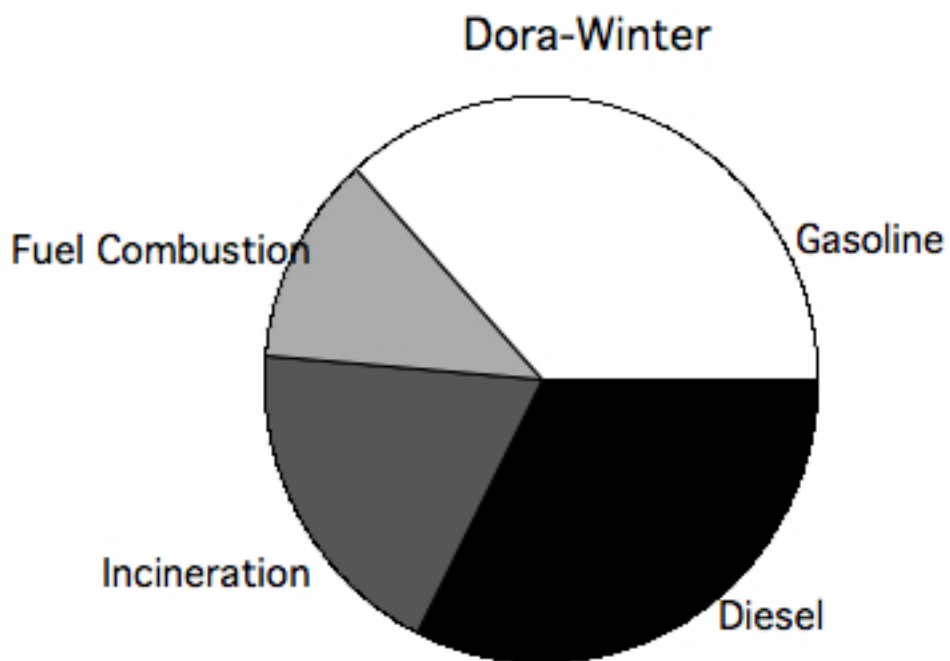


Figure 6.2: Source contributions in Dora during the winter season (2015)

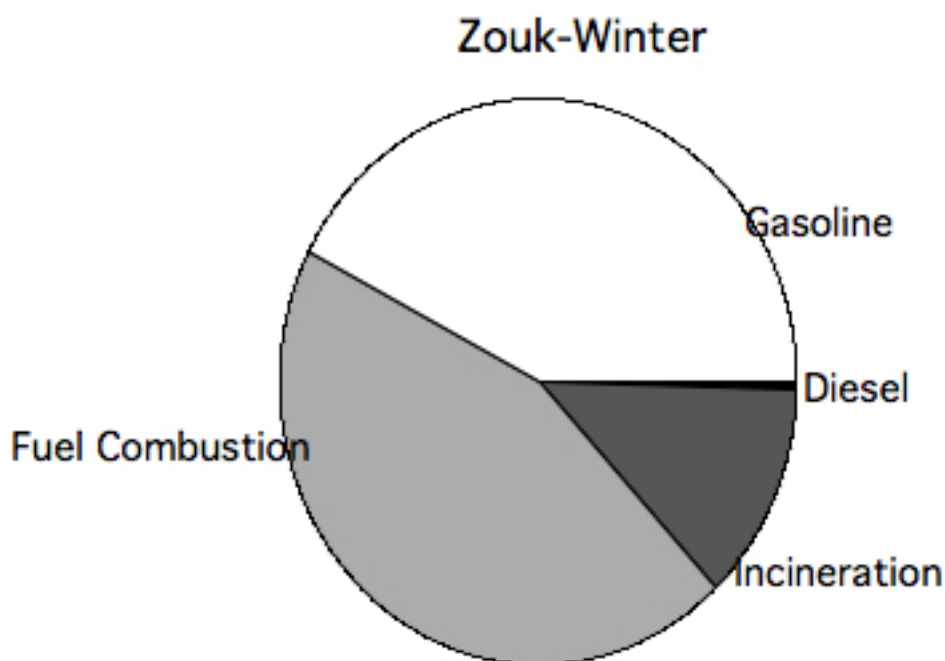


Figure 6.3: Source contributions in Zouk during the winter season (2015)

2. Summer Campaign

In summer, diesel combustion and incineration were the only prevailing sources at AUB (60 and 17%) with smaller percentages of gasoline and heavy fuel burning (7 and 5%) (Figure 6.4). Dora was highly influenced by diesel combustion (76%), incinerations (64%) and gasoline emissions (88%) except for HFO burning that reached only 5% (Figure 6.5). At Furthermore, Zouk was again majorly influenced by HFO emissions (71%) with percent contributions of diesel combustion, incineration and gasoline burning of 5, 13 and 1%, respectively (Figure 6.6). These findings prove again that the factor assignments were in accordance with the nature of each site in the summer season.

D. Conclusion

The source contributions of the total PAH emissions are relative to the prevailing characteristics of the sampling sites. Thus, PAH source plays a significant role in explaining the differences of PAH levels in each site.

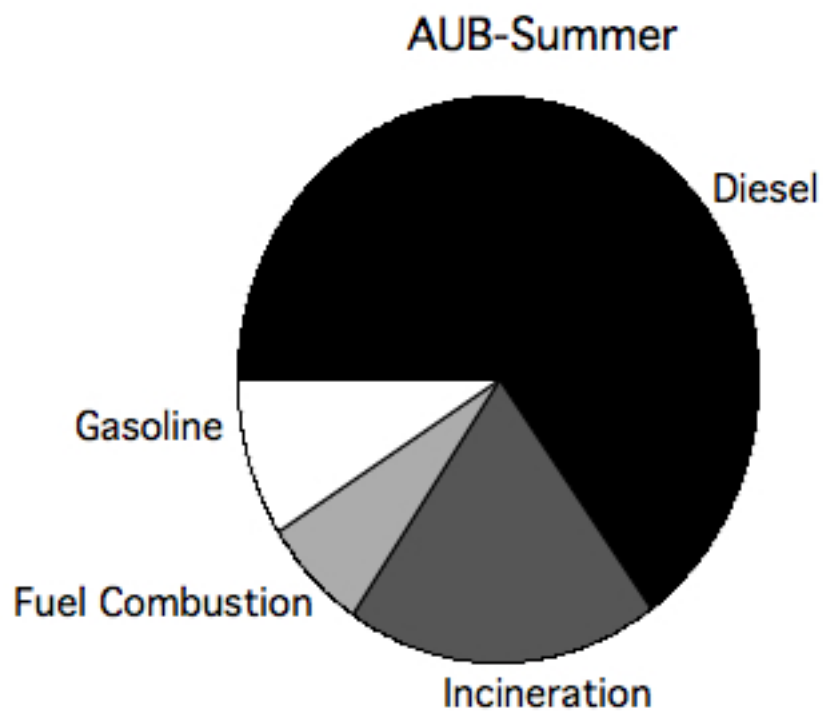


Figure 6.4: Source contributions at AUB during the summer season (2015)

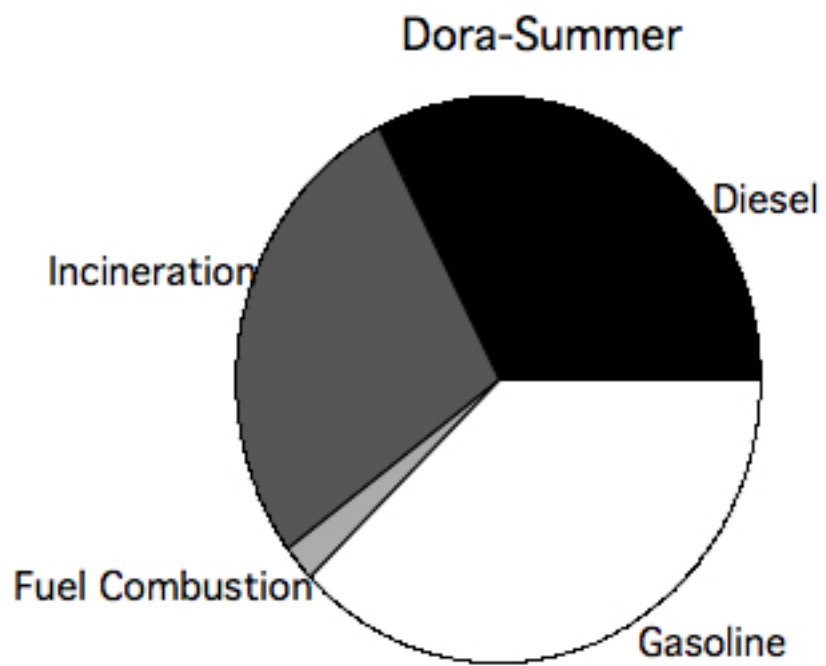


Figure 6.5: Source contributions in Dora during the winter season (2015)

