CHARACTERISTIZATION, SOURCE IDENTIFICATION AND

POTENTIAL HEALTH RISKS OF ATMOSPHERIC PM$_{2.5}$-BOUND

POLYCYCLIC AROMATIC HYDROCARBONS IN AUTO MECHANIC

WORKSHOPS AROUND UWELU MOTOR SPARE PARTS MARKET,

BENIN CITY.

By

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CERTIFICATION

This is to certify that this project work titled "Characteristization, Source Identification And Potential Health Risks Of Atmospheric $P.M_{2.5}$-Bound Polycyclic Aromatic Hydrocarbons In Auto Mechanic Workshops Around Uwelu Motor Spare Parts Market, Benin City" was carried out by Ohonba Osasumwen Yvonne with matriculation number **PG/PSC1003148** in the Department of Chemistry, Faculty of Physical Science, University of Benin, Benin City.

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DEDICATION

This piece of work is dedicated God and to my parents Mr and Mrs Ohonba

ACKNOWLEDGEMENTS

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ABSTRACT

This study investigated PM$_{2.5}$-bound polycyclic aromatic hydrocarbons (PAHs) in order to determine the seasonal changes in total PAH concentrations, to estimate carcinogenic risk of exposure and to identify possible sources by using Cluster Analysis and Principal Component Analysis, two statistical tools, and diagnostic Ratios of PAHs. The sampling period was from February to June 2019. Casella Apex-2IS PM$_{2.5}$ sampler equipped with 37-mm quartz membrane filters were operate data flow rate of 3.5Lmin –1 for 8hours.

The concentrations of 16 PAHs were determine through gas chromatography –flame ionization detector. The results revealed the PM$_{2.5}$ and total PAHs in the two seasons ranged from 2604.16 to 7351.18µg/m^3 and 585.86 to 764.07ng/m^3 respectively. The highest contributions to the total PAH level were made by Benzo(g,h,i)perylene [289.03 ng/m^3], Indeno(1,2,3-c,d)pyrene[130.51ng/m^3], Benzo(a)pyrene[122.63ng/m$^{3]}$ and Dibenz(a,h)anthracene [99.06ng/m^3] while lower values were recorded for other PAHs like Anthracene[4.40ng/m^3], Phenanthrene [3.22ng/m^3], Fluoranthene[1.7ng/m^3], Pyrene[3.65 ng/m^3], Chrysene[12.91ng/m^3], Benzo(a)Anthracene[5.27ng/m^3], Benzo(k)Fluoranthene[16.77ng/m^3] and benzo(b)Fluoranthene [72.20ng/m^3] while BAP-TEQ was 2.73×10^{-7} ng/m^3.

The PM$_{2.5}$ and total PAH concentrations were in the order March > February > May > June and exhibited significant seasonal variations. The major BAP-TEQ contributors were B(ghi)P, B(a)P, and Ind(1,2,3-cd)P. BaP accounted for 18.23% of BAP-TEQ concentrations in PM$_{2.5}$. The annual average life time excess cancer risk of PM$_{2.5}$-bound PAHs (2.51×10 -. 4ng/m3) was higher than that specified in the United States Environmental Protection Agency guidelines (1×10^{-6}). The major sources of pollution in the environment were stationary emission sources, petroleum and traffic emissions.

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1.0   INTRODUCTION AND LITERATURE REVIEW

1.1   INTRODUCTION

Motor vehicles have become essential part of today's life. Due to the inevitable wear of car engines, repair work is essential to automobile use and ownership (Williams, *et al*., 2011). Vehicles repair and maintenance need has led to the emergence of a large sector named Motor Vehicle Repair Workshop, which is also known as mechanic workshop. This is an informal sector also categorized as small and medium size enterprise. It's a labour-intensive sector, and its size of enterprise, number of workers and job characterization vary considerably (Cadwell, *et al*., 2000). Employees of all ages are routinely seen at these workshops. From health and safety point of view, this is the tough sector to tract and supervise. Hundreds and thousands of risks and hazards go unnoticed. Common occupational hazards such as physical, ergonomic, biological and chemical are found in Motor Vehicle Repair Workshop activities, due to heavy machinery, petroleum fuels/ oils, high use of solvents, smoke, particulate matter and various other pollutants. These hazards become more critical when there is a lack of awareness, controls measures and implementation of health and safety rules and regulations (Cadwell, *et al*., 2000). Repair technicians, otherwise known as mechanics, are required to apply chemicals which can be hazardous in order to perform repairs on vehicles. The application of chemicals typically involves the spraying of aerosolized agents onto a part or surface. (Spencer, *et al*., 2007). The spraying of chemicals is the most effective means of applying solvents, penetrating lubricants, and cleaners to often oddly shaped or difficult to reach parts of a vehicle (Stidman, 1999). The downside of the ease of application for these chemicals is that they become airborne and are easily inhaled into the respiratory system (Daniell, *et al*., 2010). These airborne chemicals may be organic or inorganic pollutants. Examples of such pollutants are Oxides of nitrogen (NO_x) which is formed from the combination of nitrogen dioxide (NO_2) and nitrous

<div align="center">1</div>

oxide (NO); ozone (O$_3$), particulate matter (PM- TSP, PM$_{2.5}$ and PM$_{10}$), carbon monoxide (CO), sulphur dioxide (SO$_2$) and lead (Pb). Among these, health risks associated with exposure to fine particulate matter (PM$_{2.5}$) are of significant concern, especially, given the increase in cardiovascular and respiratory disease (Murad, 2012; Shah *et al.,* 2013; Raz *et al*., 2014 and Kim *et al.,* 2015).

Particulate matter (PM) air pollution has been linked to increased morbidity and mortality rates, as well as various adverse health effects such as respiratory and cardiovascular diseases (Cakmak *et al,* 2007; Kappos*et al*., 2004; Ostro*et al*., 2007; Pope *et al*., 2004). Particulate matter with aerodynamic diameters less than 2.5 µm (PM$_{2.5}$ or fine particulate matter) are of special concern because, when inhaled, they can penetrate effectively into the respiratory system and deposit deeply in the bronchioles and alveoli of the lungs. The association of fine particles with mutagenic and carcinogenic chemicals such as polycyclic aromatic hydrocarbons (PAHs) may contribute to these acute health effects or potentially result in long-term health risks. Polycyclic aromatic hydrocarbons (PAHs) are a group of toxic pollutants formed during incomplete combustion of organic materials such as wood, fossil fuels, meat, and tobacco. They are found in automobile exhaust, wood smoke, cigarette smoke, and certain food such as barbequed food (Bostrom *et al*., 2002); thus this class of compounds is ubiquitously distributed in ambient air, food, soil, as well as in many occupational environments.

PAHs have generated considerable interest, not only because of their wide distribution in the environment, but also their carcinogenic and mutagenic potential. Benzo[a]pyrene (BAP), which is present in cigarette smoke and certain occupational environments, have been positively associated with lung cancer (Armstrong *et al*., 2004). In addition, PAHs have also been reported to have reproductive, developmental, hemato-, cardio-, neuro-, and immuno-toxicities in humans and laboratory animals. PAHs have generated considerable interest, not only because of their wide distribution in the environment, but also their carcinogenic and

mutagenic potential(ATSDR, 1995). PAHs, such as benzo[a]pyrene (BAP), which is present in cigarette smoke and certain occupational environments, have been positively associated with lung cancer (Armstrong, *et al*., 2004). In addition, PAHs have also been reported to have reproductive, developmental, hemato-, cardio-, neuro-, and immuno-toxicities in humans and laboratory animals **(ATSDR, 2001).**

Given their carcinogenic and mutagenic potential and their wide distribution resulting in exposure in the general population, PAHs have generated considerable interest; 16 PAHs have been included in U.S. EPA's list of 188 hazardous air pollutants(U.S.EPA, 1990). In ambient air, PAHs are found in both gaseous and particle phases. PAHs with 2-3 aromatic rings exist almost exclusively in the gaseous phase, while compounds with 4 or more aromatic rings are primarily associated with the particulate fraction (Eiguren-Fernandez *et al*., 2004; Li *et al*., 2006; Re-Poppi & Santiago-Silva, 2005). In addition, it has been reported that PAH-associated particles exist predominantly as fine particles, i.e., in the $PM_{2.5}$ size range, especially in areas with heavy traffic (Cancio *et al*., 2004; Duan *et al*., 2005; Ohura *et al*., 2004). Because the carcinogenic PAHs (e.g. benzo[a]pyrene and benzo[a]anthracene) are mostly associated with the particulate matter, many studies on PAHs in ambient air have been focused on PAHs bound to PM, particularly $PM_{2.5}$(Bourotte *et al*., 2005; Ohura *et al*., 2004; Sanderson *et al*., 2004; Sklorz *et al*., 2007)

1.1.1 Background of Study

Gaseous pollutants and particulate matter are released into the atmosphere at concentrations above their normal ambient level. This is caused by the increasing human activities which eventually have a measurable effect on humans, animals and plants. Particulate matter (PM) when inhaled into the human respiratory system is related to most serious health effects

including pulmonary and cardiovascular illnesses. The size of particles is directly linked to their potential for causing health problems. Environmental Protection Agency (EPA) agencies such as Federal Ministry of Environment and United State Environmental Protection Agency are concerned about particles that are 2.5 micrometre in diameter ($PM_{2.5}$)or smaller because those are the particles that generally pass through the throat and nose and enter the lungs. Once inhaled, these particles can affect the heart and lungs and cause serious health problems. The source of airborne particulates includes natural and anthropogenic processes. The most remarkable anthropogenic source with regards to quantity stem from incomplete combustion processes, such as fossil fuel and biomass burning. The rate of increase of air pollutant concentrations in developing countries such as Nigeria are higher than those in developed countries and hence atmospheric pollution is often severe in cities of developing countries all over the world. There has been significant industrial progress in Nigeria over the last three decades with the establishment of many cottage industries. This rapid industrialization has not been matched with proper planning for the control of environmental pollution problems that are usually associated with such industrial development (Okuo *et al*., 2017).

Automobiles constitute one of the major modes of transportation for conveying people and goods in any nation of the world. The usefulness of this mode of transportation is not without cost. The major cost is pollution of different magnitude (Ekong *et al*., 2012) classified the pollution cost of automobile transportation into two main groups such as operational and the maintenance cost. The operational cost of automobile transportation occurs when vehicles are driven from one place to the other while the maintenance dimension occurs during vehicle repairs. 48% of total atmospheric pollution comes from these two forms of automobile activities. Their major gaseous pollutants are sulphur dioxide, nitrogen oxide, ozone, carbon monoxide, lead and particulate matter (PM: $PM_{2.5}$, PM_{10} and TSP). International fora such as Earth Summit focused more attention on the reduction of operational cost of automobile

pollution by recommending the use of ethanol and hydrogen as alternative fuel for powering automobiles, removal of lead from gasoline, use of electric trains for inner city transportation, etc. Most of these suggestions have been implemented in some developed countries while some have been interpreted into local contents of some developing countries waiting for implementation (Earth summit, 2002). However, less attention is paid to pollution caused by the maintenance dimension of automobile transportation (auto mechanic activities). These workshops are sometimes characterized by various operators functioning in areas such as spraying or painting, welding (arc/electric), battery recharging and repairs, car servicing and maintenance (Adelekan & Abegunde, 2011). The workshop size varies depending on the number of function and services which they carry out on regular basis. Environmental pollutions arising from the activities of auto mechanics in Nigeria are not well documented except few works like (Iwegbue, 2007;Ipeaiyeda & Dawodu, 2008;Ekong *et al*., 2012)

1.1.2   Statement of Problem(s)

Air pollution is the most insidious because it is the type of pollution most difficult for humans to protect themselves from. The health impact of air pollution greatly depend on the characteristics or nature of the pollutants as well as the degree and duration of exposure.

Organic and Inorganic pollutants like PAHs and metals found in petrol and petroleum products, such as those found in the mechanic workshops, have the capacity to remain in the environment over time when exposed and hence can pose serious health effects. These may range from body pains to head ache, fatigue, respiratory problems and may even cause death when inhaled or ingested in high concentrations.

1.1.3   Justification

The increase in the number of mechanic workshops and its activities (such as auto servicing and repairs) in Nigeria due mainly to the large inflow of "Fairly Used" vehicles into the country in the late 1990s have contributed greatly to the pollution experienced within and around these workshops. The exposure to hazardous chemicals while performing automotive repair work is most likely to occur to those members of society who are least likely to be prepared for them. Several studies have been carried out on air pollution and contamination from industries and some manufacturing companiesand this has led to establishment and enforcement of emission standards while very little research has been done on the air quality surrounding automobile workshops. Also, many researchers have focused on metal pollution while scarce publications exist for PAHs.

This research was undertaken to provide baseline data on the pollution resulting from $PM_{2.5}$ bound polycyclic aromatic hydrocarbons around auto-mechanic workshops in Benin City.

Currently, no data exists in Benin City for $PM_{2.5}$ bound Polycyclic Aromatic Hydrocarbons within the ambient air of Auto-mechanic workshops. The purpose of this study was to create a profile of exposure to PAH for a typical mechanic with a view to identifying the sources as well as providing data for use in adequate environmental control.

1.1.4 Scope of Study

In this study, we analysed PAHs bound to $PM_{2.5}$ filters collected across auto mechanic workshops in uwelu motor spare-parts market which is in the North West zone of Benin City. 20-sampling locations were randomly selected after careful survey of all the mechanics workshops around the market. The sampling was carried out weekly for 5-months (February, March, April, May and June.). Meteorological data was also collected using professional weather station.

1.1.5 Aim and Objectives of the study

1.1.5.1 Aim

To characterised, source apportioned and health risks of atmospheric $PM_{2.5}$-bound the Polycyclic Aromatic Hydrocarbons around Uwelu motor spare parts in Benin City.

1.1.5.2 Objectives

The specific objectives of this study are to:

1. Determine the level of $PM_{2.5}$ using Apex2IS Casella kit in the sampling locations.

2. Assess the influence of meteorological factors such as (wind speed, wind direction, relative humidity, temperature, atmospheric pressure and solar radiation and ultra-violet radiation) on $PM_{2.5}$ concentration.

3. Characterize the concentration of $PM_{2.5}$ bound PAHs using Gas Chromatography-Flame Ionization Detector (GC-FID).

4. Draw a correlation between $PM_{2.5}$ and PAHs and meteorological parameters.

5. Estimate the degree of carcinogenicity of $PM_{2.5}$ bound PAHs using TEF and excess cancer risk factor.

6. Determine the effect of seasonal variation of PAH level

7. Determine the pollutant sources in the study area using principal component analysis and PAH diagnostic ratio.

1.2   LITERATURE REVIEW

1.2.1 Introduction

According to the USA Clean Air Act (CAA) amendments established in 1970, pollutants are classified into 2 main groups ((U.S.EPA, 1971).

These are;

- The criteria pollutants, namely, nitrogen dioxide (NO_2), sulphur dioxide (SO_2), carbon monoxide (CO), ozone (O_3), lead (Pb) and particulate matter , including particulate matter with a diameter less than 2.5 μm ($PM_{2.5}$), these can be further divided into a category of ultra-fine particulates that have a diameter less than 0.1 micrometres (μm) ($PM_{0.1}$). These small particles are generally present in relatively high concentrations in polluted air and they arise from a number of different sources (Kunzli & Perez, 2009;WHO, 2013).

- A diverse range of hazardous pollutants, including volatile and semi-volatile organic compounds and heavy metals(Sorensen *et al*., 2003). These pollutants are usually present in relatively low concentrations and they are toxic or persistent making them hazardous to human health.

It has been reported that coarse particles (PM_{10}) and fine particles ($PM_{2.5}$) in urban air have been equally potent in inducing respiratory-based hospitalisations and inflammatory responses resulting in disease exacerbation in susceptible groups (Diaz-Sanchez, 2015;Pope & Dockery, 2006). These PM subsets arising from anthropogenic sources contain transition metals, and carbonaceous fractions in the form of PAHs, both of which are known to cause chronic respiratory and cardiovascular diseases and asthma (Uzoigwe *et al*., 2013; Happo *et al*., 2008; Penn *et al*., 2005).

Despite a large body of evidence of the deleterious effects of ambient PM exposures on the cardiovascular system, relatively little attention has been given to the effects of occupational exposures, which differ from general ambient exposures in both particle type (e.g., composition), as well as exposure frequency (e.g., environmental exposures are relatively constant while occupational exposures are more variable), duration (e.g., a work-shift and working lifetime vs. an entire day and lifetime), and intensity or concentration (i.e.,

occupational exposures are generally higher than ambient levels). These differences in exposure composition, duration, frequency and population exposed may have implications on how occupational PM exposures impact CVD and how these associations are studied. For example, intense exposures may act as an acute trigger of acute coronary events for individuals with pre-existing cardiovascular disease. At the same time, differences between the general population and working populations may also have implications on how particulate exposures impact workers' cardiovascular health.

1.2.2 Particulate Matter

Airborne particulate matter is a mixture of solid particles and liquid droplets, which vary in concentration, nature and size distribution. The particles can be, for example, combustion products, dust or bio aerosols, and can act as carriers of adsorbed chemicals, bio-contaminants or condensed gases. A primary particle is a particle introduced into the air in solid or liquid form, while a secondary particle is formed in the air by gas-to-particle conversion of oxidation products of emitted precursors   The size of airborne particles is significant as it determines their dynamic properties and thus behavior in the air and fate during transport and in particular, strongly influences in which part of the respiratory tract the particles are deposited. Larger particles, due to their higher inertia are deposited in the nasal area and in the upper parts of the respiratory tract. By contrast, smaller particles that can follow the airflow to the deeper parts of the respiratory tract have a very high probability of depositing in those parts by diffusion, which is a very efficient deposition mechanism for small particles. It is, however, not only the number or mass of particles in the particular size range that is important, but also the composition of particles. The composition may determine in what way the respiratory tract reacts, or the body responds. The highest level of concentration of trace elements and toxins from anthropogenic sources and radioactivity from natural sources is related to the very small particles. The large particles carry components and elements mainly of crustal origin, mainly

from natural sources. Some particles can act as carriers of adsorbed chemicals or gases which can act as triggers for various health effects.

PM_{10} is particulate matter that is 10 microns or less in diameter, and the $PM_{2.5}$ subset includes smaller particles that are 2.5 microns or less in diameter.
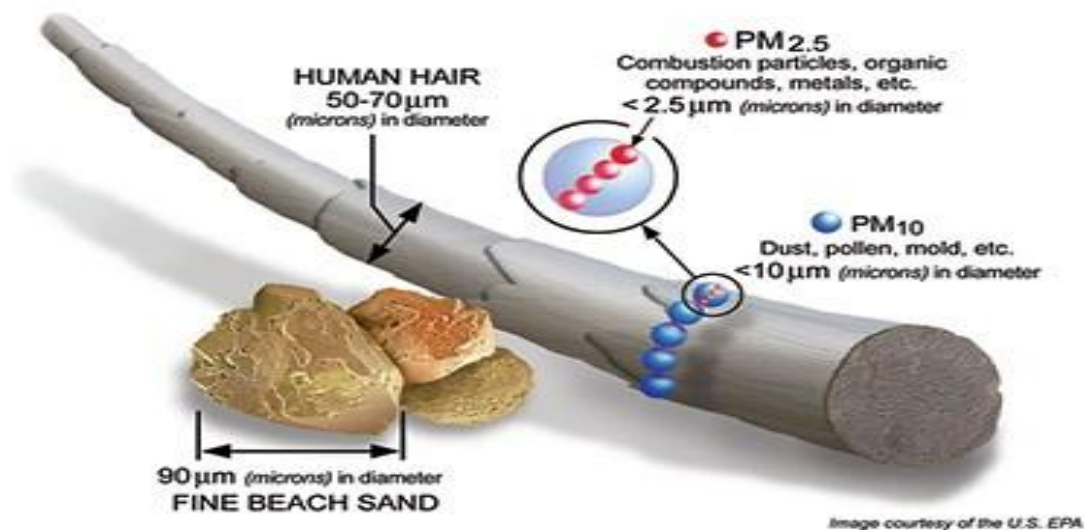
Figure 1.1: Visual Comparison of PM10, PM2.5, Human Hair, and Fine Beach Sand
Source: U.S. Environmental Protection Agency, 2012.

Within most established networks, outdoor particles are measured by PM_{10} and $PM_{2.5}$ (until recently also as TSP, total particle mass, or black smoke, BS); therefore, most of the evidence of health effects of outdoor particles is based on these measures. TSP is almost entirely dominated by particles generated by mechanical processes such as dust re-suspension, grinding, and mining. PM_{10} is sometimes dominated by particles generated by mechanical processes and sometimes by accumulation mode particles, which is an aged fraction of the

outdoor aerosol emitted by many sources such as industrial emissions, vehicle emissions, and power generation. In addition, a portion of the particles is of biogenic origin and generated from secondary processes such as photochemical processes. $PM_{2.5}$ is more likely to be dominated by accumulation mode particles, but can also include a significant fraction of mechanically generate particles. The relative contributions from different types of sources are very site specific. Increases in all-cause mortality have been observed in studies of the acute and chronic effects of particulate matter. The increase in all-cause mortality is attributable to increases in respiratory disease and cardiovascular disease mortality (Schwartz, 2004). Consistent with the observation of increases in acute mortality, there was also an increase in hospital admissions for respiratory diseases and cardiovascular diseases in association with particulate air pollution (Bascom *et al*. 1996). Subpopulations consisting of susceptible individuals how increases in symptoms, medication use and physiological parameters consistent with an exacerbation of pre-existing respiratory or cardiovascular diseases.

The PM-exposure for an individual is the concentration of particulate matter (PM) with specified characteristics that exists in a person's breathing zone over a specified period of time. Humans are normally exposed to PM from several different sources. These can be broken down into four basic (microenvironment) categories:

1) PM of outdoor origin from primary sources, such as traffic and industry, wind-blown dust from soil and from secondary sources such as PM produced by photochemical reactions.

2) PM generated by indoor sources, which include indoor combustion devices and re-suspension of general house-dust and pets.

3) PM from occupational sources, which cover a wide range of activities and they may be an extension of the domestic environment or they may be specific types of PM associated with the nature of the raw materials and the type of production process.

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4) PM due to personal habits and activities and therefore including tobacco smoking, as well as general cleaning activities

1.2.2.1 Chemical characteristics of PM$_{2.5}$

The most important chemical properties of particles include

- Elemental composition
- Secondary inorganic ions
- Carbonaceous compounds
- Organic composition

Particle organic composition

All of the combustion sources generate large amounts of volatile and semi-volatile organic compounds. Semi-volatile organic compounds can be present in the air either in the vapour or in particle form (solid or liquid). Exposure to many of the organic compounds emitted to the air has been associated with various types of health effects.

1.2.3 Polycyclic Aromatic Hydrocarbons

Polycyclic Aromatic Hydrocarbons (PAHs) are one class of compounds contained in the organic fraction of the fine particulate matter. PAHs compounds are synthesized from carbon fragments into large molecular structures in low-oxygen environments, such as occurs inside the flame envelope in the fuel-rich region of the flame structure. If the temperature is not adequate to decompose compounds upon exiting from the flame zone, then they are released into the free atmosphere and condense or are adsorbed onto the surface of particles. Many different combustion systems are known to produce PAH compounds.

The most studied PAHs is benzo[a]pyrene (B[a]P) that is a physiologically active substance that can contribute to the development of cancer in human cells.. The US EPA introduced a list of the 16 priority PAHs that include: Acenaphthene, Acenaphthylene, Anthracene, Benzo(a)anthracene, Benzo(a) pyrene, Benzo(b)fluoranthene, Benzo(g,h,i)perylene, Benzo(k)fluoranthene, Chrysene, Dibenz(a,h)anthracene, fluoranthene, fluorene, Indeno(1,2,3-cd)pyrene, Naphthalene, Phenanthrene, Pyrene. High concentrations of PAHs have been found in soot generated from wood burning stoves and coal burning stoves. PAHs have also been found in gasoline and diesel soot, and the relative abundance of individual PAH species may be different for different types of soot. This makes it is possible to use PAHs as source signatures of different types of fuels on one hand, but may also result in different health effects due to inhalation of emissions from different fuels.

1.2.4   Basic Chemistry Of PAHs

The simplest PAHs, as defined by the International Union of Pure and Applied Chemistry (IUPAC) (G.P Moss, IUPAC nomenclature for fused-ring systems), are phenanthrene and anthracene, which both contain three fused aromatic rings. PAHs may contain four to seven-member rings, but those with five or six are most common. PAHs composed only of six-membered rings are called **alternant** PAHs. Certain alternant PAHs are called **benzenoid** PAHs. The name comes from benzene, an aromatic hydrocarbon with a single, six-membered ring. PAHs containing up to six fused aromatic rings are often known as "small" PAHs, and those containing more than six aromatic rings are called "large" PAHs. Due to the availability of samples of the various small PAHs, the bulk of research on PAHs has been of those of up to six rings. The biological activity and occurrence of the large PAHs does appear to be a continuation of the small PAHs. They are found as combustion products, but at lower levels than the small PAHs due to the kinetic limitation of their production through addition of

successive rings. In addition, with many more isomers possible for larger PAHs, the occurrence of specific structures is much smaller.

1.2.5   Occurrence of PAHs

Polycyclic aromatic hydrocarbons are lipophilic, meaning they are soluble in oil. The low molecular weight PAHs are soluble in water and more volatile but as the molecular weight increase the solubility decreases as well as the volatility. Meaning that the larger compounds are less water-soluble and less volatile (i.e. less prone to evaporate). Because of these properties, PAHs in the environment are found primarily in soil, sediment and oily substances, as opposed to in water or air. However, they are also a component of concern in particulate matter suspended in air. Also, study has shown that natural crude oil and coal deposits contain significant amounts of PAHs, arising from chemical conversion of natural product molecules, such as steroids, to aromatic hydrocarbons. They are also found in processed fossil fuels, tar and various edible oils. PAHs are one of the most widespread organic pollutants. In addition to their presence in fossil fuels they are also formed by incomplete combustion of carbon containing fuels such as wood, coal, diesel, fat, tobacco, and incense as announced by British Broadcasting Co-operation(BBC NEWS, 2-08-2001) Different types of combustion yield different distributions of PAHs in both   relative amounts of individual PAHs and in which isomers are produced. Thus, coal burning produces a different mixture than motor-fuel combustion or a forest fire, making the compounds potentially useful as indicators of the burning history. Hydrocarbon emissions from fossil fuel-burning engines are regulated in developed countries.

1.2.6   Classification of PAHs

PAHs are classified based on their molecular weight as

1. Low molecular weight (LMW) the two and three member ring PAHs they are also called vapour phase PAHs. They include acenaphthene, acenaphthylene, anthracene, fluorene, and phenanthrene

2. Medium molecular weight (MMW) which include Fluoranthene and pyrene

3. High molecular weight (HMW) PAHs, the PAHs with four or more fused rings also refers to as particulate phase PAHs which include benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(g,h,i)perylene, benzo(a)pyrene, Benzo(e)pyrene, chrysene, dibenz(a,h)anthracene and indeno(1,2,3-c,d)pyrene
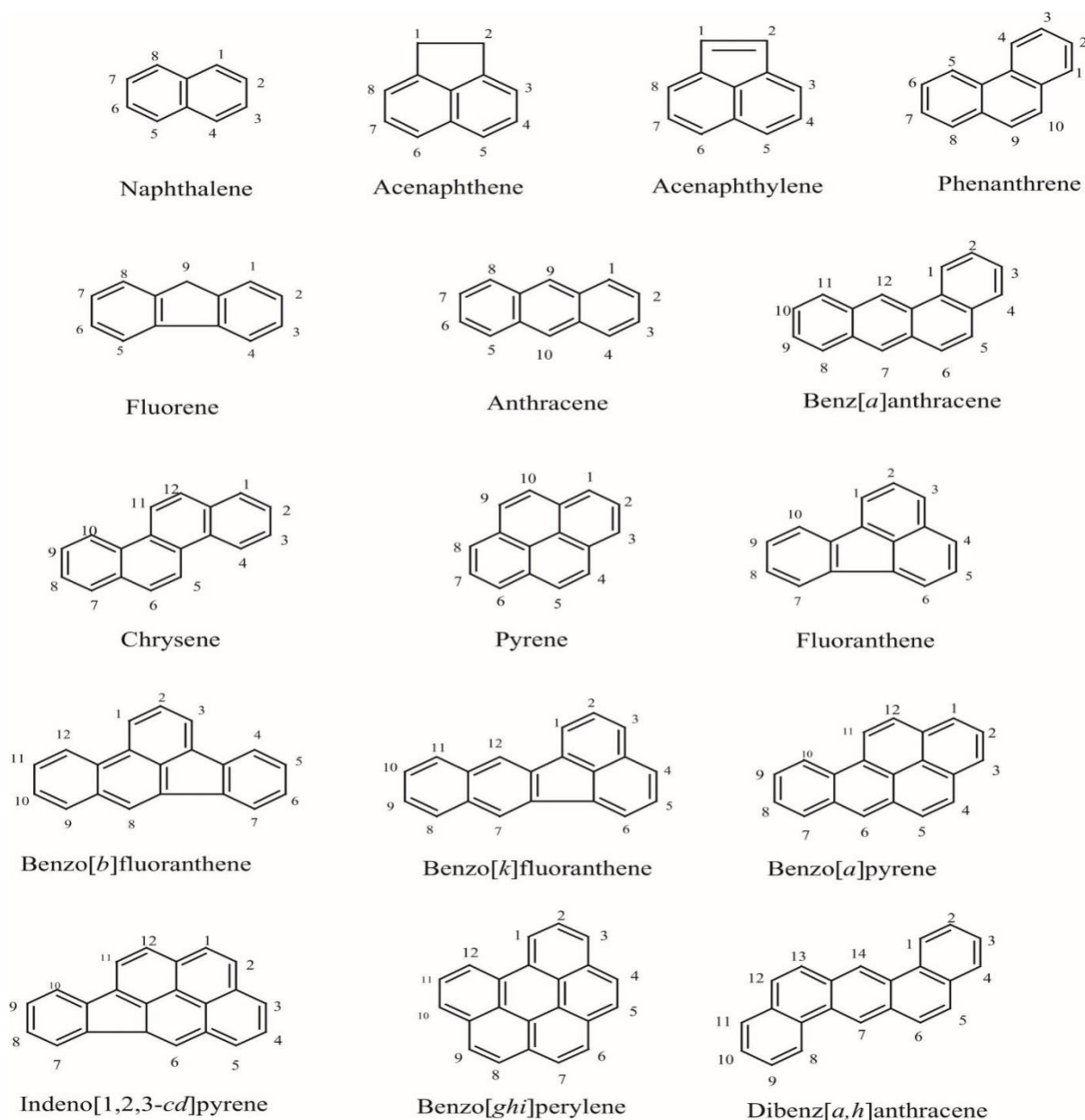
Figure 1.2: US EPA criteria PAHs

1.2.7 Formation of PAHs

PAHs may be synthesized from saturated hydrocarbons under oxygen-deficient conditions. Pyrosynthesis and pyrolysis are two main mechanisms that can explain the formation of PAHs. Low hydrocarbons form PAHs by pyrosynthesis. When the temperature exceeds 500^0C, carbon–hydrogen and carbon–carbon bond are broken to form free radicals. These radicals