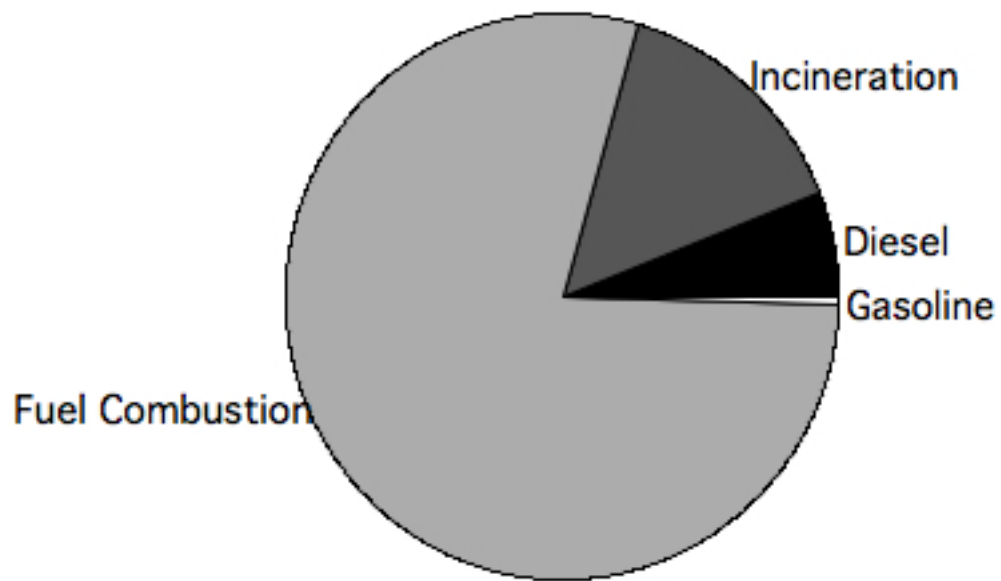


Figure 6.6: Source contributions in Zouk during the winter season (2015)

CHAPTER VII

PAHs AND DIOXINS CANCER RISK ESTIMATION

A. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are air pollutants found indoors and outdoors. Sources can include automobile exhaust, incinerations, indoor fuel used for cooking or heating, and smoking. According to the international agency of research on cancer (IARC), epidemiologic studies have shown associations of airborne PAHs with cancer (IARC 2010). US Environmental Protection Agency (USEPA) has identified 16 PAHs (Table 1.1) that we studied as priority pollutants because of their potential of inducing higher cancer risk (EPA/630/P-03/001B 2005). Benzo[a]pyrene (BaP) is classified as a Group 1 known human carcinogen (IARC 2010) and as such is the most potent congener among PAHs (WHO 1998, Boström, Gerde et al. 2002).

Dioxins are chemicals that remain intact in the environment for long periods, become widely distributed geographically, accumulate in the tissue of living organisms and are toxic to humans (StockholmConvention 2004). Furthermore one of dioxins congener, the 2, 3, 7, 8-TCDD have been associated to lung cancer by EPA (EPA 2000). As a result, many international environmental agencies including the North American Council on Environmental Cooperation (NACEC), the stockholm convention as well as EPA sought to protect human health and the environment from the danger posed PCDD/Fs and they worked on a risk-based approach to reduce or eliminate the potential impacts of these hazardous chemicals.

Several ways can be approached for the quantification of PAH and Dioxins exposure (StockholmConvention 2004, EPA/630/P-03/001B 2005). The estimation of exposure at the point of contact by measuring the chemical concentration at the interface between the person and the environment as a function of time (point-of-contact measurement) is one example. Exposure can also be estimated after it has taken place following a biological monitoring that can evaluate the amount of a chemical in the body (urine, hemoglobin and blood) and which is currently known as exposure estimation by reconstruction of internal dose. A third method adopted in this study relies on scenario evaluation that approximates the exposure. In this method, the assessor attempt to determine the concentration of chemicals first and then correlate it with the time of the individual contact with this chemical.

The scenario evaluation model for the cancer risk quantification can be calculated based on either the unit factor risk or the incremental lifetime cancer risk (ILCR).

The unit factor risk consists on the estimate of the cancer risk associated with exposure to carcinogenic substance. It is evaluated by multiplying *potency* or the *slope factor (SF)* by the carcinogen concentration C_i as follows:

$$Risk = Potency \times C_i \quad (\text{Eq:7.1})$$

The potency or the slope factor is the toxicity value that defines quantitatively the relationship between dose and response. They are derived based on data from a conducted epidemiological study (Schneider, Roller et al. 2002, EPA/630/P-03/001B 2005, Handbook 2011).

The incremental lifetime cancer risk (ILCR) consists on a time-weighted average exposure concentration. A time-weighted average dose is the total dose divided by the time period of dosing normalized to body weight usually expressed in mg/kg/day. So, this concept accounts for the individual's daily activities categorized according to the places of occurrence including indoor and outdoor environments and relates these activities to the exposure at each place and time (EPA/630/P-03/001B 2005, Zhou and Zhao 2014).

B. ILCRs calculation

ILCR represents the incremental probability of an individual to develop cancer over a lifetime as a result of exposure to a potential carcinogen through inhalation. The significance threshold for cancer risk is defined for all pollutants as a lifetime incremental cancer risk greater than 1 out of every million adults. Therefore if exposure to PAHs and dioxins released from various sources will result in more than one per one million adults exposed, the effect is considered significant.

ILCR is calculated as described in Eq. 7.2.

$$ILCR = \frac{(SF \times E \times EF \times ED \times CF)}{BW \times AT} \quad (\text{Eq.7.2})$$

Where,

SF is the cancer slope factor for BaP and 2, 3, 7, 8-TCDD inhalation exposure

EF is the exposure frequency (350 day/year)

ED is the exposure duration (43 years for adults)

CF is the conversion factor

BW is the body weight (71.3 kg for males and 59.1 for females)

AT is the average lifespan for carcinogens (25550)

E is the daily inhalation exposure level (ng/day) calculated in equation 7.3:

$$E = \sum_i C_i \times IR \times TEF_i \quad (\text{Eq.7.3})$$

where, C_i , IR and TEF are the concentration, the inhalation rate and the toxicity equivalent factor, respectively.

Being the most potent, BaP is assigned a TEF of 1 and so the total PAH exposure is defined as BaP toxic equivalency concentrations (TEQ), where all the other 15 PAH components are measured and ranked relative to BaP in terms of carcinogenicity. For example, chrysene has been determined to have 1/1000th of the carcinogenicity of BaP and therefore has a toxicity equivalency factor (TEF) of 0.001. The TEF of the remaining USEPA 16 PAH congeners are listed in (table 7.1).

As was stated in chapter IV, all dioxins congeners are ranked according to

2, 3, 7, 8-TCDD and the WHO TEF values for humans/mammals are reported in (Table 4.3).

Table 7.1: TEF values of the 16 PAHs as defined by US-EPA

PAHs	TEF
Naphtalene	0.001
Acenaphtalene	0.001
Acenaphtene	0.001
Fluorene	0.001
Phenanthrene	0.001
Anthracene	0.01
Fluoranthene	0.001
Pyrene	0.001
Benzo[a]anthracene	0.1
chrysene	0.01
Benzo[k]fluoranthene	0.1
Benzo[a]pyrene	1
Benzo[g,h,i]perylene	0.01
Dibenzo[a,h]anthracene	1
Indeno[1,2,3-cd]pyrene	0.1

For the current evaluation, it is assumed that the individual is an adult male or female living in one of the sampled areas for 24 hours and for 365 days/year. PAH and dioxins exposures that are calculated based on ambient atmospheric conditions represent a lower limit value since no other exposure routes such as ingestion and dermal contact are considered.