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combine to acetylene which further condenses with aromatic ring structures, which are resistant to thermal degradation. Figure 1 illustrates the formation of such rings starting with ethane. The tendency of hydrocarbons to form PAH structure by pyrosynthesis varies in the order— Aromatics > Cycloolefins > Olefins > Parafins (Ravindra, *et al*., 2009; Ravindra, *et al*., 2009)
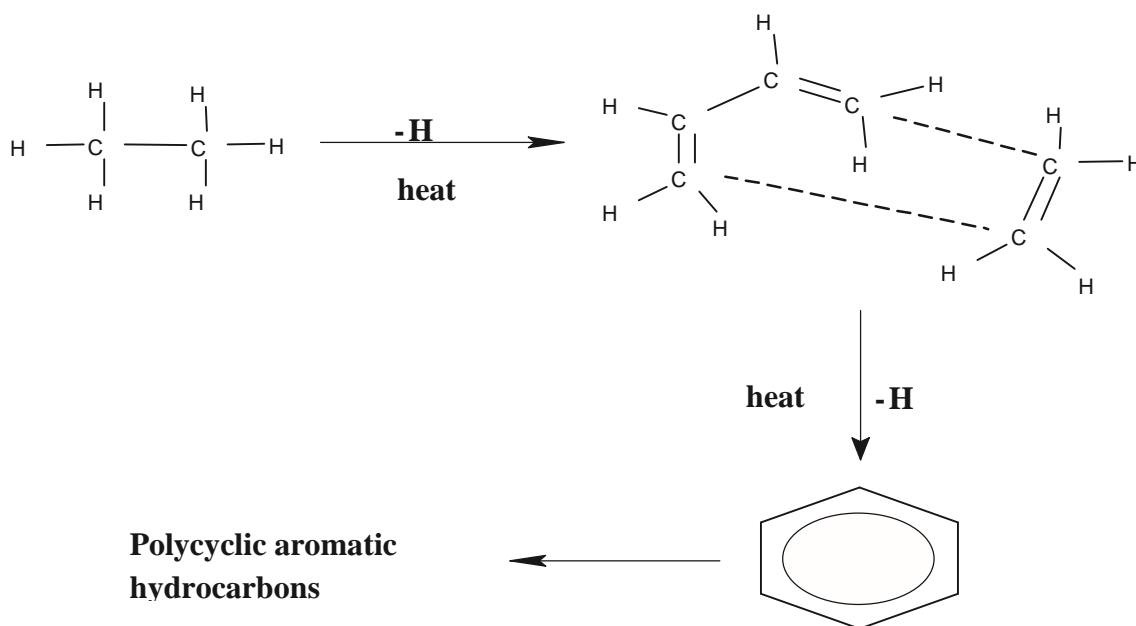
Figure 1.3: Pyrosynthesis of PAHs starting with ethane

Haynes, (1991), suggested three possible mechanisms of PAH formation during combustion, i.e. slow Diels–Alder condensations, rapid radical reactions, and ionic reaction mechanism. However, the radical formation mechanism is favoured as the combustion process within the internal combustion engine has to occur very rapidly. It would seems that gaseous hydrocarbon radicals rearrange quickly, providing the mechanism of PAHs formation and growth. The addition of hydrocarbon radicals to lower molecular weight PAHs then leads, via alkyl PAHs, to the formation of higher PAHs (Wiersum, 1996). Recently, (Lima *et al*., 2005) reviewed and

discussed some of the factors (type of fuel, amount of oxygen, and temperature) that affect the production and environmental fate of combustion-derived PAHs.

1.2.8   Polycyclic Aromatic Hydrocarbons (PAHs) as Environmental Pollutants

Polycyclic Aromatic Hydrocarbons PAHs as mentioned earlier are ubiquitous substances, that is, they are found almost everywhere and can move from one environmental media (air/atmosphere, water and soil) to the other (WGPAHs, 2001). They can persist in the environment for a long time (WHO, 2003), and have also been found to be toxic with further studies revealing them to be the most toxic pollutants among the hydrocarbon families. PAHs possess the ability to undergo biotransformation to toxic metabolites thereby resulting in adverse effects on environmental components and make them important environmental pollutants. They are released into the air from various pyrolytic sources, such as burning of fossil fuels in machines or vehicles and household or commercial burning and incineration, cigarette smoke, or from the natural sources (forest fires and volcanoes); they are usually found attached to dust particles and may be inhaled or due to their heavy molecular weight may be deposited on plants or water surface (ATSDR, 1999). PAHs are usually found in ambient air in rural, urban and suburban areas and a wide range can be found in the atmosphere (EFCS, 2010). The air or atmosphere is usually the first point of release of PAHs from several pyrolytic sources and could be inhaled directly by human (SPR, 2013).

In the atmosphere, PAHs could be transformed, degraded or deposited. Deposition could be on vegetation, animals (including birds), humans, aquatic environment and even soil. The processes that transform and degrade PAHs in the atmosphere include photolysis and reaction with NOx, N_2O_5, OH-, ozone, Sulphur dioxide SO_2, and Peroxyacetylnitrate PAN. Possible atmospheric reaction products are oxy-, hydroxy-, nitro- and hydroxynitro-PAH derivatives. Photochemical oxidation of a number of PAHs has also been reported with the formation of nitrated PAHs, quinones, phenols, and dihydrodiols. Reaction with ozone or

Peroxyacetylnitrate yields diones; Nitrogen oxide reactions yield nitro and dinitro PAHs. Sulphonic acids have also been formed from reaction with sulphur dioxide. Some of these breakdown products are mutagenic and studies have shown that these products could be more toxic than the parent PAHs compounds (ATSDR, 1995). PAHs like many air pollutants reduce air quality. When such air is inhaled, it can produce certain dangerous health defects and this also depends on the length of exposure and the quantity exposed to. Studies have further found that the quantity of PAHs found in the atmosphere in cold season could be more than those found in hot season (EFCS, 2010). This could be related to the absence of sunlight that could act to break down the PAHs (by photodecomposition) and the probable increase in burning to keep warm that could increase heating emissions in the atmosphere. On the contrary however, observation has shown that there is likely to be more fire incidence or outbreak in the dry season than in the wet season which are the two major seasons prevalent in Nigeria (the study area); and could therefore increase the amount of heating emission and probably PAHs in the atmosphere.

1.2.9   Sources of Polycyclic Aromatic Hydrocarbons (PAHs)

PAHs have been found to be almost ubiquitous since they are found everywhere (WHO, 2003) even in interstellar medium (Allamandola *et al*., 2003); their source would therefore be related to almost everything in the environment and its usage or that of it components. Sources of Polycyclic Aromatic Hydrocarbons PAHs in the environment could be grouped into:

• originating sources

• emitting sources

1.2.9.1   Originating sources of PAHs

If source inventories are lacking or incomplete, the first task is to clarify whether the known or unknown sources of PAHs are petrogenic, pyrogenic or natural. This is usually accomplished

by observing PAH fingerprints that show the relative PAH abundances (Douglas *et al*. 2007). For example, the relative distribution of PAHs in each homologous family is used to differentiate compositional changes during the degradation of oil spills (Wang *et al*., 1999). Once released to the environment, the PAHs are prone to a wide variety of degradation processes, including evaporation, dissolution, dispersion, emulsification, adsorption on suspended materials, microbial degradation (biotic or biodegradation), photo-oxidation, and interaction among the contaminants and sediments (Kim *et al*., 2009). Degradation substantively changes the physicochemical properties and relative abundances of even the highest MW PAHs, and such changes must be considered when identifying and quantifying PAH sources (Wang *et al*., 2004).

(a)   Biogenic/digenetic

Digenetic PAHs are produced during the slow transformation of organic materials in lake sediments, whereas biogenic or phylogenetic PAHs are produced by plants, algae/phytoplankton and microorganisms (Venkatesan, 1988). Perylene (Pr) is produced under several conditions: by digenesis and biosynthesis from terrestrial precursors (perylenequinone pigment) or other organic matter; under anoxic conditions; and in soil and subtidal, marine and freshwater sediments (Boll *et al,* 2008; Guo *et al*., 2007). In the tropics, termite nests may act as a perylene source in soil (Barra *et al*, 2007). If perylene does not correlate with the total organic carbon, then the perylene is likely to have a natural origin(Luo *et al*., 2008). In such a case, perylene may not yield its source of organic matter, although it can be a useful tracer for water and for depositional conditions (Budzinski *et al*., 1997). For instance, assuming a biogenic perylene origin, (BBC NEWS, 2-08-2001). (Page *et al*., 1996) used perylene depth gradients to show lack of vertical mixing.

Other PAHs such as benzo(*b*)fluoranthene (BbF), phenanthrene (P) and naphthalene (N) can originate from vascular land plants or termite activity (Tobiszewski & Namiesnik, 2012). Benzo(*a*)pyrene can be biosynthesized by certain bacteria and plants (Peters *et al*., 2005). Retene (RET) can be produced from the anaerobic microbial degradation of dehydroabietic acid (present in tire particles in urban areas) in soils and sediments (Mandalakis *et al*., 2002). Perylene or biogenic-diagenetic PAHs also potentially have anthropogenic sources. PER has been detected in trace amounts after pyrolytic processessuch as coal pyrolysis in municipal incinerator waste products and automotive emissions (Abrajano *et al*., 2003; Luo *et al*., 2008). Retene has other anthropogenic sources, such as fresh oil, diesel, exhaust emissions from heavy-duty diesel fuels, pulp/paper mill effluents, and emissions from coals(Yan *et al*., 2005).

(b) Petrogenic sources:

Petrogenic sources of PAHs are due to the intentional or accidental release of petroleum or the refined products from workshops and factories that utilise the products, production tank farms, leaking underground storage pipes, pipeline vandals and other oil spillage actions(ATSDR, 1995).

According to the work done by (Neff*et al*., 2004), a typical petroleum fraction may contain 0.2 to more than 7% total Polycyclic Aromatic Hydrocarbons. Petrogenic PAHs from unrefined petroleum sources are found to be mostly of the two to three ringed, low molecular weight compounds; the higher molecular weight fractions are usually at low concentration less than 100mg/kg (Neff *et al*., 2004). The refined products contain the same PAHs as in the parent petroleum as well as small amounts produced by catalytic cracking and other refining processes.

Also, the PAHs fractions in different refined oils vary depending on the distillation temperature range of the product; consequently, the two ringed PAHs – naphthalene and alkyl naphthalene

are present in gasoline fuels while diesel fuels, home heating oils and engine oils may contain the four ringed PAHs as well as other aromatic hydrocarbons(Neff *et al*., 2004). Most of the PAHs from petrogenic sources contain an alkyl group on one or more of the aromatic carbons and those in the refined products are usually more abundant than those of the parent compounds in petroleum(Neff *et al*., 2004). Benzo(a)pyrene whose origin is from petroleum hydrocarbons is considered to be probably and possibly carcinogenic in human (ATSDR, 1999).

(c)   Pyrolytic Sources:

This is the major source of PAHs with three or more rings in the environment (Neff *et al*., 2004). Pyrolysis has to do with heating or loosing composition of a substance by heating (Hogg, 2006). PAHs are released into the environment due to incomplete combustion of organic compounds in fossil fuels or hydrocarbon oils (WHO, 2003). Combustion is said to be complete when the application of heat breaks up molecules with the ultimate production of carbon (iv) oxide and water (Lau *et al*., 2010). When combustion is incomplete, or the combusted fuel products or oil cool quickly, the small organic chemicals may condense to form new chemicals which include PAHs; these are the pyrolytic polycyclic hydrocarbons PAHs (Neff *et al*., 2004). Examples of human activities that generate PAHs from pyrolytic source are: residential or commercial burning or cooking (including frying, broiling, and smoking), asphalt production, coal tar production, industrial or vehicular exhaust from diesel and petroleum engines, vehicular fumes from highway traffic, burning of garbage and incineration (WHO, 2003).

PAHs from pyrolytic sources are usually complex and are dominated by the four to five and six ringed fractions. The rings usually have their homologous series dominated by the un-alkylated parent compound or they may contain a homologue with only one or two alkyl substituents (Neff *et al*., 2004). This, according to(Neff, 1979) as cited by (Neff *et al*., 2004) is determined by the temperature of formation in a given pyrolytic PAHs fraction and there exist an inverse relationship between the temperature of formation and the abundance of alkyl

carbons. An example is coal tar (which is produced due to high temperature baking of hard coal in a reducing atmosphere to produce coke and manufactured gas); it is a type of high temperature pyrolytic polycyclic aromatic hydrocarbons and will likely contain few alkyl groups and more unalkylated groups. However, further treatment (such as distillation) of the tar could alter the composition and sometimes produce the two and three ringed PAHs fractions (such as creosote)(Neff *et al.*, 2004).

Pyrolytic-anthropogenic sources of PAHs could also be linked to the natural sources. This is because of the heating or pyrolysis that occurs during diagenesis (conversion of sediments into rocks or reconstitution of crystals to form a new product). This process however happens naturally and is not known to be directly caused by human intervention (Lau *et al.*, 2010). Some literature reviews classified diagenesis of biogenic material which is grouped in this report as well as in many other reports as natural source as a pyrolytic or pyrogenic PAHs source. The purpose of classification or grouping is for clarity and understanding based on perception of individual and not in any way meant to be contradictory.

1.2.9.2   Emitting Sources of PAHs

This can be divided into natural and anthropogenic sources
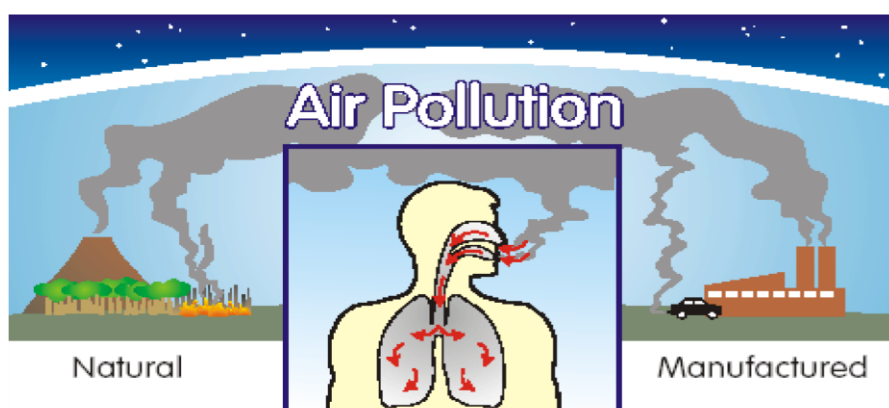
Figure 1.4: Air pollution from natural and anthropogenic release of PAHs

(a) Natural Source

The natural sources of PAHs are from thermal geologic reactions that involves rapid chemical and biological transformation of organic precursors (Neff *et al*., 2004) from living or recently living plants or animals (biogenic material), such as wood, coal, limestone, pearls or chalk (Hogg, 2006). Natural sources of PAHs also include underground oil seeps, discharge from chlorophylls plants, fungi and bacteria (Bouwmeester *et al*., 2006). The natural sources of PAHs are not usually considered as adding to the bulk of the pollutant in the environment (Kostopoulou *et al*., 2009). This source of emission can be subdivided into two

    i. Terrestrial source

  ii. Cosmic source

(i)   Terrestrial source

Terrestrial sources of PAHs include the non-anthropogenic burning of forests, woodland, and moorland due to lightning strikes. Volcanic eruptions may also emit PAHs, but no data regarding these emissions in atmosphere were found. Wild and Jones have estimated that the contribution from these sources to overall PAHs emission may be negligible (Wild & Jones, 1995).

In nature, PAHs may be formed in three ways:

1. High-temperature pyrolysis of organic materials.

2. Low to moderate temperature diagenesis of sedimentary organic material to form fossil fuels; and

3. Direct biosynthesis by microbes and plants(Neff, 1979).

A number of PAHs are generated by biogenic precursors which are common constituents of terrestrial higher plants, through diagenetic process (Bouloubassi & Saliot, 1993). Some authors suggest that PAHs can be synthesized by unicellular algae, higher plants or bacteria, but at the same time others conclude that organisms accumulate PAHs rather than synthesize

them (Wilcke, 2000). It is commonly accepted that predators accumulate non-metabolized pollutants and thus have higher levels than their food supply (Cripps, 1992).

Meteorological conditions (such as wind, temperature, and humidity) and fuel type (e.g. moisture content, green vs. seasoned wood) may play an important role in the degree of natural PAH production.

(ii) Cosmic Source

Among the cosmic source of PAHs are carbonaceous chondrites, which originate in the main asteroid belt and are not associated with life (Halasinski *et al*., 2005). The PAHs in chondrites appear to be the product of a high-temperature synthesis. However they may be the thermal alteration of pre-existing aliphatic compounds. Thermal alteration requires the presence of low-temperature mineral phases such as magnetite and hydrated phyllosilicates for their formation.

(b) Anthropogenic Sources

Anthropogenic has to do with sources that involve human and human interventions in the environment. Such interventions are those that spring up from day to day activities of human that involves utilisation and incomplete combustion of hydrocarbons in oil (WHO, 2003). The emission of PAHs from a particular source depends on the processes involved for production of materials (Manoli *et al*., 2004). During low temperature activities like biomass burning, PAHs having low molecular weight are formed whereas PAHs having maximum molecular weight are formed in the atmosphere during high temperature activities like combustion of fuels in engines, incinerations (Mostert *et al*., 2010).

Examples of major anthropogenic source are;

i. Domestic emission

ii. Mobile emission

iii. Industrial emission

(i)   Domestic emission

Domestic emissions are predominantly associated with the burning of coal, oil, gas, garbage, or other organic substances like tobacco or char broiled meat. Furthermore, wood, dried animal-dung-cake and crop waste (agricultural residue) use in biofuel are also used extensively for cooking in developing nations as noted by (WHO, 2002). It was also noted from WHO report that over 75% people in China, India, and South East Asia, and 50–75% people in parts of South America and Africa use these solid fuels for daily cooking. Low-temperature bio-fuel combustion has the potential to result in higher emissions of PAHs than high-temperature industrial sources. The majority of PAHs in the biomass fuel smoke were of low molecular weight and mostly volatile, with more than 86% of total PAHs found in vapour phase The partial combustion of coal, which has a hydrogen-to-carbon ratio 0.1, is a major source of PAH compounds. Domestic combustion of solid fuels makes a significant contribution to the total PAHs emission. The emissions rate in domestic heating are greatly influenced by the nature of fuel (wood type presence of foliage) and combustion conditions such as temperature, moisture, and availability of oxygen (Standley & Simoneit, 1987). Further, it has also been noticed that smouldering combustion emit 4–5 times more PAHs than flaming combustion (Jenkins *et al.*, 1996)

(ii)   Mobile emission

Mobile sources are also example of petrogenic emission which includes the emission from vehicles such as aircraft, shipping, railways, automobiles, off-road vehicles, and machinery. The emission of PAHs from these sources is a function of engine type, load and age, fuel type and quality (e.g. aromaticity), PAH accumulation in lubricant oil, lubricant oil combustion, and driving mode, including cold starting and emission control. (Paturel *et al.*, 1996) found that the start conditions of vehicles, hot or cold engine, have only a little influence on the mass repartition of the PAHs in gaseous or particulate phase. Further, the study suggests that there

are very high emissions of PAHs under cold start, particularly with gasoline cars at low speed. Similarly, (Devos *et al*., 2006) found that cold start PAHs emission are around 10 times higher for gasoline vehicles than for diesel vehicles. Most of the studies show that the emissions from vehicle exhaust (diesel, leaded and unleaded gasoline) are the largest contributors of PAHs in urban areas (Marr *et al*., 2006). Diesel fuelled vehicles have higher particulate emissions than gasoline fuelled vehicles.

The production of PAHs from gasoline automobiles depends on the air/fuel ratio. It has been found that the amount of PAHs in engine exhaust decreases with a leaner mixture. For example, (Jones *et al*., 2004) found that as the air/fuel combustion ratio increased, the high molecular weight PAHs (4202 amu) diminished rapidly. The use of catalytic converters has also been shown to have a significant effect on the reduction of the PAHs concentration in the exhaust gases. It is estimated that over 2,500,000 tons of tires were produced per year in European Union and with a similar estimation for the USA.(Larnesjo¨, 1999) has indicated that the dominant PAHs in the tire tread are fluoranthene, pyrene, benzo(g,h,i)perylene, and coronene. The PAHs content of tires is dependent on the manufacturer and the year of manufacture.

(iii) Industrial source

The most important industrial sources of PAHs include primary aluminium production (in particular plants using Soderberg process), coke production(e.g. as part of iron and steel production), creosote and wood preservation, waste incineration, cement manufacture, petrochemical and related industries, bitumen and asphalt industries, rubber tire manufacturing, and commercial heat/power production(PAHs Position Paper, 2001).

1.2.10 Environmental fate of PAHs

Once emitted to the atmosphere, molecular mass influences the fate of the gaseous PAH mixtures. Heavier PAHs (> four rings) tend to adsorb to particulate matter, while lighter PAH (< four rings) tend to remain gaseous until removed via precipitation (Skupinska *et al*., 2004).
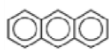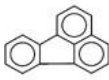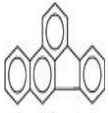
1.2.11 Priority PAHs
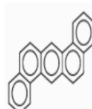
The United States Agency for Toxic Substances and Disease Registry has considered 17 priority PAHs (Table 1.1) based on their toxicological profile (ATSDR, 1995), although the health effects of individual PAHs are not exactly alike. These 16 PAHs were chosen to be included in the priority list because

(1) More information is available on them than on others;

(2) They are suspected to be more harmful than others, and they exhibit harmful effects that are representative of PAHs in general;

(3) There is a greater chance for exposure to these PAHs than to the others; and

(4) Of all the PAHs studies so far, these exhibited the highest concentrations.

Table1.1: EPA 16 priority PAH compounds and their properties

Structure	Name	Formula	Molecular Weight	Melting Point(^{0}C)	Boiling Point(^{0}c)
	Naphthalene (Nap)	C10H8	128	80.26	218
	Acenaphthalene (Ace)	C12H10	154	95	96
	Acenaphthylene (Acy)	C12H8	152	92.93	265-275
	Fluorene (Flo)	C13H10	166	116-117	295
	Phenanthrene (phen)	C14H10	178	100	340
	Anthracene (Anth)	C14H10	178	218	340-342
	Fluoranthene (Flan)	C16H12	202	100.8	375
	Pyrene (pyr)	C16H10	202	156	393-404
	Benzo[a]anthracene (B[a]A)	C18H12	228	158	438
	Chrysene (chry)	C18H12	228	254	448
	Benzo[b]fluoranthene (B[b]F)	C20H12	252	168.3	No data

	Benzo[k]fluoranthene (B[k]F)	C20H12	252	215	489
	Benzo[a]pyrene (B[a]P)	C20H12	252	179- 179.3	495
	Dibenz [a,h]anthracene (D[ah]A)	C22H14	278	262	No data
	Benzo[g,h,i]perylene (B[ghi]P)	C22H12	176	273	550
	Indeno[1,2,3-c,d]pyrene (Ind[1,2,3-cd]P)	C22H12	276	163.6	530

SOURCE: US EPA 2002

1.2.12 Uses of PAHs

They are mostly used as intermediaries in pharmaceutical, agricultural product, photographic products, thermosetting plastic, lubricating materials, and other chemical industries (ATSDR, 2010). However, the general uses of some PAHs are:

- Acenaphthene: manufacture of pigments, dyes, plastics, pesticides and pharmaceuticals.

- Anthracene: diluent for wood preservatives and manufacture of dyes and pigments.

- Fluoranthene: manufacture of agrochemicals, dyes and pharmaceuticals.

- Fluorene: manufacture of pharmaceuticals, pigments, dyes, pesticides and thermoset plastic.

- Phenanthrene: manufacture of resins and pesticides.

- Pyrene: manufacture of pigments.

Other PAHs may be contained in asphalt used for the construction of roads, in addition to roofing tar. Furthermore, specific refined products, of precise PAHs, are used also in the field of electronics, functional plastics, and liquid crystals.

1.2.13 Routes of Exposure

Some exposure may involve more than one route simultaneously, affecting the total absorbed dose (such as dermal and inhalation exposure from contaminated air). All non-workplace sources of exposure, such as diet, smoking, and burning of coal and wood, should be taken into consideration. PAH concentrations in air can vary from less than 5 to 200 000 nanograms/cubic metre (ng/m^3) (Georgiadis & Kyrtopoulos, 1999). Although environmental air levels are lower than those associated with specific occupational exposures, they are of public health concern when spread over large urban populations (Zmirou *et al*., 2000).

1.2.14 Effects of PAHs and toxicology

The effect of PAHs are enumerated below

1.2.14.1 Environmental Effects

PAHs are usually released into the air, or they evaporate into the air when they are released to soil or water (INCHEM, 1998). PAHs often adsorb to dust particles in atmosphere, where they undergo photo oxidation in the presence of sunlight, especially when they are adsorbed to particles. This oxidation process can break down the chemical over a period of days to week (Santodonato *et al*, 1981). Since PAHs are generally insoluble in water, they are generally found adsorbed on particulate and precipitated in the bottom of lakes and rivers, or solubilized in any oily matter which may contaminate water. Sediments, and soil, mixed microbial population in sediment/water system may degrade some PAHs over a period of weeks to months (ATSDR 2010).

The toxicity of PAHs is affected by metabolism and photo-oxidation, and they are generally more toxic in the presence of ultraviolet light. PAHs have moderate to high acute toxicity to aquatic life and birds. PAHs in soil are unlikely to exert toxic effect on terrestrial invertebrates, except when soil is contaminated (Peter, 2003).Adverse effects on these organism include tumours, adverse effects on reproduction, development and immunity, mammals can absorb PAHs by various routes e.g. inhalation, dermal contact and ingestion (Igwe and Ukaogo 2015). Plant can absorb PAHs from soils through their roots and translocate them to other plant parts. Uptake rates are generally governed by concentration, water solubility and their physicochemical state as well as soil type. PAH – induced phyto-toxic effect are rare. Certain plant contain substances that can protect against effect, whereas other can synthesize PAH that act as growth hormones (ATSDR 2010).PAHs are moderately persistent in the environment, and can bio-accumulate. The concentration of PAHs found in fish and shell fish are expected to be much higher than in the environment from which they are taken. Bioaccumulation has

been also shown in terrestrial invertebrate, however PAHs metabolism is sufficient to prevent bio-magnification(Borosky, 1999).

1.2.14.2 Health Effects

The effects on human health will depend mainly on the length and extend of exposure, the amount or concentration of PAHs one is exposed to, and of course the innate toxicity of the PAHs, and whether exposure occurs via inhalation, ingestion or skin contact. A variety of other factors can also affect health impacts, including subjective facts such as pre-existing health status and age(Collins *et al*., 1998).

(a) Acute or Short-Term Health Effects.

The ability of PAHs to induce short-term health effects in human is not clear. Intakes of PAHs occur via ingestion, inhalation or dermal (skin) exposure to contaminated soil/dust and from inhalation of PAHs vapours. Tilling the dry soil can result in ingestion of small but measurable amount of soil. Occupational exposure to high level of pollutant mixture containing PAHs has resulted in symptoms such as eye irritation, nausea, vomiting, diarrhoea and confusion(Collins *et al*., 1998).

However, it is not known which components of the mixture where responsible for the effect and other compounds commonly found with PAHs may be the cause of these symptoms.

(b) Chronic or Long-term Health Effects

Health effect from chronic or long-term exposure to PAHs may include decrease immune function, cataract, kidney and liver damage (e.g. jaundice), breathing problems, asthma like symptoms and lung function abnormalities and repeated contact with skin may induce redness and skin inflammation. Naphthalene, a specific PAH, can cause the breakdown of red blood cell if inhaled or ingested in large amounts (Collins *et al*., 1998). If exposed to PAHs, the

harmful effect that may occur largely depend on the way people are exposed (BBC News,2001).

(c) Carcinogenicity

Although un-metabolized PAHs can have toxic effect, a major concern is the ability of the reactive metabolites, such as epoxides and dihydrodiols, of some PAHs to bind to cellular proteins and DNA. The resulting biochemical disruption and cell damage leads to Mutations, developmental malformation, tumours, and cancer. Evidence indicates that mixtures of PAHs are carcinogenic to humans (Grimmer *et al*., 1988). The evidence came primarily from occupational studies of workers exposed to mixtures containing PAHs and those long-term studies have shown an increase in risk of predominantly skin and lung, but as well as bladder and gastrointestinal cancers. However, it is not clear from these studies whether exposure to PAHs was the main cause as workers were simultaneously exposed to other cancer – causing agent (e.g. aromatic amines) (Grimmer *et al* 1988). Animals exposed to certain level of some PAH over long period in laboratory studies have developed lung cancer from inhalation, stomach cancer from ingesting PAHs in food and skin contact. BaP is the most common PAH to cause cancer in animal and this compound is notable for being the first chemical carcinogen to bed is covered. Based on the available evidence both the International Agency for Research on cancer (IARC, 1983) classified a number of PAHs as carcinogenic to animal and some PAH – rich mixture as carcinogenic to human (Igwe & Ukaogo, 2015). The EPA has classified seven PAH compound as probable human carcinogens: BaA, BaP, BbF, BkF, chrysene, dibenz(ah)anthracene, and indeno(1,2,3-cd)pyrene. Other studies include Benzo(ghi)perylene (Jung *et al*., 2001). Subsequent US studies among coke oven workers confirmed excessive lung cancer mortality, with the suggestion of excessive genito-urinary system cancer mortality.

(d) Mutagenicity

Mutagenesis is the process in which mutation occurs. Mutation occurs when a DNA gene is damaged or changed in such a way as to alter the genetic message carried by that gene. A mutagen is an agent or substance that can bring about a permanent alteration to the physical composition of a DNA gene such that the genetic message is changed. Once the gene has been damaged, the mRNA (messenger ribonucleic acid) transcribed from that gene will now carry an altered message. The polypeptide (or amino acid chain) made by translating the altered mRNA will now contain a different sequence of amino acids(Blamire, 2000).

Mutagenic actions occur due to genotoxicity; genotoxicity plays important role in the carcinogenicity process and probably in some forms of developmental toxicity (Buha & Lah, 2011). Genotoxic substances are those that are capable of altering DNA, thereby causing cancer or mutation (Mosby's medical dictionary, 2009). Genotoxic effects for some PAHs have been demonstrated both in rodents and in vitro tests using mammalian (including human) cell lines (Buha & Lah, 2011). Most of the PAHs are not genotoxic by themselves and they need to be metabolised to the diol epoxides which react with DNA, thus inducing mutagenic actions (Buha & Lah, 2011).

(e) Teratogenicity

Teratogenicity is the process of action of a teratogen. According to medical dictionary definition, a teratogen is an agent or factor that causes malformation of the embryo or can disrupt the development of an embryo or foetus in a pregnant mother's womb especially in early pregnancy; they could be toxic chemicals radiation, viruses, alcohol, smoking, certain prescription drugs and numerous other agents (Mosby's Medical dictionary, 2009).