In Table 7.2, spatial and temporal comparison of PAH cancer risk are reported. Computed ILCRs for the respective summer and winter were 0.5×10^{-6} and 1×10^{-6} at AUB, 1×10^{-6} and 3×10^{-6} at Zouk and 2×10^{-6} and 3×10^{-6} at Dora. Summer inhalation ILCR values are higher than those calculated for the winter despite the fact that the total PAH concentration was found to be higher during winter. This can be explained by the higher concentrations of PAH congeners having relatively high TEF in the summer, namely benzo[a]pyrene (TEF = 1), benzo[a]anthracene (TEF = 0.1 as well as for dibenzo[a,h]anthracene (TEF = 1) which was detected in Zouk.

Table 7.2: inhalation incremental lifetime cancer risk (ILCR) values in the studied sites during winter and summer seasons

	Winter			Summer		
	AUB	Zouk	Dora	AUB	Zouk	Dora
Ei (ng/day)	9.8	18.6	47.5	19.2	64.9	75.7
ILCRs	5E-07	1E-06	2E-06	1E-06	3E-06	4E-06

In Table 7.3, only a spatial comparison of PAHs, dioxins and total cancer risk, respectively was reported where total cancer risk is obtained by summing up both PAH and dioxin ILCRs.. At AUB, PAH, dioxins as well as the total ILCRs were the lowest in comparison with the remaining sites. Dora registered the highest cancer probabilities for PAH and dioxin exposures. At last, although it has smaller ILCRs than those reported in Dora, Zouk was considered to be at high risk as well.

Table 4: Total inhalation incremental lifetime cancer risk (ILCR) values in the studied sites

	AUB	Zouk	Dora
PAH ILCRs	1E-06	3E-06	4E-06
Dioxin ILCRs	1E-09	1E-08	3E-08
Total ILCRs	1E-06	3E-06	4E-06

C. Scenario evaluation

In the computation model previously mentioned, the ILCR values were calculated assuming the person lives all year for more than 40 years in one of the site location. A more realistic scenario would be to develop a probabilistic risk assessment taking into account the indoor and outdoor environments and locations a person might be exposed to while carrying a normal daily routine.

Outdoor concentrations were based on the ambient PAH and dioxin concentrations obtained from this study. Whereas indoor concentrations were split into two sources:

- 70% outdoor infiltration through doors (by an increment of 2.10^{-4} %) windows (an increment of 10^{-4}) and in presence of air-conditioner (an increment of 0.2%) according to the American Society of Heating, Refrigerating, and Air-Conditioning Engineers (ASHRAE).
- 30% indoor activities including resting activities where PAHs' Indoor/outdoor ratio is equal to 0.7, gas cooking activity where indoor/outdoor ratio is equal to 1.8 and smoking activity where this ratio is equal to 2 (Brochu, Ducré-Robitaille et al. 2006). We assume that we have no major emission of dioxins from indoor activities.

Indoor concentration were reported in three different environments taking in consideration all activities and exchange rates.

In order to put all the mentioned parameters in the context of someone's lifestyle, we introduce Adam.

Who is Adam?

Adam is a male of 27 years old who weighs 70 kg. Adam lives in Zouk and is employed by AUB. He takes the bus to work every day and makes a bus connection in Dora. He works out frequently and socializes with his friends during weekends.

As stated IR is defined as the inhalation rate and TEQ as the toxicity equivalents ($C_i \times \text{TEF}$),

In order to determine ED, exposure scenarios for weekdays and weekends are proposed.

Weekday, Saturday and Sunday proposal scenarios

Exposure duration was determined by dividing 24 hours of the day into intervals lasting according to the defined activities.

During a weekday scenario (figure 7.1), Adam wakes up at 7 a.m., takes his coffee and smoking break that lasts one hour. He then takes two buses from Zouk to Dora and from Dora to AUB where he begins work at 9 a.m. He works for 7 hours interrupted by a one-hour lunch break at 2 p.m. After work, Adam goes to the gym for 2 hours, rests and smokes before getting back home following the same morning route (AUB-Dora-Zouk). Once at home, Adam prepares his dinner, eats, watches TV and sleeps at midnight.

During a Saturday scenario (figure 7.2), Adam wakes up at 10 a.m., goes to the supermarket for two hours and once home he starts cooking. He then takes lunch, naps

for two hours to receive his guests for arguileh at 5 p.m. He watches a movie with his friends and gets to bed at midnight as well.

On Sunday (figure 7.3), Adam wakes up also at 10 a.m. He jogs for two hours, cooks, eats, and naps before he prepares himself to go out for dinner. At midnight, he goes to bed.

Applying the scenarios described above, inhalation daily exposure levels of both PAHs and dioxins were found to be 5.8, 17.8 and 10.5 ng/day for a weekday, Saturday and Sunday, respectively. Computed ILCRs were more than one in one million which means according to EPA, WHO and Health Canada, Adam is at high potential risk.