There is growing evidence that prenatal exposure to air pollutants have adverse effects on foetal growth and early child neurodevelopment. Molecular and epidemiological research has shown

that foetuses and infants are more susceptible than adults to the harmful effects of a variety of environmental contaminants, including PAHs (Padmini *et al.,* 2009). Studies carried out on animals have revealed that teratogenic or embryotoxic effects occurred when experimental animals such as mice were exposed to PAHs such as benzo(a) anthracene, benzo(a)pyrene, and naphthalene; Laboratory studies conducted on these organisms have demonstrated that ingestion of high levels of benzo(a)pyrene during pregnancy resulted in birth defects and decreased body weight in the offspring (Buha & Lah, 2011). Other studies have also shown that fish embryos and larvae are highly sensitive to PAHs mixtures from a variety of sources, including creosote wood preservatives, oil sands and sediments impacted by urbanisation (Incardona *et al*., 2008). It is not known whether these effects can occur in humans. However, the centre for children's Environmental Health reports studies demonstrate that exposure of PAH pollution during pregnancy is related to similar adverse birth outcomes including how birth weight, premature delivery, heart inflammations. High prenatal exposure to PAH is also associated with lower IQ at age three, increased behavioural problems at ages of six and eight and childhood asthma cord blood of exposed babies shows DNA damage that has been linked to cancer (Igwe &Ukaogo 2015).

(f) Genotoxicity

Genotoxic effects for some PAHs been demonstrated in rodents using mammalian cell lines. Most of the PAHs are not genotoxic by themselves and they need to be metabolized to the diol exposed which react with DNA, thus inducing genotoxic damage. Genotoxicity plays important role in the carcinogenicity process and maybe in some forms of developmental toxicity as well [ATSDR 2010].

Table 1.2: summary of Health effect of some PAH

PAHs	Effects	Reference
Anthrancene	Toxic, skin sensitizer , eye irritation, nausea, vomiting, diarrhea and confusion	(ATSDR, 2009)
Acenaphthylene	Toxic , eye irritation.	(ATSDR, 2010)
Benzo(a)anthrance	Toxic, Carcinogenic, heart malformations, childhood asthma, skin irritations.	(Luch , 2005)
Benzo(b)fluoranthene	Toxic	(Luch, 2005)
Pyrene	Toxic , eye irritation	(ATSDR, 2010)
Benzo(a)pyrene	Carcinogenic, mutagenic, birth defects, decrease in body weight, toxic, skin irritants, leukemia, heart malformations, childhood asthma eye irritation, nausea, vomiting, diarrhea and confusion.	(ATSDR,2009; Cross et al., 2010; Luch, 2005)
Chrysene	Toxic, Carcinogenic , kidney and liver damage and jaundice cataracts	(Luch,2005; ATSDR,2009)
Benzo(b)fluoranthene	Toxic, Carcinogenic	(Luch , 2005)
Benzo(k)fluoranthene	Toxic, Carcinogenic ,Tumors of the gastrointestinal tract and lungs	(Cross *et al* 2010)
Naphthalene	Toxic, Skin irritants, Breakdown of red blood cell, heart malformations, childhood asthma, eye irritation,	(ATSDR, 2009)

	nausea, vomiting, diarrhea and confusion	
Dibenz(a,h)anthracene	Carcinogenic, toxic, cataracts, kidney and liver damage and jaundice cataracts.	(ATSDR, 2009)
Indeno(1,2,3-cd)pyrene	Carcinogenic, toxic, increase in mammary tumors in rat kidney and liver damage and jaundice cataracts	(ATSDR, 2009)
Benzo(g,h,i)perylene	Carcinogenic (although not to humans), genotoxic	

Source; Luch, 2005

1.2.15 Toxicity equivalency factors (TEF) and Rick of Carcinogenicity of PAHs

Toxicity equivalent factor (TEF) evaluation is the most popular method used to identify the toxicity of PAHs. Seven PAHs have been identified by the United States Environmental Protection Agency (USEPA) and the International Agency for Research on Cancer (IARC) to be of high risk to humans and are therefore used to assess the level of pollution in the environment. They are benzo[a]pyrene, dibenzo[a,h]anthracene, benz[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, indeno[1,2,3-cd]pyrene and chrysene. Aside their confirmed carcinogenicity, all the seven PAHs were also found genotoxic alongside benzo[g,h,i]perylene that was not classified as being carcinogenic to humans. The USEPA, therefore, established toxicity equivalency factors (TEFs) for the quantification of their level of toxicity. The highest TEF of 1 was assigned to benzo[a]pyrene while lower values as shown in Table 4 were assigned to other PAHs.

Table 1.3: TEF value for various PAHs

PAH	TEF
Benzo[a]anthracene	0.1
Chrysene	0.01
Benzo[b]fluoranthene	0.1
Benzo[k]fluoranthene	0.1
Benzo[a]pyrene	1
Dibenz[a,h]anthracene	1
Indeno[1,2,3-cd]pyrene	0.1
Benzo(g,h,i)perylene	0.01

TEFs of individual PAHs have been reported by many researchers. Toxicity equivalency concentrations (TEQs) are calculated as the product of summing up the values obtained by TEF values and concentrations of PAHs. The toxicity equation is given by;

$$TEQ = \Sigma \ (C_i \ x \ TEF_i) \qquad\qquad [1.1]$$

where,

TEQ: toxic equivalent concentration

Ci: concentration of PAHi.

Petry *et al*., 1996used TEFs in assessing occupational and environmental health risks associated with exposure to airborne mixtures of PAHs. They used information of the ratio between airborne concentrations of B[a]p equivalents to the concentrations of B[a]p alone, which could indicate the variation of risk for the different environments. Individual PAH-based

BaPeq toxicity estimates were up to one order of magnitude higher than estimates based on BaP concentration measurements and B[a]p-risk from a risk assessment of lung cancer related to occupational exposure. Vyskocil *et al*., (2004) reported that 1.73% of the cancer suffered by Beijing inhabitants in 2007 was related to inhalation of PAHs in ambient air. Residents of the city run an increasing of cancer caused by the inhalation of ambient air containing HAPs, such as PAHs

The association as projected by the office of Environmental Health Hazard Assessment (OEHHA, 2005), Sacramento, California, for estimating carcinogenic risk associated with PAH emissions is expressed below

$$\text{Carcinogenic risk} = [\text{PAH}\} \text{ X TEF X } UR_{BaP} \qquad [1.2]$$

$$= BaP_{eq} \text{ X } UR_{BaP} \qquad [1.3]$$

Where [PAH] = Total PAH concentration for individual PAHs

TEF = Total Equivalence Factor for the individual PAHs

UR_{BaP} = Inhalation cancer unit risk factor of BaP $\Rightarrow$ (1 X $10^{-6} \mu g/m^3$)

UR_{BaP} is estimated from Cancer Potential Factor (CPF) From the relation

UR = CPF X 20m^3/(70kg X CV)

This estimated value for UR is coined by relating the average weight of 70kg for human and 20m^3 of average inhalation. (OEHHA, 2005)

1.2.16   Source markers

This is also known as tracer or signature. Specific PAHs have been suggested as being indicators for certain processes that release PAHs into the environment. These PAHs are called source markers, tracers, or signatures. The PAH concentration profile and ratio can be used to

determine the contribution of different sources to their concentrations in air. Li & Kamens (1993) characterized PAH signatures for three combustion sources, i.e. residential wood combustion, gasoline spark ignition emissions, and diesel engine emissions. Normalization is a general statistical approach to reduce the anomalies in large data sets and it was found that the normalized PAH signatures gave better results than un-normalized signatures (Li & Kamens, 1993)

Furtherrmore, it was possible to distinguish between the above-mentioned sources when a smaller source contributed more than 10% of the total. Khalili *et al*., 1995 determined the chemical composition (source finger prints) of the major sources of airborne PAHs in the Chicago metropolitan area, from 1990 to 1992. They found that two or three-ring PAHs were responsible for 92%, 65%, 74%, 99%, and 80% of the total concentration of the measured 20 PAHs from highway tunnels, diesel engine, petrol engines, coke oven, and wood combustion samples, respectively. Six-ring PAHs such as indeno[1,2,3-c,d] pyrene and benzo[g,h,i] pyrene were mostly below the detection limit in the highway tunnels, diesel and petrol engine samples (Khalili *et al*., 1995).

1.2.17 PAH Diagnostic or Binary Ratio

In many studies, the sources of polycyclic aromatic hydrocarbons (PAHs) in various environmental samples have been qualitatively determined by the various molecular diagnostic ratios. PAHs diagnostic ratios are widely used to identify anthropogenic sources of PAHs emission. It involves comparing ratios of pairs of frequently found PAH emissions. Emission factors are useful for the estimation of the amount of air pollutants (e.g. PAHs) released and therefore for setting national and international environmental policies for protection strategies and regulations (Ravindra *et al*., 2008). The ambient PAH concentrations and their diagnostic ratios indicate the different sources of PAHs in the environment (Guo *et al*., 2003).For

example, a widely used concentration ratio is the anthracene (Ant)/[Ant + phenanthrene (Phe)], and if this is lower than 0.10, it is taken as indicative of non-burnt fossil fuel, whereas if this ratio exceeds 0.10, this suggests combustion sources. Similarly, many other ratios exist as shown in table 1.4 and are used to reveal petrogenic or pyrogenic origin, fuel or wood combustion, or traffic related sources. When these ratios are used to determine the sources, it is hypothesized that paired chemicals are diluted to a similar extent and that the ratios remain constant en route from sources to receptors, although in many cases it has been proven that this does not happen (Zhang *et al*., 2005). For example, PAHs resulting from the use of coal, oil, and wood are low in coronene relative to B[a]P, while mobile source combustion emissions from diesel and petroleum use are high in benzo[g,h,i]perylene and coronene relative to B[a]P . The ratio of these PAHs can be used to distinguish between traffic dominated PAH profiles and other sources. PAHs profiles have been used to identify vehicle emission following the use of unleaded gasoline in many countries and the unsuitability of lead as a vehicle sources marker. The diversity in PAH sources could also be characterized from diagnostic ratios. As shown in Table 1.4, many studies have developed and used a specific value of PAH diagnostic ratio for a source category. Studies reported in the table also indicate that it is further possible to differentiate the traffic emission in to gasoline or diesel exhaust as shown by Khalili *et al*. (1995), Guo *et al*. (2003), Fang *et al*., 2004, and Ravindra *et al*. (2006a). suggested indeno[1,2,3-c,d]pyrene/(indeno[1,2,3-cd) pyrene+benzo[g,h,i]perylene ratio of 0.62 for wood burning, whereas (Kavouras *et al*., 2001) used a ratio between 0.35 and 0.70 indicating diesel emission. Hence, it would be difficult to differentiate diesel emission from biomass emission based only on one proposed diagnostic ratio (indeno[1,2,3-c,d] pyrene/indeno[1,2,3-c,d]pyrene+benzo[g,h,i]perylene). However, the diagnostic ratios method should be used with caution because it is often difficult to discriminate between some sources (Ravindra *et al*.,

2006a). The ratio can be altered due to the reactivity of some PAH species with other atmospheric species, such as ozone and/or oxides of nitrogen. (Ravindra *et al*, 2008).

Table 1.4: PAH diagnostic ratios

Diagnosis ratio	Value	Sources
Ind[1,2,3-cd]p / (Ind[1,2,3-cd)p+	0.18	Cars
B[ghi]P)	0.37	Diesel
	0.56	Coal
	0.62	Wood burning
	0.35–0.70	Diesel emissions
Flo / (flo + pyr)	>0.5	Diesel
	<0.5	Gasoline
B[a]P / (B[a]P + chry)	0.5	Diesel
	0.73	Gasoline
Benzo[b]fluoranthene/ benzo[k]fluoranthene	>0.5	Diesel
B[a]P/benzo[ghi]perylene	0.5–06	Traffic emission
	>1.25	Brown coal [b]
Indeno[1,2,3- cd)pyrene/benzo[ghi]perylene	<0.4	Gasoline
	~1	Diesel
Fluoranthene/benzo[e]pyrene	3.5±0.5	Automobile-exhaust
Pyr /B[a]P	~10	Diesel engine
	~1	Gasoline-engine
Fluo/pyr	0.6	Vehicluar
Anth/(Anth + Phen)	< 0.1	petrogenic
	>0.1	pyrolytic

Source: Ravinda *et al*, 2008

1.2.18 Collection of PAH samples

PAHs in the atmosphere are mainly collected by two sampling models: active sampling and passive sampling. Active sampling uses deposition or adsorption of target PAH compounds on filters or sorbent materials, through the collection of air particulates onto filters or into sorbent tubes, using a pump. PAHs accumulated on filters or sorbent materials are returned to the laboratory for analysis. In many applications, filters such as quartz fibre filters, glass fibre filters and cellulose filters are used to collect PAHs associated with particulate matter. These filters are highly vulnerable to losing the collected PAHs via volatilization and thus precautions need to be taken to minimise the loss of LMW PAHs. For collecting gaseous PAHs, commonly used sorbents include XAD-2 resin and polyurethanefoam (PUF) because of their high collection efficiencies, chemical stability, easy extractability and low cost. However, limitations on active sampling include the very high costs of sampling and the loss or volatilization of PAHs during the sampling and handling process. "These disadvantages can be alleviated by using passive sampling methods, which are based on free flow of analyte molecules from the sampled medium to a collecting medium as a result of differences in chemical potentials" (Caslavsky *et al*., 2004; Lee & Vu, 2010).

In this study, $PM_{2.5}$samples were collected by active sampling using Apex 2IS casella pump.

1.2.19 Sample Extraction Methods

The extraction of samples can be carry out using different method depending desired extraction efficiency and financial considerations

1.2.19.1   Soxhlet Extraction.

Basically, in the Soxhlet extraction technique, the solid sample is placed into an extraction thimble which is then extracted using an appropriate solvent via the reflux cycle. Once the

solvent is boiled, the vapour passes through a bypass arm into the condenser, where it condenses and drips back onto the solvent in the thimble. As the solvent reaches the top of the siphon arm, the solvent and extract are siphoned back onto the lower flask whereby the solvent re-boils, and the cycle is repeated until all the sample is completely extracted into the lower flask. The main disadvantage of this extraction process is the use of large volumes of solvent. In addition, this method is very labour intensive and time consuming, as the solvent has to be refluxed up to 24-48 hours to achieve considerable extraction efficiencies (Dean & Xiong, 2000). Other minor drawbacks of using the Soxhlet apparatus include the likelihood of sample carryover, the need to fractionise extracts to avoid heavy contamination of GC injection port, and the unfeasibility of re-dissolving dried Soxhlet extracts (Mì`ege *et al*., 1998). The efficiency of the Soxhlet extraction increases with molecular weight, reaching an efficiency range of 84– 100% for PAHs with more than 4 rings (Smith *et al*., 2006)

1.2.19.2   Ultrasonic Agitation/Sonication.

The ultrasonic agitation, also known as sonication, is a technique which engages the acoustic energy of ultrasonic waves with a minimum frequency of 16 kHz in fluid, causing rapid compression and rarefaction of fluid movement which results in the cavitation phenomenon, that is, the reoccurring formation and collapse of micro-bubbles. This agitation can be performed either by immersing a sonicator transducer also known as an ultrasonic horn into the sample solvent mixture or placing the sample solvent mixture directly into a sonication bath. The desired ultrasound is generated by means of piezoelectric ceramic attached either to the ultrasonic horn or the walls of the sonication bath.

Study has shown that sonication was better than the Soxhlet because it provided higher extraction efficiencies, was more economical and easily operated (Sun *et al*., 1998). Likewise,

it was noted by Guerin that similar levels of extraction efficiency to the Soxhlet extraction method could be attained through vigorous sonication (Guerin, 1998).

The power amplitude and duration of sonication need to be carefully controlled in order to avoid extensive exposure to the irradiation which may degrade the contaminants in the sample and reduce the extraction rates of PAHs. The decrease in efficiency during excessive sonication is due to an increase in broken carbonaceous particles and additional contact surface area which adsorbs the PAHs more readily, causing a reversed adsorption cycle of PAHs (Stephens Jr *et al*., 1994). Additionally, further separation techniques such as centrifugation or filtration are required after the extraction process. The following benefits of using ultrasonic assisted extraction are short extraction time, high sample throughput and the small amounts of solvent required.