Exposure Duration to PAHs during a Weekday

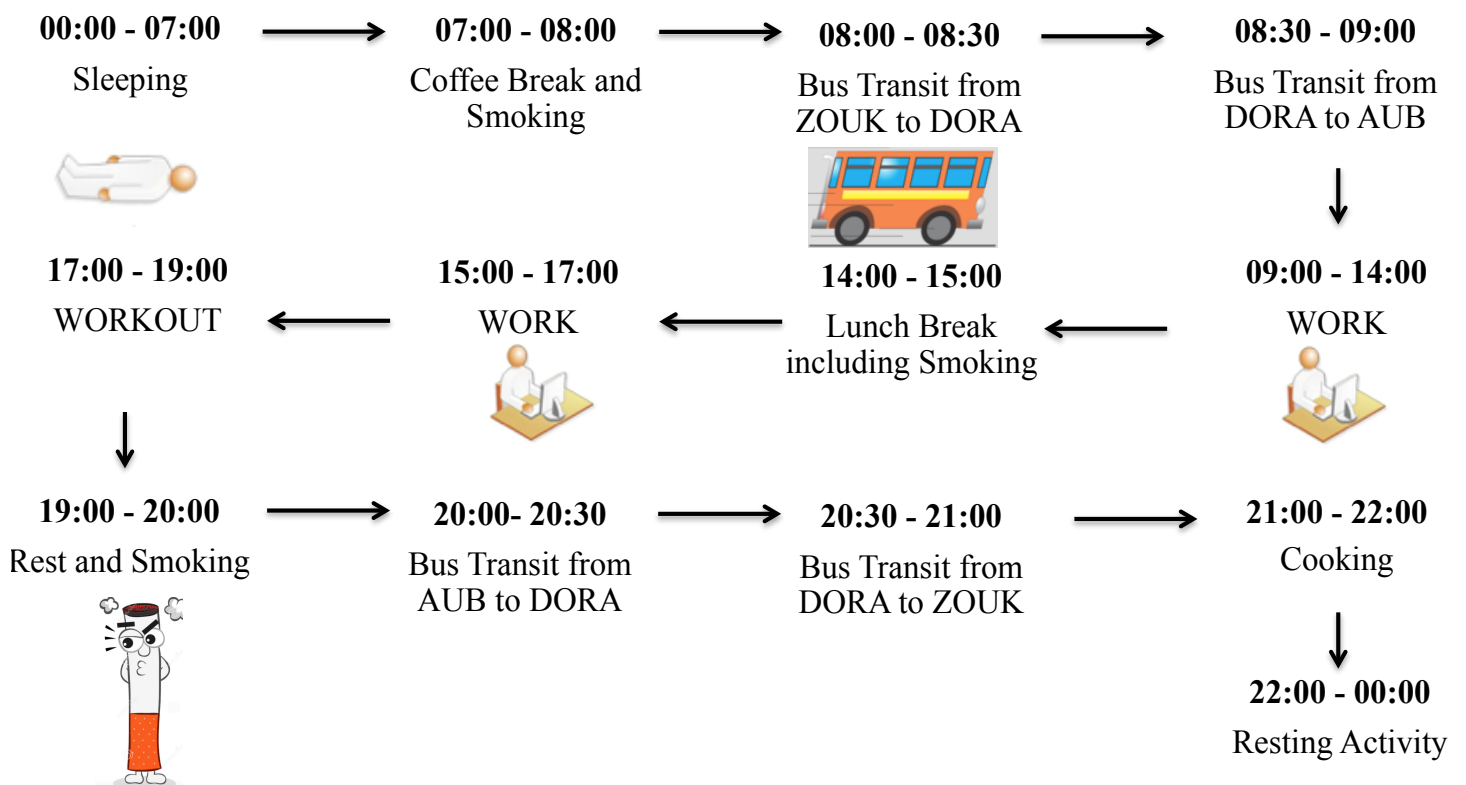


Figure 7.6: Weekday Scenario

Exposure Duration to PAHs during a Saturday

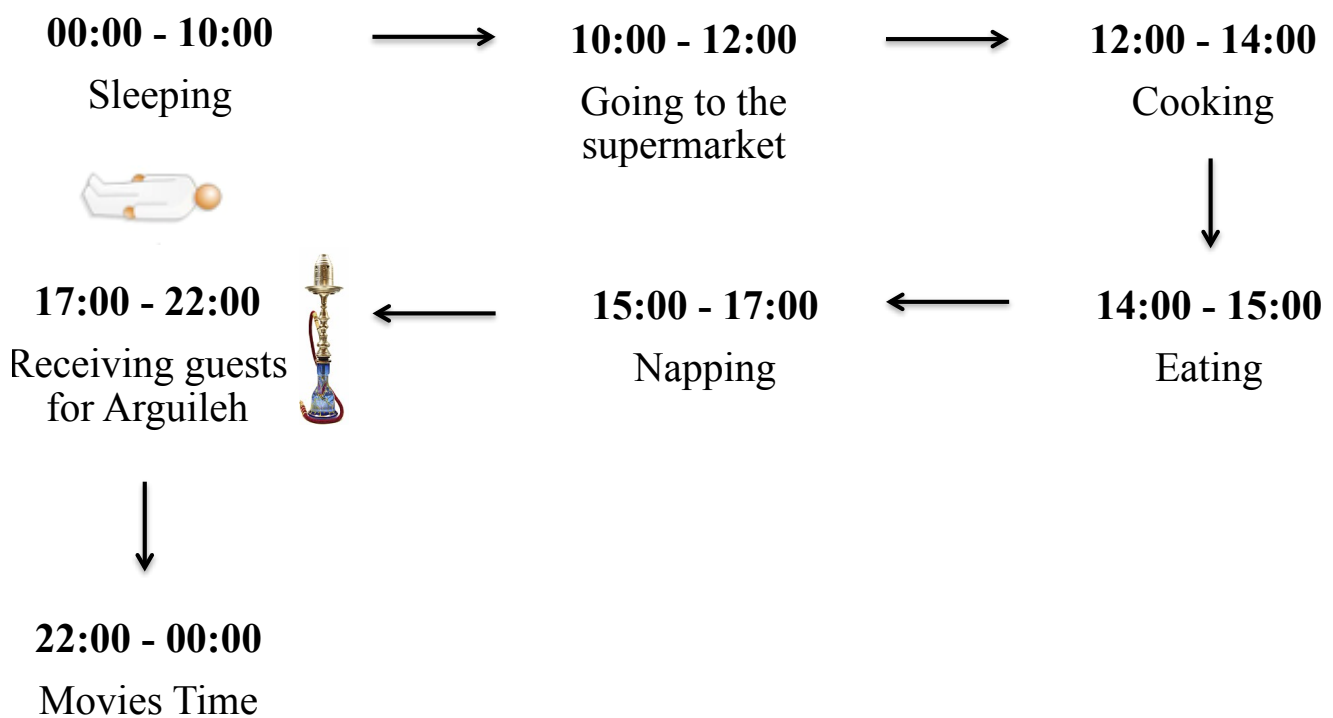


Figure 7.7: Saturday Scenario

Exposure Duration to PAHs during a Sunday

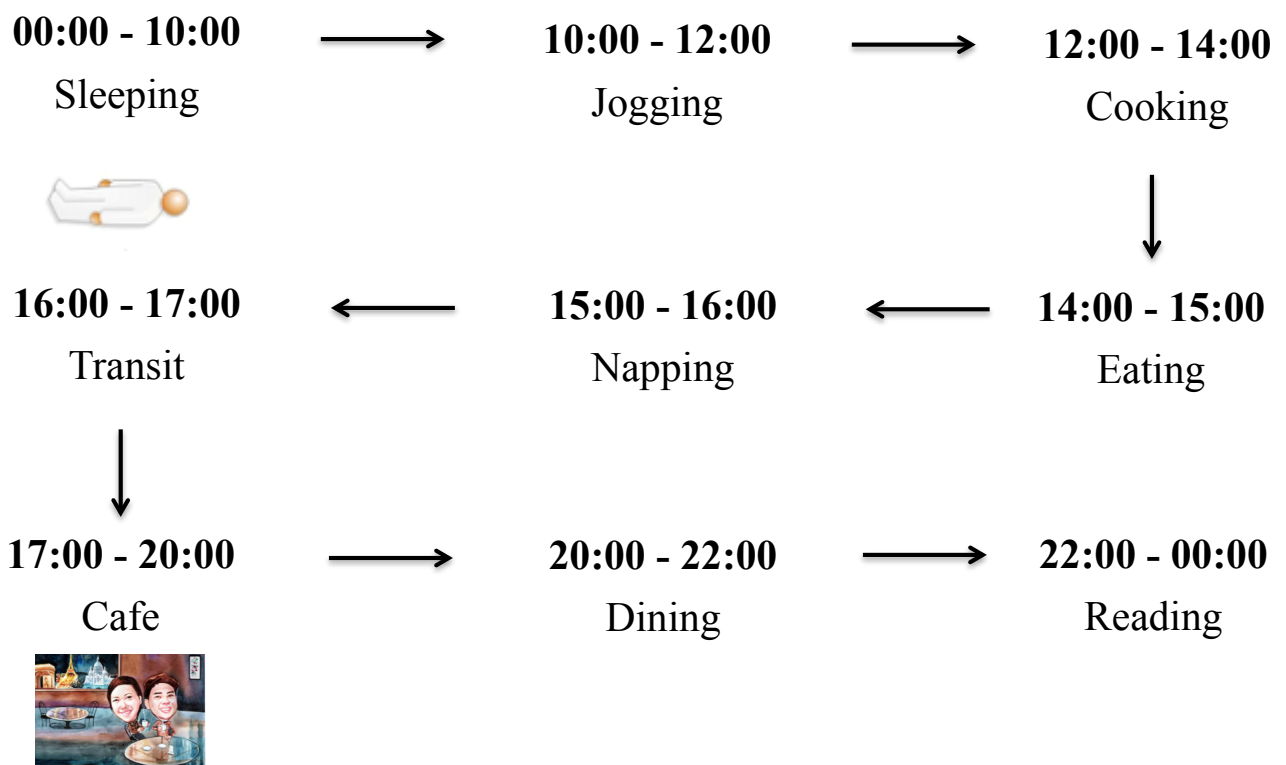


Figure 8: Sunday Scenario

CHAPTER VIII

CONCLUSIONS

This study presents for the first time the characterization of polycyclic aromatic hydrocarbons (PAHs) and dioxins in the atmosphere. PAHs and PCDD/Fs are distributed ubiquitously in the ambient air, which lead to a wide exposure in the general population and therefore induce adverse health effects. In the atmosphere, they originate from natural sources; however, their presence in populated urban areas is significantly influenced by anthropogenic emissions.

Results of the spatial variations of PAHs and dioxin concentrations in three representative sites (AUB, Zouk and Dora) showed how the local emission at the sampling locations affects their levels. AUB, a representative of an urban background site, had the lowest concentrations of PAHs and PCDD/Fs. Zouk Mikalel, an urban residential site, showed levels higher than AUB but the highest concentrations were recorded in the urban industrial site of Dora. Furthermore, the temporal study of PAHs provided a clear variation between two winter and summer 2015. Light PAHs were higher during winter at the three sites due to the occurrence of the inversion layer and higher local emissions in the form of domestic heating. In the summer lower values can be explained the enhancement of the photodegradation reactions in presence of the intense light. As for heavy PAH amounts in the Zouk, higher levels in summer were attributed to the elevated emissions from the power plant. This was clearly indicated by the increase in the concentrations of the marker of heavy fuel oil burning namely

benzo[a]pyrene, benzo[a]anthracene and chrysene. Similarly the increase in waste incineration during the summer sampling in Dora contributed in the elevation of the benzo[a]anthracene and chrysene concentrations.

Using PMF, the contribution of the different sources in each site conform the description of the sampling location. Being an urban background site, AUB showed lowest contribution of the investigated sources. Zouk was majorly affected by heavy fuel oil burning released from the power plant stacks, whereas Dora had the highest contribution of gasoline, diesel and incinerations.

From a health perspective, all data was used to estimate the cancer risk after exposure to both PAHs and PCDD/Fs. Average ILCRs were 0.75×10^{-6} , 2×10^{-6} and 2.5×10^{-6} at AUB, Zouk and Dora respectively, which means that a person living either in Zouk or Dora will be at high risk to develop cancer.

This study permits the evaluation of the cancer risk associated with daily exposure of the Lebanese population. For future directions, it is suggested that the study of PAH levels is coupled with meteorological and geographical data as well as the ground emission inventory of the studied area.

BIBLIOGRAPHY

1. Boström, C.-E., et al. (2002). "Cancer risk assessment, indicators, and guidelines for polycyclic aromatic hydrocarbons in the ambient air." *Environmental health perspectives* **110**(Suppl 3): 451.
2. Brochu, P., et al. (2006). "Physiological daily inhalation rates for free-living individuals aged 1 month to 96 years, using data from doubly labeled water measurements: a proposal for air quality criteria, standard calculations and health risk assessment." *Human and Ecological Risk Assessment* **12**(4): 675-701.
3. EPA/630/P-03/001B (2005). "Guidelines for Carcinogen Risk Assessment."
4. Handbook, E. F. (2011). Inhalation rates.
5. IARC (2010). IARC Monographs on the Evaluation of Carcinogenic Risks to Humans. **92**.
6. IARC (2010). Some non-heterocyclic polycyclic aromatic hydrocarbons and some related exposures. IARC monographs on the evaluation of carcinogenic risks to humans/World Health Organization, International Agency for Research on Cancer. **92**: 1.
7. Schneider, K., et al. (2002). "Cancer risk assessment for oral exposure to PAH mixtures." *Journal of Applied Toxicology* **22**(1): 73-83.
8. WHO (1998). Selected non-heterocyclic polycyclic aromatic hydrocarbons.
9. Zhou, B. and B. Zhao (2014). "Analysis of intervention strategies for inhalation exposure to polycyclic aromatic hydrocarbons and associated lung cancer risk based on a Monte Carlo population exposure assessment model." *PloS one* **9**(1): 1-11.
10. Benzo[g,h,i]perylene entry. *Environmental Contaminants Encyclopedia*. (1997).
11. addo, v. p., bidleman, T.F, Brorstrom-Lunden, E, builtjes, P.J.H, Dutchak, S, Duyzer, J.H, Gryning, S, Jones, K.C, Van djik, H.F.G, Van Jaarsveld, J.A. (1999). "Atmospheric transport and deposition of pesticides: an assessment of current knowledge." *Water Air Soil Pollution* **115**: 245-256.
12. Agency, I. E. (2006a). *Energy Statistics and Balances of Non-OECD Countries , 2003-2004*.
13. Barakat, A. (2001). PAHs and petroleum markers in the atmospheric environment of Alexandria City, Egypt. ABSTRACTS OF PAPERS OF THE AMERICAN CHEMICAL SOCIETY, AMER CHEMICAL SOC 1155 16TH ST, NW, WASHINGTON, DC 20036 USA.

14. Chen, S.-J., et al. (2007). "Emissions of polycyclic aromatic hydrocarbons (PAHs) from the pyrolysis of scrap tires." *Atmospheric Environment* **41**(6): 1209-1220.
15. Chmielewski, A. G., et al. (2010). "Electron beam technology for multipollutant emissions control from heavy fuel oil-fired boiler." *Journal of the Air & Waste Management Association* **60**(8): 932-938.
16. Cooper, D. (2001). "Exhaust emissions from high speed passenger ferries." *Atmospheric Environment* **35**(24): 4189-4200.
17. Duran, A., et al. (2001). "Simulation of atmospheric PAH emissions from diesel engines." *Chemosphere* **44**(5): 921-924.
18. Dyke, P. H., et al. (2003). "PCB and PAH releases from power stations and waste incineration processes in the UK." *Chemosphere* **50**(4): 469-480.
19. Galarneau, E., et al. (2007). "Estimation of atmospheric emissions of six semivolatile polycyclic aromatic hydrocarbons in southern Canada and the United States by use of an emissions processing system." *Environmental Science & Technology* **41**(12): 4205-4213.
20. Gambino, M., et al. (2000). Regulated and unregulated emissions reduction with retrofit catalytic after-treatment on small two stroke SI engine, SAE Technical Paper.
21. Guo, H., et al. (2003). "Particle-associated polycyclic aromatic hydrocarbons in urban air of Hong Kong." *Atmospheric Environment* **37**(38): 5307-5317.
22. Hopke, P. K. (2000). A guide to positive matrix factorization. Workshop on UNMIX and PMF as Applied to PM2.
23. Hopke, P. K. (2008). "The use of source apportionment for air quality management and health assessments." *Journal of Toxicology and Environmental Health, Part A* **71**(9-10): 555-563.
24. Jang, E., et al. (2013). "Source apportionment of polycyclic aromatic hydrocarbons in urban air using positive matrix factorization and spatial distribution analysis." *Atmospheric Environment* **79**: 271-285.
25. Khalili, N. R., et al. (1995). "PAH source fingerprints for coke ovens, diesel and, gasoline engines, highway tunnels, and wood combustion emissions." *Atmospheric Environment* **29**(4): 533-542.
26. Larsen, R. K. and J. E. Baker (2003). "Source apportionment of polycyclic aromatic hydrocarbons in the urban atmosphere: a comparison of three methods." *Environmental Science & Technology* **37**(9): 1873-1881.

27. Li, C.-T., et al. (1999). "PAH emission from the industrial boilers." *Journal of Hazardous Materials* **69**(1): 1-11.
28. Li, W.-H., et al. (2012). "Concentrations and sources of PAHs in surface sediments of the Fenhe reservoir and watershed, China." *Ecotoxicology and environmental safety* **75**: 198-206.
29. Ma, W.-L., et al. (2010). "Seasonal variations of sources of polycyclic aromatic hydrocarbons (PAHs) to a northeastern urban city, China." *Chemosphere* **79**(4): 441-447.
30. Marchand, N., et al. (2004). "Polycyclic aromatic hydrocarbons (PAHs) in the atmospheres of two French alpine valleys: sources and temporal patterns." *Atmospheric Chemistry and Physics* **4**(5): 1167-1181.
31. Mari, M., et al. (2010). "Inferences over the sources and processes affecting polycyclic aromatic hydrocarbons in the atmosphere derived from measured data." *Science of the Total Environment* **408**(11): 2387-2393.
32. Marr, L. C., et al. (1999). "Characterization of polycyclic aromatic hydrocarbons in motor vehicle fuels and exhaust emissions." *Environmental Science & Technology* **33**(18): 3091-3099.
33. Miguel, A. H., et al. (1998). "On-road emissions of particulate polycyclic aromatic hydrocarbons and black carbon from gasoline and diesel vehicles." *Environmental Science & Technology* **32**(4): 450-455.
34. Miller, L., et al. (2010). "Intra-urban correlation and spatial variability of air toxics across an international airshed in Detroit, Michigan (USA) and Windsor, Ontario (Canada)." *Atmospheric Environment* **44**(9): 1162-1174.
35. Motelay-Massei, A., et al. (2007). "PAHs in the bulk atmospheric deposition of the Seine river basin: source identification and apportionment by ratios, multivariate statistical techniques and scanning electron microscopy." *Chemosphere* **67**(2): 312-321.
36. NAEI (1970 to 2001). 15th Annual Report from the UK National Atmospheric Emissions Inventory (NAEI). Annual Report National Environmental Technology Centre.
37. Oros, D. and B. Simoneit (2000). "Identification and emission rates of molecular tracers in coal smoke particulate matter." *Fuel* **79**(5): 515-536.
38. paper, P. p. (2001). "Ambient air pollution by polycyclic aromatic hydrocarbons (PAH)." Office for Official Publications of the European Communities, Luxembourg.
39. Pisupati, S. V., et al. (2000). "An investigation on polycyclic aromatic hydrocarbon emissions from pulverized coal combustion systems." *Journal of Hazardous Materials* **74**(1): 91-107.