1.2.19.3   Mechanical Agitation.

This simple, low-cost method uses agitation or mixing action to extract the PAHs from samples in a shake-flask placed onto a rotary shaker, or with a magnetic stirrer submersed into the flask directly. Although it is an easy handling method with minimal glassware and smaller volumes of extraction solvent, this method has not been as widely used as the Soxhlet and sonication due to the lower extraction efficiency and unsatisfactory quantitative results (Graham *et al*., 2006). Although some studies reported that this method was comparable to the Soxhlet technique, the results obtained using mechanical shaking showed larger variations and less selectivity due to the difficulty in quantifying the PAHs extracts (Berset *et al*., 1999). Comparable results were only attainable with long shaking times to extend the contact time with solvent (Kalbe *et al*., 2008).

1.2.19.4   Microwave-Assisted Extraction (MAE).

Another highly instrumental extraction technique is the MAE whereby both solvent and samples are subjected to heat radiation energy attained from electromagnetic wavelengths between 1m and 1 mm, with frequencies of 300MHz to 300 GHz. Microwave radiation is preferred compared to conventional heating due to its rapid heating which is reproducible and has less energy losses. Modern designs of the microwave ovens include carousels which can hold at least twelve extraction vessels allowing simultaneous multiple extractions. The main advantages of the MAE method are the reductions in solvent usage and time. In comparison to SFE, the cost of MAE is moderately lower (Wang *et al*., 2007). Additionally, this unique heating mechanism provides selective interaction with polar molecules which greatly enhances the extraction efficiency of PAHs (Letellier *et al*., 1999).

The major drawback of this method however is that the solvent needs to be physically removed from the sample matrix upon completion of the extraction prior to further analysis. In certain cases whereby samples are pre-treated with activated copper bars to assist the extraction process, the removal of this copper is necessary for a cleaner extract (Mi`ege *et al*, 1998).

In this study, extraction was carried out using Sonication method

1.2.20 Analysis of PAHs

Polycyclic Aromatic Hydrocarbons from various samples can be quantified by passing them through chemical analysis in the laboratory. The method applied depends on the sample source; whether it is from food sample or from environmental media. It is also determined by the type of analysis required at a given time. Chemical analysis could be required for legislation, monitoring for detection of frauds or compliance to limits, and monitoring for exposure limits in risk assessment procedure (Anklam *et al*., 2006).

No matter the sample source of the PAHs, extraction and pre-concentration steps are usually required for sample enrichment especially when the source is from uncontaminated aqueous samples (WHO, 2003). Several extraction techniques have been used to extract PAHs from various sample sources. For environmental samples, solid-liquid and liquid-liquid extraction have been used for soil, sediment and water samples; some of the methods used are Soxhlet Extraction SE, Supercritical Fluid Extraction SFE and Pressurised Liquid Extraction(Anklam *et al*., 2006). Even simpler extraction techniques, such as liquid extraction at room temperature on a shaking device, were shown to be suitable for extracting PAHs from soil. These methods have been proven and approved by US Environmental Protection Agency US EPA has been effective for extracting the 16 PAHs that are considered to be of priority (Anklam, et al., 2006).

After extraction, the next stage in the analytical process of PAHs is sample clean-up. This stage is necessary in order to remove any co-extractives (compounds that are extracted together with the PAHs in the extraction process) and produce a pure PAHs sample for chromatographic analysis. Examples of extracts that could be present are: aliphatic hydrocarbons, porphrins, chlorins and carotenoids. Sample clean-up and consequently pre-concentration could take place during adsorption chromatography with silica gel, alumina or florisil (Anklam *et al*., 2006) and during fractional distillation into aliphatic and aromatic fractions using activated alumina (neutral) column with n-hexane and Dichloromethane. The n-hexane removes the aliphatic hydrocarbons while Dichloromethane separates the aromatic fraction.

The clean-up method required depend largely on the selectivity of the applied extraction techniques and on the chromatographic method to be applied later on the pure sample; for instance, SFE extracts of urban air particles in a particular analysis carried out to monitor PAHs contained fewer co-extractives than SE or PLE extracts. And this was attributed to the fact that SE and PLE apply non-polar organic solvents which also dissolves humic acids and aliphatic

hydrocarbons; subsequently, silica gel or alumina was used for the clean-up during adsorption chromatography (Anklam *et al*., 2006)..

After the clean-up, a pre-concentrated sample is derived which could still be pass through a further concentration process by placing the extract in a rotary vacuum evaporator or by exposing the extracts to laboratory room temperature for at least 24 hours until a concentrated extract of about 0.5-1.0ml is gotten. The concentration or sample enrichment could also be achieved by means of a suitable enrichment device – under a gentle Nitrogen gas stream (Kanchananayoon & Tatrahun, 2008).

The next stage is the actual analysis of the prepared samples and the method usually employed for PAHs is CHROMATOGRAPHY. Gas chromatography with mass spectrometry GC-MS detection operated in selected ion monitoring SIM as well as high performance liquid chromatography with fluorescence detection HPLC-FLD are methods that have been used for analysis of PAHs. The International Standard Organisation ISO standard 13877:1998 describes a method for the determination of PAHs in soil by HPLC, and very recently published standard ISO 18287:2006 for the determination of PAHs in soil by GC-MS (Anklam *et al*., 2006). Also, in WHO guidelines report for drinking water quality, gas chromatography with flame ionisation detection GC-FID was used for analysing PAHs in drinking water (WHO, 2003).

1.2.20.1 Gas Chromatography

Chromatography is a mixture separating technique for compounds containing several solutes. It is suitable for identification of the various compounds present in a mixture of solutes as well as determining the amount present; it is therefore a useful tool for qualitative and quantitative analysis of chemical samples. The method involves the use of a solvent which could be gas, liquid or adsorbent medium (paper or gel) moving over another solvent; they are usually

classified as having a stationary and a mobile phase(SHU, 2013). There are many techniques in Chromatography, and Gas Chromatography GC is one of them; there is also liquid chromatography in which the mobile phase is a suitable solvent and adsorption chromatography in which the mobile phase is a suitable solid. The major difference between them is in the type of mobile phasing used (SHU, 2013). Gas Chromatography has been extensively utilised in scientific research to analyse and identify substances. It has been estimated that 10-20% of known compounds can be estimated by GC (www.chem.agilent.com) and it is one of the preferred technique for PAHs analysis because of the way it works.

Gas chromatography has illustrated in the diagram (fig.1.5) below works by using a gas called the carrier gas to move the solutes or samples (usually in the liquid state) when they are vaporised in a heating column through a stationary phase such that they are analysed and the result are read through a detector attached to the column.
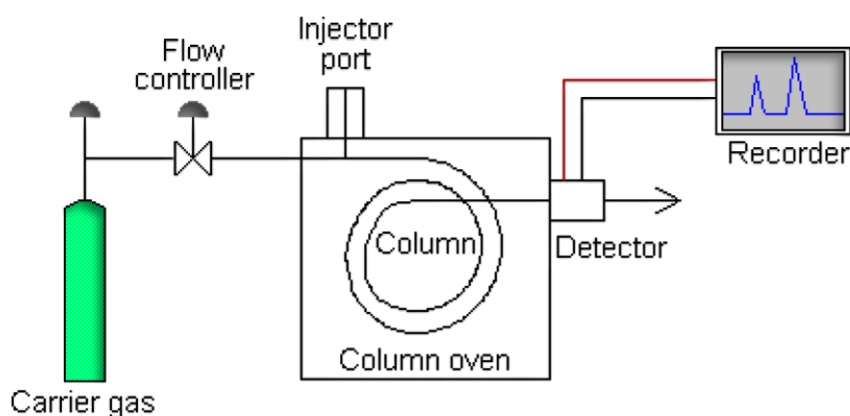
Figure 1.5: Schematic representation of a Gas Chromatography

Adapted from: Sheffield Hallam University SHU, Biosciences. www.teaching.shu.ac.uk

To be suitable for GC, the solutes must be sufficiently volatile and stable to high temperature; if the solutes do not decompose at high temperature when heated, then it is suitable for GC analyses. This is one of the reasons why GC is preferred for analysis of PAHs (www.chem.agilent.com).

The sample to be analysed is introduced into the column through the injector by means of a micro-syringe, it is heated by the oven in the heating column and moved by the carrier gas which is usually an inert gas (such as: nitrogen, argon, helium or carbon (iv) oxide) through the column until they have been analysed and detected by a monitoring device which sends the signal to a recorder. The solute with the lowest temperature emerges first followed by the next until all the compounds present in the sample have been analysed. The emergence of the samples is determined by their physical properties and temperature and composition of the heating column. As the solutes emerge in the detector, the readings are recorded as electronic signal on the monitor and this is what is read as the chromatogram. The ideal chromatogram is a closely spaced wave signal plotted against the elapse time with different peaks for different solutes. The peak of the chromatogram indicates the quantity of that solute present in the mixture while the retention time which is the time it takes before the sample elapses could be used to determine the type or identify the compound present. However, using the chromatogram peak and the retention time alone is not enough to know the quantity and type of the solute present. A known standard which is a pure sample containing similar solutes is subjected to similar column condition and the chromatogram peaks and retention times compare with that of the unknown sample and the result is determined. One condition necessary to have good chromatogram peak and hence good result is to ensure that only a small amount of the solutes sample is injected into the column; this will ensure that the emerging chromatograms are not overlapped and therefore measured distinctly.

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The detector is also another important part of the GC components as it is the one that determines the type of reading that will be produce by the recorder. It is therefore necessary that the detector be very effective in detecting the result of the analysis and in yielding a good signal for recording. There are a few detectors used with chromatography in PAHs analysis and they include fluorescent detector, flame ionisation detector and mass spectrometry.

1.2.20.2   Flame Ionisation Detector *(FID)*

FID is a robust and easy to use method for analysing organic compounds including PAHs in gas chromatography. It is a mass flow dependent detector; this means that the signal produced is related to the rate at which solutes enter the detector. Gas Chromatography with flame ionisation detector GC-FID uses support gases such as hydrogen and air and has a detectability value of 100pg and dynamic range of $10^{7.}$ Unlike some other detectors in which dilution with make-up gas lowers their response, GC-FID is unaffected by the make-up gas.

In GC-FID, effluent (which is the sample to be analysed) from the column is mixed with hydrogen and air and ignited. The flame produced by the burning of organic compounds produces ions and electrons which can conduct electricity through it. A large electrical potential is applied at the burner tip, and a collector electrode is located above the flame. The current resulting from the pyrolysis of any organic compounds is measured. The diagram below in fig.1.6 illustrates a Flame Ionisation Detector.
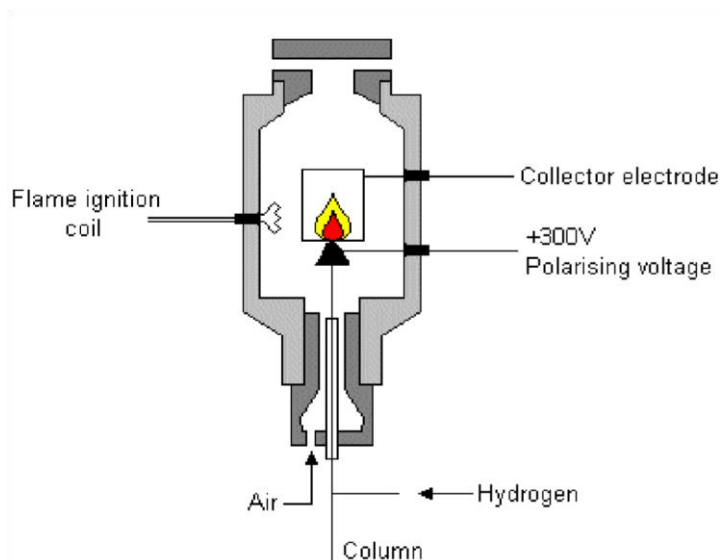
Figure 1.6: Schematic representation of a Flame Ionisation Detector FID

Adapted from: Sheffield Hallam University SHU, Biosciences. www.teaching.shu.ac.uk.

The advantages of using FID in GC are

- It is a useful general detector for the analysis of organic compounds;

- It has high sensitivity,

- It has a large linear response range, and low noise,

- It is also robust and easy to use.

However, it major disadvantage is that, it destroys the sample. This means that the sample used for the analysis is used up in the process. An example of a detector that does not use up the sample during analytical process is mass spectrometry and it has been used in GC for analysis of organic compounds including PAHs (www.teaching.shu.ac.uk.).

<center>**CHAPTER TWO**</center>

2.0   MATERIALS AND METHOD

2.1   SAMPLING LOCATION

This study was carried out in eight (8) auto-mechanic workshops randomly chosen around Uwelu Motor Spare Parts Market which is located in the North-West zone of Benin City, Edo state, Nigeria.   The metropolis lies between latitude $6^{o}2355N$ to $6^{o}2739N$ and longitude $5^{o}3618E$ to $5^{o}4430E$, it has a tropical climate characterized by two distinct conditions of wet and dry seasons. The dry season starts in December and lasts till March while the wet season starts in April and lasts till November. Temperature across the state is relatively high with a very narrow variation in seasonal and diurnal range; 22°C - 36°C and an annual rainfall of above 600mm with mean relative humidity of above 80%.

All sampling locations were fairly similar.   They were chosen based on the following criteria

1. Presence of at least 3 mechanical activities such as general engine repair and servicing, welding, panel beating, electrical repair, paint/body repair, A/C repair etc
2. Absence of trees at least 50m from the repair shop
3. Minimum distance of 100m from major roads

2.1.1   Activities, Practices and Types of Waste Generated in the Study Area

The workshops in the study are arranged in clusters. The area had a range of activities which include auto servicing and maintenance, battery charging and repair, panel beating, welding (arc/electric), spraying, electrical repair and painting. Of all these activities, the most common that was practiced daily were the auto servicing and maintenance, battery repair, panel beating, welding, electrical repair and painting. These activities were based on the various skilled operators functioning in different units within the workshop

<center>54</center>
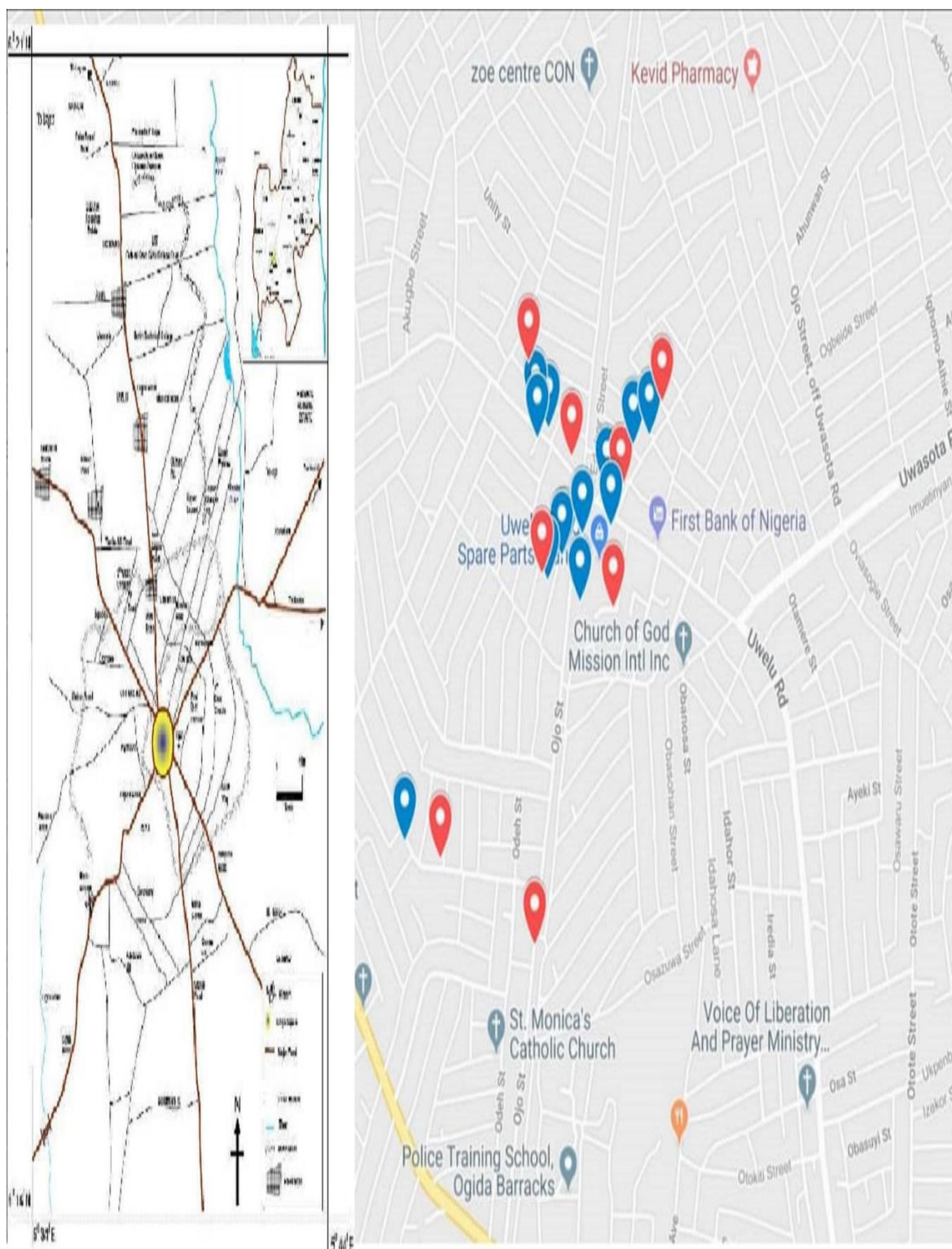
Figure 2.1   Map of Benin city and Uwelu environ showing sampling locations