40. Ravindra, K., et al. (2006). "Seasonal and site-specific variation in vapour and aerosol phase PAHs over Flanders (Belgium) and their relation with anthropogenic activities." *Atmospheric Environment* **40**(4): 771-785.
41. Ravindra, K., et al. (2008). "Atmospheric polycyclic aromatic hydrocarbons: source attribution, emission factors and regulation." *Atmospheric Environment* **42**(13): 2895-2921.
42. Rogge, W. F., et al. (1993). "Sources of fine organic aerosol. 2. Noncatalyst and catalyst-equipped automobiles and heavy-duty diesel trucks." *Environmental Science & Technology* **27**(4): 636-651.
43. ROY J. IRWIN, N. P. S. (1997). ENVIRONMENTAL CONTAMINANTS ENCYCLOPEDIA BENZO(G,H,I)PERYLENE ENTRY.
44. Schauer, J. J., et al. (1999). "Measurement of emissions from air pollution sources. 2. C1 through C30 organic compounds from medium duty diesel trucks." *Environmental Science & Technology* **33**(10): 1578-1587.
45. Schauer, J. J., et al. (2002). "Measurement of emissions from air pollution sources. 5. C1-C32 organic compounds from gasoline-powered motor vehicles." *Environmental Science & Technology* **36**(6): 1169-1180.
46. Sofowote, U. M., et al. (2008). "Source apportionment of PAH in Hamilton Harbour suspended sediments: comparison of two factor analysis methods." *Environmental Science & Technology* **42**(16): 6007-6014.
47. Song, Y., et al. (2007). "Source apportionment of ambient volatile organic compounds in Beijing." *Environmental Science & Technology* **41**(12): 4348-4353.
48. Srivastava, A. and V. Jain (2007). "Size distribution and source identification of total suspended particulate matter and associated heavy metals in the urban atmosphere of Delhi." *Chemosphere* **68**(3): 579-589.
49. Vardoulakis, S., et al. (2008). "Impact and uncertainty of a traffic management intervention: population exposure to polycyclic aromatic hydrocarbons." *Science of the Total Environment* **394**(2): 244-251.
50. Venkataraman, C., et al. (1994). "Size distributions of polycyclic aromatic hydrocarbons and elemental carbon. 1. Sampling, measurement methods, and source characterization." *Environmental Science & Technology* **28**(4): 555-562.
51. Viana, M., et al. (2008). "Source apportionment of particulate matter in Europe: a review of methods and results." *Journal of Aerosol Science* **39**(10): 827-849.

52. Wang, D., et al. (2009). "Application of positive matrix factorization to identify potential sources of PAHs in soil of Dalian, China." *Environmental Pollution* **157**(5): 1559-1564.
53. Westerholm, R. and H. Li (1994). "A multivariate statistical analysis of fuel-related polycyclic aromatic hydrocarbon emissions from heavy-duty diesel vehicles." *Environmental Science & Technology* **28**(5): 965-972.
54. Yang, H.-H., et al. (1998). "PAH emission from various industrial stacks." *Journal of Hazardous Materials* **60**(2): 159-174.
55. Zhang, Y. and S. Tao (2009). "Global atmospheric emission inventory of polycyclic aromatic hydrocarbons (PAHs) for 2004." *Atmospheric Environment* **43**(4): 812-819.
56. Millman, A., et al. (2008). "Air pollution threatens the health of children in China." *Pediatrics* **122**(3): 620-628.
57. Sippula, O., et al. (2009). "Comparison of particle emissions from small heavy fuel oil and wood-fired boilers." *Atmospheric Environment* **43**(32): 4855-4864.
58. Jawdeh, G. A. (2006). "Lebanon Country Situation Report."
59. Lohmann, R., et al. (2000). "A comparative study of the gas-particle partitioning of PCDD/Fs, PCBs, and PAHs." *Environmental Science & Technology* **34**(23): 4943-4951.
60. Mandalakis, M., et al. (2002). "Gas-particle concentrations and distribution of aliphatic hydrocarbons, PAHs, PCBs and PCDD/Fs in the atmosphere of Athens (Greece)." *Atmospheric Environment* **36**(25): 4023-4035.
61. N.Pitts, B. J. F.-P. a. J. (2000). *Chemistry of the upper and lower atmosphere.*
62. Stockholm Convention (2004).
63. UNEP (2013). *Results of the global survey on concentrations in human milk of persistence organic pollutants by the United Nations Environment Programme and the World Health Organization.*
64. Arey, J., et al. (1967). "Polycyclic aromatic hydrocarbon and nitroarene concentrations in ambient air during a wintertime high-NO_x episode in the Los Angeles basin." *Atmospheric Environment* (1967) **21**(6): 1437-1444.
65. Baek, S., et al. (1991). "A review of atmospheric polycyclic aromatic hydrocarbons: sources, fate and behavior." *Water, air, and soil pollution* **60**(3-4): 279-300.
66. Caricchia, A. M., et al. (1999). "Polycyclic aromatic hydrocarbons in the urban atmospheric particulate matter in the city of Naples (Italy)." *Atmospheric Environment* **33**(23): 3731-3738.

67. Greenberg, A., et al. (1985). "Polycyclic aromatic hydrocarbons in New Jersey: a comparison of winter and summer concentrations over a two-year period." *Atmospheric Environment* (1967) **19**(8): 1325-1339.
68. Harrison, R. M., et al. (1996). "Source apportionment of atmospheric polycyclic aromatic hydrocarbons collected from an urban location in Birmingham, UK." *Environmental Science & Technology* **30**(3): 825-832.
69. Li, Z., et al. (2009). "Characterization of PM 2.5-bound polycyclic aromatic hydrocarbons in Atlanta—seasonal variations at urban, suburban, and rural ambient air monitoring sites." *Atmospheric Environment* **43**(27): 4187-4193.
70. Mastral, A. M., et al. (2003). "Spatial and temporal PAH concentrations in Zaragoza, Spain." *Science of the Total Environment* **307**(1): 111-124.
71. Menichini, E. (1992). "Urban air pollution by polycyclic aromatic hydrocarbons: levels and sources of variability." *Science of the Total Environment* **116**(1): 109-135.
72. Menichini, E., et al. (1999). "The temporal variability of the profile of carcinogenic polycyclic aromatic hydrocarbons in urban air: a study in a medium traffic area in Rome, 1993–1998." *Atmospheric Environment* **33**(23): 3739-3750.
73. N.Pitts, B. J. F.-P. a. J. (2000). *Chemistry of the upper and lower atmosphere*.
74. addo, v. p., bidleman, T.F, Brorstrom-Lunden, E, builtjes, P.J.H, Dutchak, S, Duyzer, J.H, Gryning, S, Jones, K.C, Van djik, H.F.G, Van Jaarsveld, J.A. (1999). "Atmospheric transport and deposition of pesticides: an assessment of current knowledge." *Water Air Soil Pollution* **115**: 245-256.
75. Agency, I. E. (2006a). *Energy Statistics and Balances of Non-OECD Countries , 2003-2004*.
76. Arey, J., et al. (1967). "Polycyclic aromatic hydrocarbon and nitroarene concentrations in ambient air during a wintertime high-NO_x episode in the Los Angeles basin." *Atmospheric Environment* (1967) **21**(6): 1437-1444.
77. ATSDR (1995). ATSDR (Agency for toxic substances and disease registry. u. c. Prepared by Clement International Corp. **205**: 88-0608.
78. Baek, S., et al. (1991). "A review of atmospheric polycyclic aromatic hydrocarbons: sources, fate and behavior." *Water, air, and soil pollution* **60**(3-4): 279-300.
79. Barakat, A. (2001). PAHs and petroleum markers in the atmospheric environment of Alexandria City, Egypt. ABSTRACTS OF PAPERS OF THE AMERICAN

CHEMICAL SOCIETY, AMER CHEMICAL SOC 1155 16TH ST, NW,
WASHINGTON, DC 20036 USA.

80. Barrie, L., et al. (1997). "Sources, occurrence and pathways." J. Jensen, K. Adare et R. Shearer (éd.), Canadian Arctic contaminants assessment report. Ministère des Affaires indiennes et du Nord, Ottawa (Ont.).
81. Boström, C.-E., et al. (2002). "Cancer risk assessment, indicators, and guidelines for polycyclic aromatic hydrocarbons in the ambient air." *Environmental health perspectives* **110**(Suppl 3): 451.
82. Brochu, P., et al. (2006). "Physiological daily inhalation rates for free-living individuals aged 1 month to 96 years, using data from doubly labeled water measurements: a proposal for air quality criteria, standard calculations and health risk assessment." *Human and Ecological Risk Assessment* **12**(4): 675-701.
83. Cakmak, S., et al. (2007). "Air pollution and mortality in Chile: susceptibility among the elderly." *Environmental health perspectives*: 524-527.
84. Caricchia, A. M., et al. (1999). "Polycyclic aromatic hydrocarbons in the urban atmospheric particulate matter in the city of Naples (Italy)." *Atmospheric Environment* **33**(23): 3731-3738.
85. Chen, S.-J., et al. (2007). "Emissions of polycyclic aromatic hydrocarbons (PAHs) from the pyrolysis of scrap tires." *Atmospheric Environment* **41**(6): 1209-1220.
86. Chmielewski, A. G., et al. (2010). "Electron beam technology for multipollutant emissions control from heavy fuel oil-fired boiler." *Journal of the Air & Waste Management Association* **60**(8): 932-938.
87. Cooper, D. (2001). "Exhaust emissions from high speed passenger ferries." *Atmospheric Environment* **35**(24): 4189-4200.
88. Duran, A., et al. (2001). "Simulation of atmospheric PAH emissions from diesel engines." *Chemosphere* **44**(5): 921-924.
89. Dyke, P. H., et al. (2003). "PCB and PAH releases from power stations and waste incineration processes in the UK." *Chemosphere* **50**(4): 469-480.
90. EPA/630/P-03/001B (2005). "Guidlines for Carcinogen Risk Assessment."
91. Galarneau, E., et al. (2007). "Estimation of atmospheric emissions of six semivolatile polycyclic aromatic hydrocarbons in southern Canada and the United States by use of an emissions processing system." *Environmental Science & Technology* **41**(12): 4205-4213.
92. Gambino, M., et al. (2000). Regulated and unregulated emissions reduction with retrofit catalytic after-treatment on small two stroke SI engine, SAE Technical Paper.

93. Greenberg, A., et al. (1985). "Polycyclic aromatic hydrocarbons in New Jersey: a comparison of winter and summer concentrations over a two-year period." *Atmospheric Environment* (1967) **19**(8): 1325-1339.
94. Guo, H., et al. (2003). "Particle-associated polycyclic aromatic hydrocarbons in urban air of Hong Kong." *Atmospheric Environment* **37**(38): 5307-5317.
95. Handbook, E. F. (2011). Inhalation rates.
96. Harrison, R. M., et al. (1996). "Source apportionment of atmospheric polycyclic aromatic hydrocarbons collected from an urban location in Birmingham, UK." *Environmental Science & Technology* **30**(3): 825-832.
97. Hopke, P. K. (2000). A guide to positive matrix factorization. Workshop on UNMIX and PMF as Applied to PM2.
98. Hopke, P. K. (2008). "The use of source apportionment for air quality management and health assessments." *Journal of Toxicology and Environmental Health, Part A* **71**(9-10): 555-563.
99. IARC (2010). IARC Monographs on the Evaluation of Carcinogenic Risks to Humans. **92**.
100. IARC (2010). Some non-heterocyclic polycyclic aromatic hydrocarbons and some related exposures. IARC monographs on the evaluation of carcinogenic risks to humans/World Health Organization, International Agency for Research on Cancer. **92**: 1.
101. Jang, E., et al. (2013). "Source apportionment of polycyclic aromatic hydrocarbons in urban air using positive matrix factorization and spatial distribution analysis." *Atmospheric Environment* **79**: 271-285.
102. Jawdeh, G. A. (2006). "Lebanon Country Situation Report."
103. Jones, K. C. and P. De Voogt (1999). "Persistent organic pollutants (POPs): state of the science." *Environmental Pollution* **100**(1): 209-221.
104. Khalili, N. R., et al. (1995). "PAH source fingerprints for coke ovens, diesel and, gasoline engines, highway tunnels, and wood combustion emissions." *Atmospheric Environment* **29**(4): 533-542.
105. Larsen, R. K. and J. E. Baker (2003). "Source apportionment of polycyclic aromatic hydrocarbons in the urban atmosphere: a comparison of three methods." *Environmental Science & Technology* **37**(9): 1873-1881.

106. Lawley, P. (1989). "Mutagens as carcinogens: development of current concepts." *Mutation Research/Fundamental and Molecular Mechanisms of Mutagenesis* **213**(1): 3-25.
107. Lebowitz, M. (1996). "Epidemiological studies of the respiratory effects of air pollution." *European Respiratory Journal* **9**(5): 1029-1054.
108. Li, C.-T., et al. (1999). "PAH emission from the industrial boilers." *Journal of Hazardous Materials* **69**(1): 1-11.
109. Li, Z., et al. (2009). "Characterization of PM 2.5-bound polycyclic aromatic hydrocarbons in Atlanta—seasonal variations at urban, suburban, and rural ambient air monitoring sites." *Atmospheric Environment* **43**(27): 4187-4193.
110. Lohmann, R., et al. (2000). "A comparative study of the gas-particle partitioning of PCDD/Fs, PCBs, and PAHs." *Environmental Science & Technology* **34**(23): 4943-4951.
111. Ma, W.-L., et al. (2010). "Seasonal variations of sources of polycyclic aromatic hydrocarbons (PAHs) to a northeastern urban city, China." *Chemosphere* **79**(4): 441-447.
112. Manahan, S. E. (1999). *Industrial ecology: environmental chemistry and hazardous waste*, CRC Press.
113. Mandalakis, M., et al. (2002). "Gas-particle concentrations and distribution of aliphatic hydrocarbons, PAHs, PCBs and PCDD/Fs in the atmosphere of Athens (Greece)." *Atmospheric Environment* **36**(25): 4023-4035.
114. Marchand, N., et al. (2004). "Polycyclic aromatic hydrocarbons (PAHs) in the atmospheres of two French alpine valleys: sources and temporal patterns." *Atmospheric Chemistry and Physics* **4**(5): 1167-1181.
115. Mari, M., et al. (2010). "Inferences over the sources and processes affecting polycyclic aromatic hydrocarbons in the atmosphere derived from measured data." *Science of the Total Environment* **408**(11): 2387-2393.
116. Marr, L. C., et al. (1999). "Characterization of polycyclic aromatic hydrocarbons in motor vehicle fuels and exhaust emissions." *Environmental Science & Technology* **33**(18): 3091-3099.
117. Martínez, K., et al. (2006). "PCDD/Fs in ambient air: TSP and PM 10 sampler comparison." *Atmospheric Environment* **40**(3): 567-573.
118. Mastral, A. M., et al. (2003). "Spatial and temporal PAH concentrations in Zaragoza, Spain." *Science of the Total Environment* **307**(1): 111-124.