Source: google maps 2019

Table 2.1: Coordinates of sampling locations

S/no	Latitude	Longitude

1	6.3721090	5.584539
2	6.3779350	5.589140
3	6.3779148	5.589063
4	6.3774468	5.588533
5	6.3775565	5.588315
6	6.3803503	5.588568
7	6.3803460	5.588568
8	6.3806094	5.588077
9	6.3724543	5.583226
10	6.3801628	5.588145
11	6.3816280	5.587822
12	6.3770366	5.589735
13	6.3769261	5.589826
14	6.3783252	5.589822
15	6.3791364	5.590729
16	6.3791558	5.591252
17	6.3800378	5.591703
18	6.3802184	5.592307
19	6.3804487	5.592692
20	6.3704570	5.588049

2.2   REAGENTS, APPARATUS AND INTRUMENTS

REAGENT USED

- Acetone (HPLC grade)

- Dichloromethane (HPLC grade)

- Silica gel

- Nitrogen gas

APPARATUS/ INSTRUMENTS USED

- Glassware (conical flasks, measuring cylinder, forceps, GC vials,)

- Retort stand and clamps

- Tweezers

- Dessicator

- Syringes – 15ml

- Ultrasonic bath (Sonication bath)

- Apex 2IS Casella pump (Bedford, UK)

- Conical Inhalable sampler (Bedford,UK)

- Quartz filter – 37mm diameter

- Poly urethane foams, PUF

- Gas Chromatograms fitted with Flame Ionization Detector , GC-FID

- Muffle furnace

- Professional weather station

- Analytical weighing balance

2.3   PREPARATION FOR SAMPLING

PUF for sampling were first pre-cleaned with DCM in an Ultrasonic Bath for 15 minutes and purged at room temperature with nitrogen gas till dry (USEPA, 2006). The Quartz filters were baked at 450-500°C for 4 hours in a muffle furnace and stored in a DCM pre-treated dark plastic bag to prevent photo-oxidation and sealed.

The quartz filter and PUF were equilibrated in a desiccator for 48 hours before sampling to eliminate the effect of humidity and weighed using a four digit weighing balance to obtain accurate PM measurements.

The Casella pump was calibrated before each sampling to meet the recommended flow rates.

2.4   SAMPLING PROCEDURE

PM$_{2.5}$ and TSP samples were collected using Apex2IS Casella standard pump coupled with a conical inhalable sampling head at a height of 1.5-2.0 meters above the ground and at a flow rate of 3.5L/M (litre per minute). Sampling was carried out between February and June 2019. Eight sampling locations were chosen at random and sampling was carried out twice in these locations, once in the dry season and once in the wet season. The sampling was carried out for eight (8) hours, from 8am to 4pm.

After each sampling, the sampling head containing the quartz filter and PUF were kept in the desiccator overnight. The next morning the sampling head, quartz filter and PUF were collectively and separately weighed. The difference in the initial and final weights were calculated to get the mass of PM$_{2.5}$ and TSP. The quartz filters were transferred into a 100ml brown bottle containing 25ml of Acetone/DCM (1:1). The bottle was then sealed and wrapped in aluminium foil and stored at 4°C for extraction and analysis.

Plate 2.1: Casella pump and conical inhalable sampler

2.4.1 Collection of Meteorological Data

Temperature, humidity, rainfall, wind speed, wind direction, solar radiation and UV index were measured during the sampling using an automatic weather equipment mounted 2.5-3.0 meters above the ground at all sampling locations. It was programmed to collect data at 5-minute interval and stored in memory, the data was then downloaded to a laptop.

Plate 2.2: Professional weather station equipment

2.5 SAMPLE PREPARATION AND ANALYSIS

2.5.1 SAMPLE PREPARATION

Glassware were properly washed with distilled water and then finally rinsed with dichloromethane to dry out any water molecules present. Thereafter, the glassware was baked in a dry oven at a temperature set at 120°C for about 30 minutes.

2.5.1.1 Sample Extraction

Tweezers were used to carefully transfer the filters into the conical flask and 10ml of a mixture of dichloromethane (DCM) and Acetone 1:1 ratio (5ml each) was then added into the flasks and the samples were extracted into the solvents by ultrasonic method of extraction for thirty (30) minutes.

2.5.1.2 Extract concentration and clean-up

The extracts were further concentrated by passing a gentle stream of nitrogen over it until one 1ml concentrate was obtained. Then the concentrate was transferred into a chromatographic column well packed with silica and little sodium sulphate anhydrous which served as a drying agent to remove any traces of water. The cleaned extract was blown down and concentrate obtained was transfer into GC vials.

2.5.2 Sample Analysis

Sample analysis was carried out using a HP Agilent technology 6890 GC system equipped with a flame ionization detector, samples and standards of 1μL were injected in split/splitless mode (1.5 minutes split time). Polycyclic aromatic hydrocarbon (PAH) analytes separation was carried out on a 30m low polarity GC column (30m,0.25mm ID,0.25μm film thickness) with the carrier gas; helium (He). The temperature was set at 100°C. This was then ramped to 330°C at a rate of 4°C/min and held for 30minutes. The oven was then allowed to cool to the initial temperature ready for another injection. The GC conditions are shown in the table below.

Table 2.2 GC conditions employed in PAH analysis

Injection	Split flow, 275°C, surge pressure= 80kPa for 1.5minutes
Column	HP 5MS 30m, 0.25mm × 0.25μm, helium gas
Oven programme	Start at 100°C,held for 2minutes ,then ramp at 10°C/min to 190°C (held for 8mins) then 10°C/min to 330°C (held for 30mins)

2.6 QUALITY ASSURANCE/QUALITY CONTROL

Prior to analysis, to prevent PAH degradation and losses, the samples were preserved by carefully folding each filter with the collected particulates (on the inside) wrapped in aluminium foil and then kept in the freezer at very low temperature.

The conical flasks used were firstly rinsed with distilled water, DCM and thereafter baked in a drying oven at 110°C for 30minutes to remove all interfering organics.

During sonication, the bath was calibrated to room temperature to avoid degradation any thermally sensitive analytes,

CHAPTER THREE

3.0   RESULTS AND DISCUSSION

This section on the results and discussion is subdivided into five sub-sections;

(i)   Fine particulate matter

(ii)   PAH analysis

(iii)   Meteorological Parameters

(iv)   Source identification Analysis

(v)   Estimation of Toxicity and Carcinogenicity for potential health impact.

3.1 Results and Discussion of Fine Particulate PM$_{2.5}$

The values for the PM$_{2.5}$ concentration obtained from each sampling location is presented below in Table 3.1a. The monthly average concentration is in bold.

Table 3.1a: Concentration of PM$_{2.5}$ (µg/m³) obtained in the various sampling location from February to June.

Month	Locations	PM.2.5 (µg/m³)
February	1	7440.47
	2	6845.23
	3	8630.95
	4	6488.09
	Mean ± SD	**7351.185 ± 813.43**
March	5	5357.14
	6	5238.09
	7	4464.29
	8	4821.43
	Mean ± SD	**4970.23 ± 408.07**
April	9	4702.38
	10	3273.8
	11	3630.95
	12	3690.47
	Mean ± SD	**3824.4± 613.56**
May	13	3571.42
	14	3035.71
	15	3035.71
	16	2916.67
	Mean ± SD	**3139.87 ± 293.11**
June	17	2976.19
	18	2678.57
	19	2440.47
	20	2321.43
	Mean ±SD	**2604.16 ± 289.06**

In February, $PM_{2.5}$ levels ranged from 6488.09µg/m^3 to 8630.95µg/m^3. It ranged from 2604.16µg/m^3 to 3139.87 µg/m^3. When compared to the World Health Organization (WHO, 2006) air quality guideline for $PM_{2.5}$ which is 25 µg/m^3 for 24 hour mean, the $PM_{2.5}$ values obtained for this study far exceeds the guideline.

The concentration of $PM_{2.5}$ for February and March which represent the dry season were 7351.185µg/m^3 and 4970.23µg/m^3 respectively which are 294 and 199 fold the value of WHO guideline. During the month of May and June, which are representative of the wet season, the concentration of $PM_{2.5}$ were 3139.87 µg/m^3 and 2604.16µg/m^3 which are 126 and 104 fold the value of WHO guideline value.

The observed high values $PM_{2.5}$ during the dry season could be as a result of accumulated dust since February and March are the last months of the dry season and the prolonged absence of precipitation which helps the cleansing of the environment, and high wind speed due to characteristic harmattan season, which was just exiting, which aids the circulation of dust in the environment and increases particulates in the atmosphere.

For the wet season, $PM_{2.5}$ values as expected declined. This is most likely as a result of the emergence of the rainy season. Precipitation reduces the concentration of air pollutants in the atmosphere, particularly dust/particulate matter pollution.

The values obtained in all site during dry and wet season clearly violates the stipulated limit as they are all above the stated unit 25µg/m^3.

Generally, the high values may also be attributed to the nature of activities taking place in the sampling location. Samples were collected from auto-mechanic workshop where so many activities like repair and maintenance of vehicles are carried out. Also activities from welding and motor spray painting which was a major factor considered during the site location.

Emissions from generators used during welding activities, all these activities releases particulates into the environment.
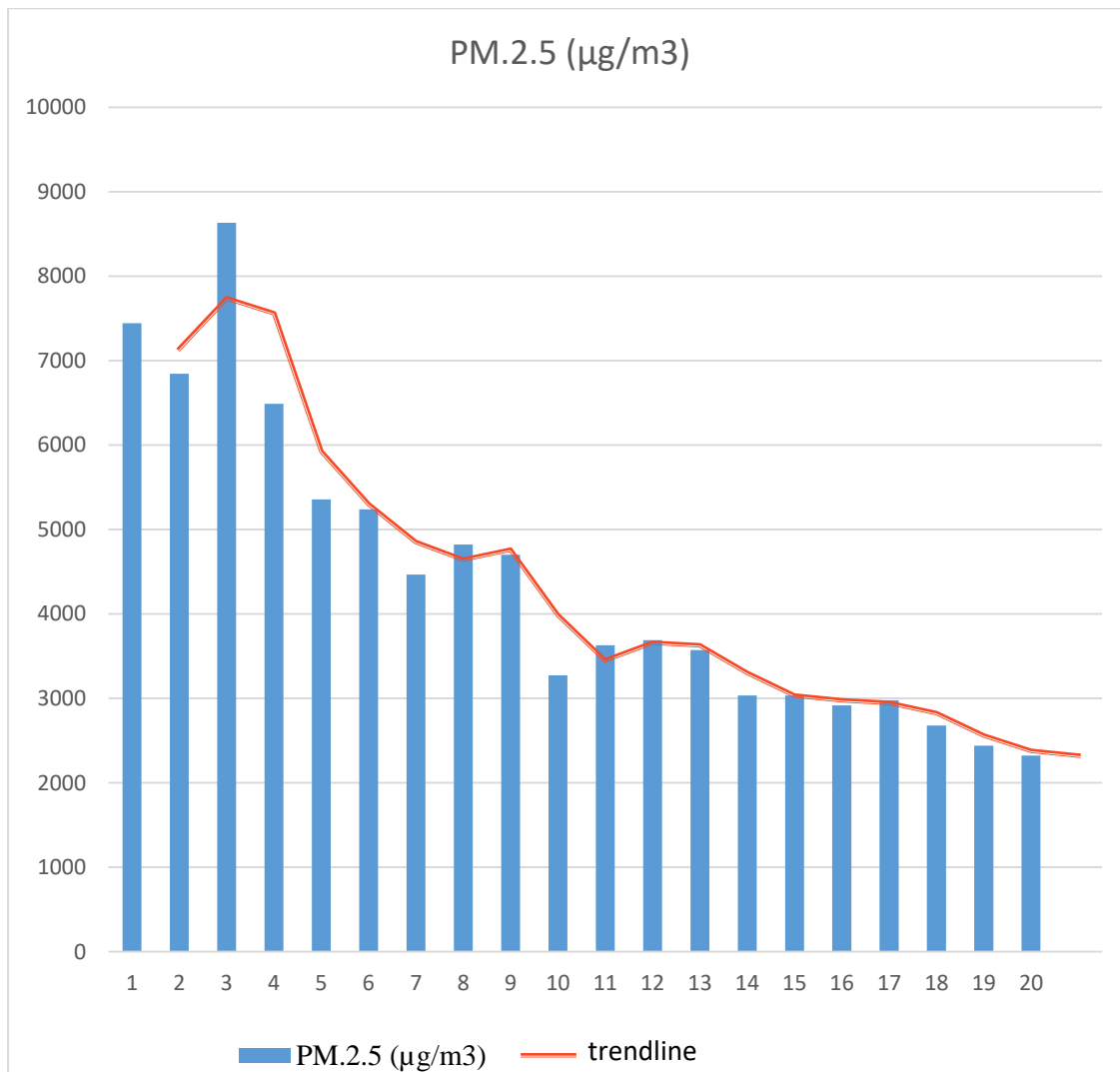
Figure 3.1   Bar chart and trend line showing the gradual decline in PM$_{2.5}$concentration for the sampling period

Table 3.1b: Comparison of PM$_{2.5}$ Result (µg/m^3) of this study with other studies.

S/N	SITE/LOCATIONS	PM$_{2.5}$ VALUES (µg/m^3)	REFERENCES
1	Urban/Benin City	1284.72-3020.84	Ediagbonya *et al.,* 2016
2	Urban/Lagos (Industrial area)	For wet season- 14.00-32.67 For dry season- 18.67-34.67	Okuo *et al.,* 2017
3	Urban/Benin City (Auto-mechanic workshops)	For wet 2604.16-3139.81 For dry 4970.23-7351.185	Current Study
4	Urban/ Rural Delta state	104170- 218750 for urban 104170-312500 for rural	Ediagbonya *et al,* 2012

In Sapele, the concentration ranged from 104.17 µg/m^3- 2187.50 mg/m^3 for urban area and 104.17 µg/m^3-416.69 mg/m^3 for rural area. This shows a clearly significant increase in the concentration of PM$_{2.5}$ for urban areas which is due to the difference in activities taking place in the locations. The mean concentration of Particulates for his study were also significantly higher than he concentration found in this study.