119. Menichini, E. (1992). "Urban air pollution by polycyclic aromatic hydrocarbons: levels and sources of variability." *Science of the Total Environment* **116**(1): 109-135.
120. Menichini, E., et al. (1999). "The temporal variability of the profile of carcinogenic polycyclic aromatic hydrocarbons in urban air: a study in a medium traffic area in Rome, 1993–1998." *Atmospheric Environment* **33**(23): 3739-3750.
121. Miguel, A. H., et al. (1998). "On-road emissions of particulate polycyclic aromatic hydrocarbons and black carbon from gasoline and diesel vehicles." *Environmental Science & Technology* **32**(4): 450-455.
122. Miller, L., et al. (2010). "Intra-urban correlation and spatial variability of air toxics across an international airshed in Detroit, Michigan (USA) and Windsor, Ontario (Canada)." *Atmospheric Environment* **44**(9): 1162-1174.
123. Millman, A., et al. (2008). "Air pollution threatens the health of children in China." *Pediatrics* **122**(3): 620-628.
124. Motelay-Massei, A., et al. (2007). "PAHs in the bulk atmospheric deposition of the Seine river basin: source identification and apportionment by ratios, multivariate statistical techniques and scanning electron microscopy." *Chemosphere* **67**(2): 312-321.
125. N.Pitts, B. J. F.-P. a. J. (2000). *Chemistry of the upper and lower atmosphere*.
126. NAEI (1970 to 2001). 15th Annual Report from the UK National Atmospheric Emissions Inventory (NAEI). Annual Report National Environmental Technology Centre.
127. Oros, D. and B. Simoneit (2000). "Identification and emission rates of molecular tracers in coal smoke particulate matter." *Fuel* **79**(5): 515-536.
128. Ostro, B., et al. (2007). "The effects of components of fine particulate air pollution on mortality in California: results from CALFINE." *Environmental health perspectives*: 13-19.
129. paper, P. p. (2001). "Ambient air pollution by polycyclic aromatic hydrocarbons (PAH)." Office for Official Publications of the European Communities, Luxembourg.
130. Pisupati, S. V., et al. (2000). "An investigation on polycyclic aromatic hydrocarbon emissions from pulverized coal combustion systems." *Journal of Hazardous Materials* **74**(1): 91-107.
131. Pope III, C. A. and D. W. Dockery (2006). "Health effects of fine particulate air pollution: lines that connect." *Journal of the Air & Waste Management Association* **56**(6): 709-742.
132. Rappe, C. (1993). "Sources of exposure, environmental concentrations and exposure assessment of PCDDs and PCDFs." *Chemosphere* **27**(1): 211-225.

133. Ravindra, K., et al. (2006). "Seasonal and site-specific variation in vapour and aerosol phase PAHs over Flanders (Belgium) and their relation with anthropogenic activities." *Atmospheric Environment* **40**(4): 771-785.
134. Ravindra, K., et al. (2008). "Atmospheric polycyclic aromatic hydrocarbons: source attribution, emission factors and regulation." *Atmospheric Environment* **42**(13): 2895-2921.
135. Ré-Poppi, N. and M. Santiago-Silva (2005). "Polycyclic aromatic hydrocarbons and other selected organic compounds in ambient air of Campo Grande City, Brazil." *Atmospheric Environment* **39**(16): 2839-2850.
136. Rogge, W. F., et al. (1993). "Sources of fine organic aerosol. 2. Noncatalyst and catalyst-equipped automobiles and heavy-duty diesel trucks." *Environmental Science & Technology* **27**(4): 636-651.
137. ROY J. IRWIN, N. P. S. (1997). ENVIRONMENTAL CONTAMINANTS ENCYCLOPEDIA BENZO(G,H,I)PERYLENE ENTRY.
138. Schauer, J. J., et al. (1999). "Measurement of emissions from air pollution sources. 2. C1 through C30 organic compounds from medium duty diesel trucks." *Environmental Science & Technology* **33**(10): 1578-1587.
139. Schauer, J. J., et al. (2002). "Measurement of emissions from air pollution sources. 5. C1-C32 organic compounds from gasoline-powered motor vehicles." *Environmental Science & Technology* **36**(6): 1169-1180.
140. Schneider, K., et al. (2002). "Cancer risk assessment for oral exposure to PAH mixtures." *Journal of Applied Toxicology* **22**(1): 73-83.
141. Sippula, O., et al. (2009). "Comparison of particle emissions from small heavy fuel oil and wood-fired boilers." *Atmospheric Environment* **43**(32): 4855-4864.
142. Sofowote, U. M., et al. (2008). "Source apportionment of PAH in Hamilton Harbour suspended sediments: comparison of two factor analysis methods." *Environmental Science & Technology* **42**(16): 6007-6014.
143. Song, Y., et al. (2007). "Source apportionment of ambient volatile organic compounds in Beijing." *Environmental Science & Technology* **41**(12): 4348-4353.
144. Srivastava, A. and V. Jain (2007). "Size distribution and source identification of total suspended particulate matter and associated heavy metals in the urban atmosphere of Delhi." *Chemosphere* **68**(3): 579-589.
145. StockholmConvention (2004).

146. Stockholm Convention (2004). The Stockholm Convention on Persistent Organic Pollutants.
147. UNEP (2013). Results of the global survey on concentrations in human milk of persistent organic pollutants by the United Nations Environment Programme and the World Health Organization.
148. USEPA (1999). Compendium Method TO-13A. Determination of Polycyclic Aromatic Hydrocarbons (PAHs) in Ambient Air Using Gas Chromatography/Mass Spectrometry (GC/MS).
149. Vallack, H. W., et al. (1998). "Controlling persistent organic pollutants—what next?" *Environmental Toxicology and Pharmacology* **6**(3): 143-175.
150. Van den Berg, M., et al. (1998). "Toxic equivalency factors (TEFs) for PCBs, PCDDs, PCDFs for humans and wildlife." *Environmental health perspectives* **106**(12): 775.
151. van Drooge, B. L. and P. P. Ballesta (2009). "Seasonal and daily source apportionment of polycyclic aromatic hydrocarbon concentrations in PM₁₀ in a semirural European area." *Environmental Science & Technology* **43**(19): 7310-7316.
152. Vardoulakis, S., et al. (2008). "Impact and uncertainty of a traffic management intervention: population exposure to polycyclic aromatic hydrocarbons." *Science of the Total Environment* **394**(2): 244-251.
153. Venkataraman, C., et al. (1994). "Size distributions of polycyclic aromatic hydrocarbons and elemental carbon. 1. Sampling, measurement methods, and source characterization." *Environmental Science & Technology* **28**(4): 555-562.
154. Viana, M., et al. (2008). "Source apportionment of particulate matter in Europe: a review of methods and results." *Journal of Aerosol Science* **39**(10): 827-849.
155. Wang, D., et al. (2009). "Application of positive matrix factorization to identify potential sources of PAHs in soil of Dalian, China." *Environmental Pollution* **157**(5): 1559-1564.
156. Westerholm, R. and H. Li (1994). "A multivariate statistical analysis of fuel-related polycyclic aromatic hydrocarbon emissions from heavy-duty diesel vehicles." *Environmental Science & Technology* **28**(5): 965-972.
157. Whitby, K., et al. (1972). "The aerosol size distribution of Los Angeles smog." *Journal of Colloid and Interface Science* **39**(1): 177-204.
158. WHO (1998). Selected non-heterocyclic polycyclic aromatic hydrocarbons.
159. Yang, H.-H., et al. (1998). "PAH emission from various industrial stacks." *Journal of Hazardous Materials* **60**(2): 159-174.

160. Zhang, Y. and S. Tao (2009). "Global atmospheric emission inventory of polycyclic aromatic hydrocarbons (PAHs) for 2004." *Atmospheric Environment* **43**(4): 812-819.
161. Zhou, B. and B. Zhao (2014). "Analysis of intervention strategies for inhalation exposure to polycyclic aromatic hydrocarbons and associated lung cancer risk based on a Monte Carlo population exposure assessment model." *PloS one* **9**(1): 1-11.