In Lagos, Okuo *et al.,* 2017, the highest concentration of PM$_{2.5}$ recorded during dry season was 34.67µg/m^3 and during the wet season 32.67µg/m^3. This value was below regulatory limit but differs greatly from those obtained from this study, this might be as a result of difference in the activities been carried out in the various sampling site. Studied conducted in Lagos was in an Industrial area with less particulate generating anthropogenic activities than that in this study

with anthropogenic activities like motor spray painting, welding, panel beating, emissions from generators used during welding activities, vehicular traffic emissions, and spill of used oil which all release particles into the atmosphere.

3.2 Result and Discussion for Analysis of PAHs

Table 3.2: Total concentration of the USEPA sixteen PAHs obtained around sample location arranged by monthly average and overall average.

PAH Component	February ng/m³	March ng/m³	April ng/m³	May ng/m³	June ng/m³	Total mean and SD ng/m³
Naphthylene	ND	ND	ND	ND	ND	ND
Acenaphthylene	ND	ND	ND	ND	ND	ND
Acenaphthene	ND	ND	ND	ND	ND	ND
Fluorene	ND	ND	ND	ND	ND	ND
Anthracene	6.42	4.02	5.54	5.22	0.85	4.41±2.17
Phenanthrene	2.98	4.39	2.75	5.25	0.71	3.22±1.74
Fluoranthene	1.65	2	1.7	1.7	1.45	1.70±0.20
Pyrene	4.9	4.52	2.66	3.57	2.6	3.65±1.05
Benzo(a) anthracene	6.05	5.41	5.34	4.81	4.74	5.27±0.53
Chrysene	11.84	12.47	16.93	13.16	10.16	12.91±2.51
Benzo(k)fluoranthene	16.77	17.95	25.36	11.23	12.53	16.77±5.56
Benzo(b)fluoranthene	58.53	63.55	123.88	59.13	55.93	72.20±29.02
Benzo(a)pyrene	132.07	130.08	118.01	118.49	114.48	122.63±7.90
Indeno(1,2,3–cd)pyrene	118.78	166.97	141.91	102.47	122.4	130.51±24.74
Dibenz(a,h)anthracene	71.61	97.85	77.53	189.72	58.59	99.06±52.62
Benzo(g,h,i)perylene	289.62	284.08	516.53	153.5	201.42	289.03±139.49
Total PAH (ng/m³)	721.21	764.07	984.24	668.26	585.86	744.73±149.48

ND = Not Detected

The concentrations of the studied PAH samples are shown in Table 3.2. The average values (in ng/m^3) are mean values for the 4 sampling locations which were covered in a month. Individual concentrations were below the detection limit for acenaphthylene, acenaphthene, Naphthylene and fluorene. The obtained concentrations values are probably underestimated due to volatilization of the low molecular weight compounds. The highest contributions to the total PAH level were made by Benzo(g,h,i)perylene [232.16 ng/m^3], Indeno(1,2,3-c,d)pyrene [127.66 ng/m^3], Benzo(a)pyrene[123.78 ng/m$^{3]}$ and Dibenz(a,h)anthracene while lower values were recorded for other PAHs like Anthracene[4.13 ng/m^3], Phenanthrene [3.33 ng/m^3], Fluoranthene[1.7 ng/m^3], Pyrene[3.90 ng/m^3], Chrysene[11.91 ng/m^3], Benzo(a)Anthracene[5.25 ng/m^3], Benzo(k)Fluoranthene[14.62 ng/m^3] and benzo(b)Fluoranthene[59.29 ng/m^3].

Benzo[a]anthracene, Chrysene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo[a]pyrene and Indeno(1,2,3-cd)pyrene have been classified as possible carcinogenic to humans. In this study, these PAHs represented about 65% of the Total PAH which is an indication of significant contamination. HMW compounds contributed 99% to the total PAH concentration. These HMW PAHs are generally derived from pyrolytic origin (Qiao*et al*., 2006; Sanders *et al*., 2002; Dahle *et al*., 2003).

Mean levels of individual PAHs in the dry season for ranged from 1.65ng/m^3 low for Fluoranthene to 289.62 ng/m^3 high for Benzo (g,h,i)perylene both in February. Mean values ranged from 2 ng/m^3 low for Fluoranthene to 284.08 ng/m^3 high for Benzo (g,h,i)perylene in March. This could indicate that the activities within that environment are influencing the mechanic site a in similar way. The concentration obtained for all PAHs all showed slight increase in the month of March.In the rainy season, individual PAH ranged from 0.85ng/m^{3}low in anthracene to 201.42ng/m^{3}high for Benzo(g,h,i)perylene. A general observation from PAH

levels result in the rainy season, at the study location is that, lower amounts were detected in the rainy season compared to the dry season.
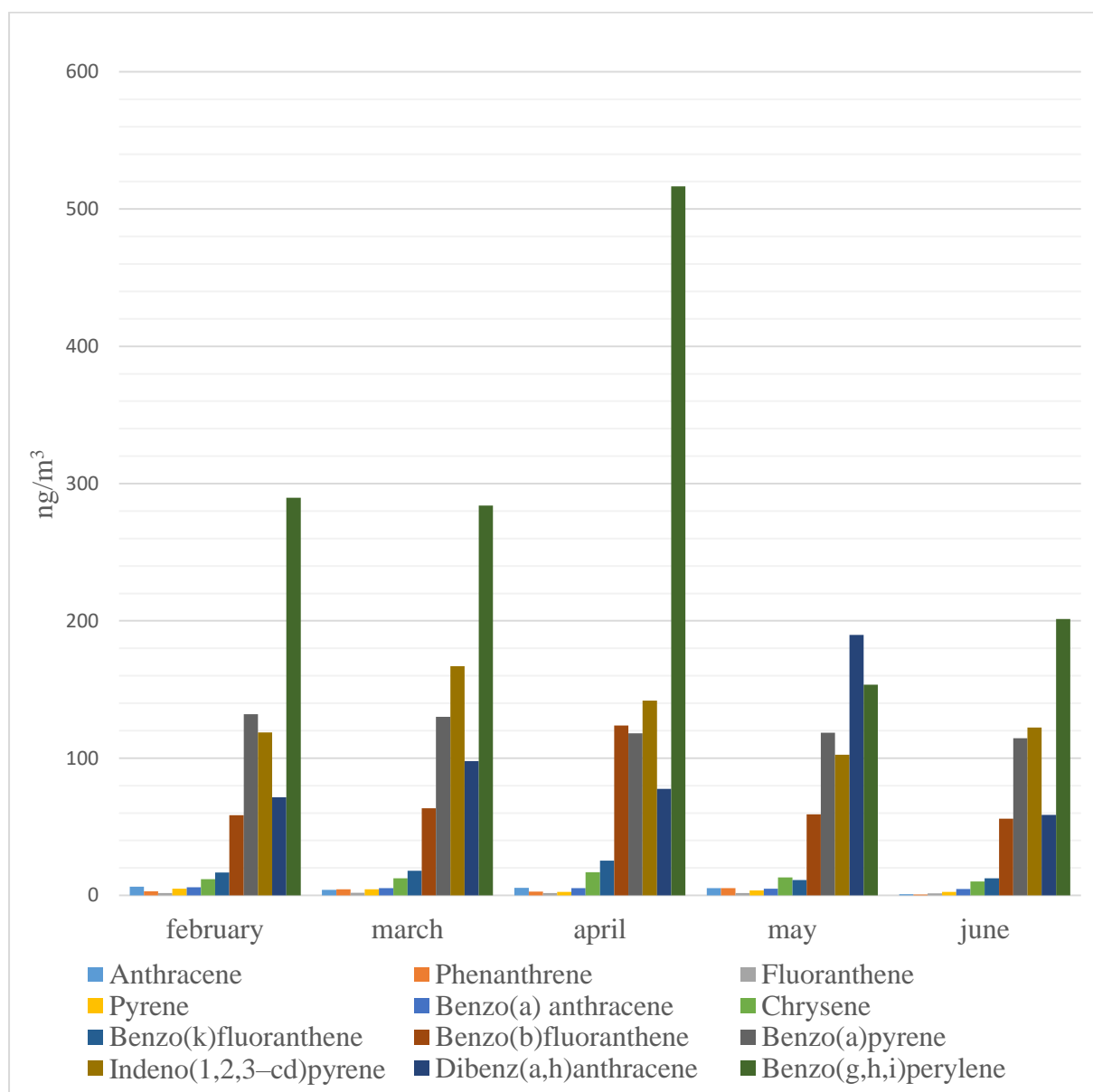
Figure 3.2a Bar chart showing the trend in PAH concentration for the sampling period.

The seasonal behaviour of the origin of PAH emissions is mostly associated with meteorological conditions and soil volatilization. Figure 3.4 summarises the average concentrations and distribution pattern across the sampling period. A similar trend was observed in Benzo(g,h,i)perylene, Benzo(b)Fluoranthene, Benzo(k)Fluoranthene and Indeno(1,2,3-c,d)pyrene with a higher concentration in March, 2019. It may be due to heavy

rainfall during the period. There was a general decline in the concentration of all PAHs from the dry season to the wet season in May and June with the exception of Dibenz(a,h)anthracene and Phenanthrene which saw spikes in concentration in May. The rain may have assisted in bringing down the particulate matters released into the atmosphere to settle onto the soil. In the case of rainfall or when the temperature drops they form dry or wet deposits on plants, soil and in the hydrosphere from the atmosphere, but when the temperature rises, they volatilize into the atmosphere from these environmental media (Chun, 2011; Tham *et al*., 2008).
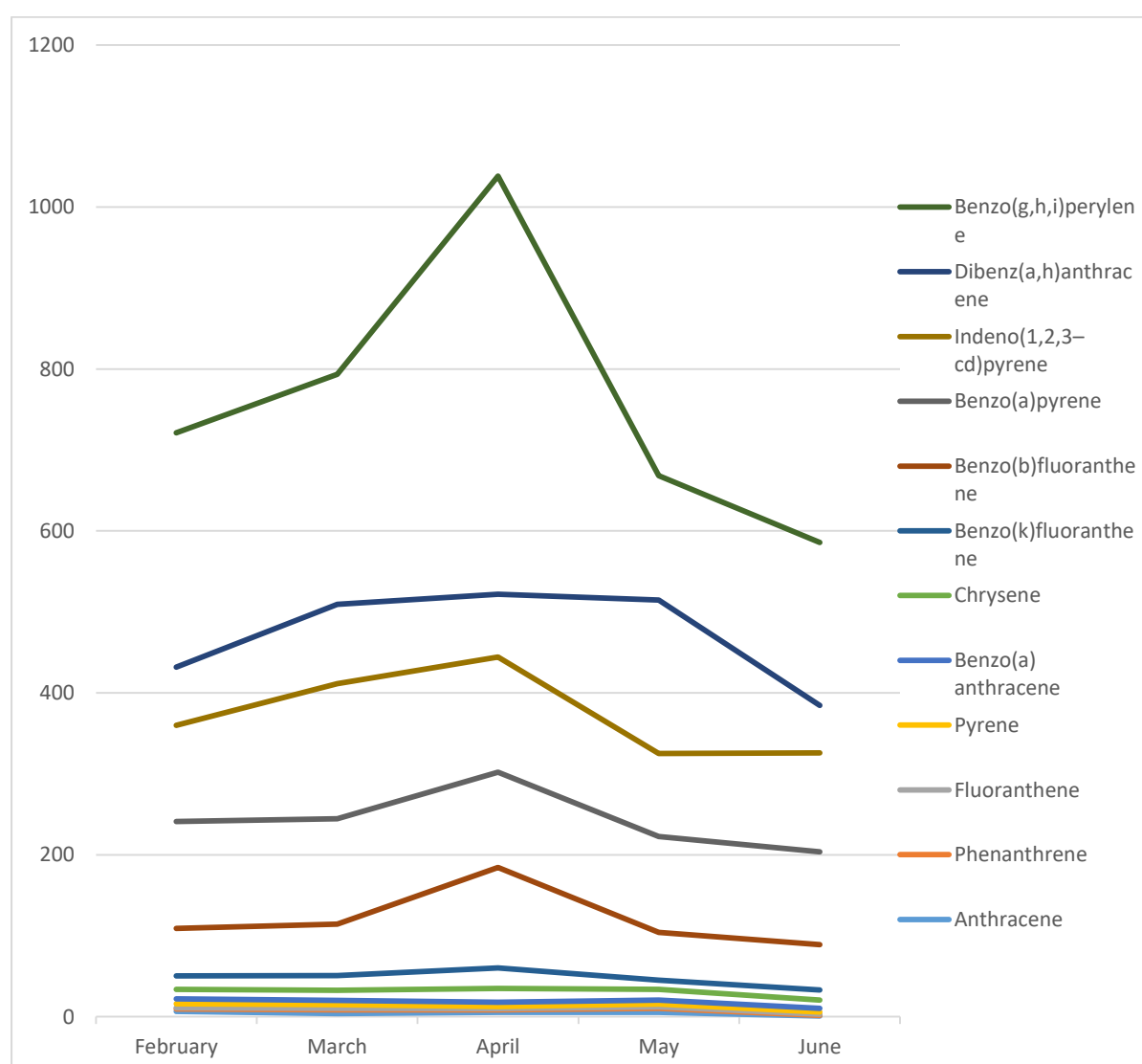
Figure 3.2b: Line graph showing the trend in monthly PAH concentration from February to June

The OSHA PEL (permissible exposure levels) for PAHs in the workplace is $0.2mg/m^3$ for 8hour TWA (time-weighted average) (Buha & Lah, 2011). The average PAH concentration from this study is $0.000685mg/m^3$ which is much lower. I is also lower than the National Institute for Occupational Safety and Health (NIOSH) workplace recommended exposure limit for PAHs which is $0.1 mg/m^3$ for coal tar pitch volatile agents for a 10-hour workday, 40-hour workweek (Buha & Lah, 2011).

3.3 Result and Discussion of Meteorological Parameters

Table 3.3.1 Meteorological Parameters obtained from the sampling locations for the months of February, March, May and June.

Meterological parameters	February	March	April	May	June
Ultra-violet radiation (μW/m2)	944.12±65.31	1,034.97±96.57	1135.44±80.43	801.41±35.62	651.25±85.06
Pressure (mmHg)	749.8±0.76	748.81±0.33	748.18±0.10	749.72±0.53	750.82±0.30
Solar radiation (W/m2)	589.45±140.78	656.44±145.49	777.95±133.95	526.59±101.73	529.80±90.15
Wind Direction (o)	191.81±19.68	184.91±6.49	194.28±20.81	183.84±30.44	190.78±49.75
Humidity (%)	75.09±2.35	72.91±1.42	69.25±1.51	74.06±1.72	74.91±1.49
Temperature (°C)	30.51±0.45	31.17±0.26	31.91±0.20	30.10±0.25	29.84±0.35
Wind Speed (km/h)	6.01±0.46	5.5±0.24	5.45±0.51	5.68±0.43	6.69±0.63

Ultra-violet radiation increased steadily from February (944.12 μW/m2) and peaked in April (1135.44 μW/m2) from then it started to decline. A similar pattern was observed for solar radiation which increased from February (589.45 μW/m2) to April (777.95 μW/m2) and then went on a decline, and Temperature with February mean of 30.51°C and April Mean of 31.91°C. a reverse pattern was observed in Pressure, with February mean of 749.8mmHg and April mean of 748.18mmHg which was the lowest value for the sampling season, from there, it went on a steady increase to peak in June at 750.82mmHg, and in Humidity with February

mean of 75.09% and April mean of 69.25% which was the lowest value for the sampling season, from there, it went on a steady increase to peak in June at 74.91%, and in Wind Speed with February mean of 6.01Km/h and April mean of 5.45Km/h which was the lowest value for the sampling season, then it went on a steady increase to peak in June at 6.69Km/h
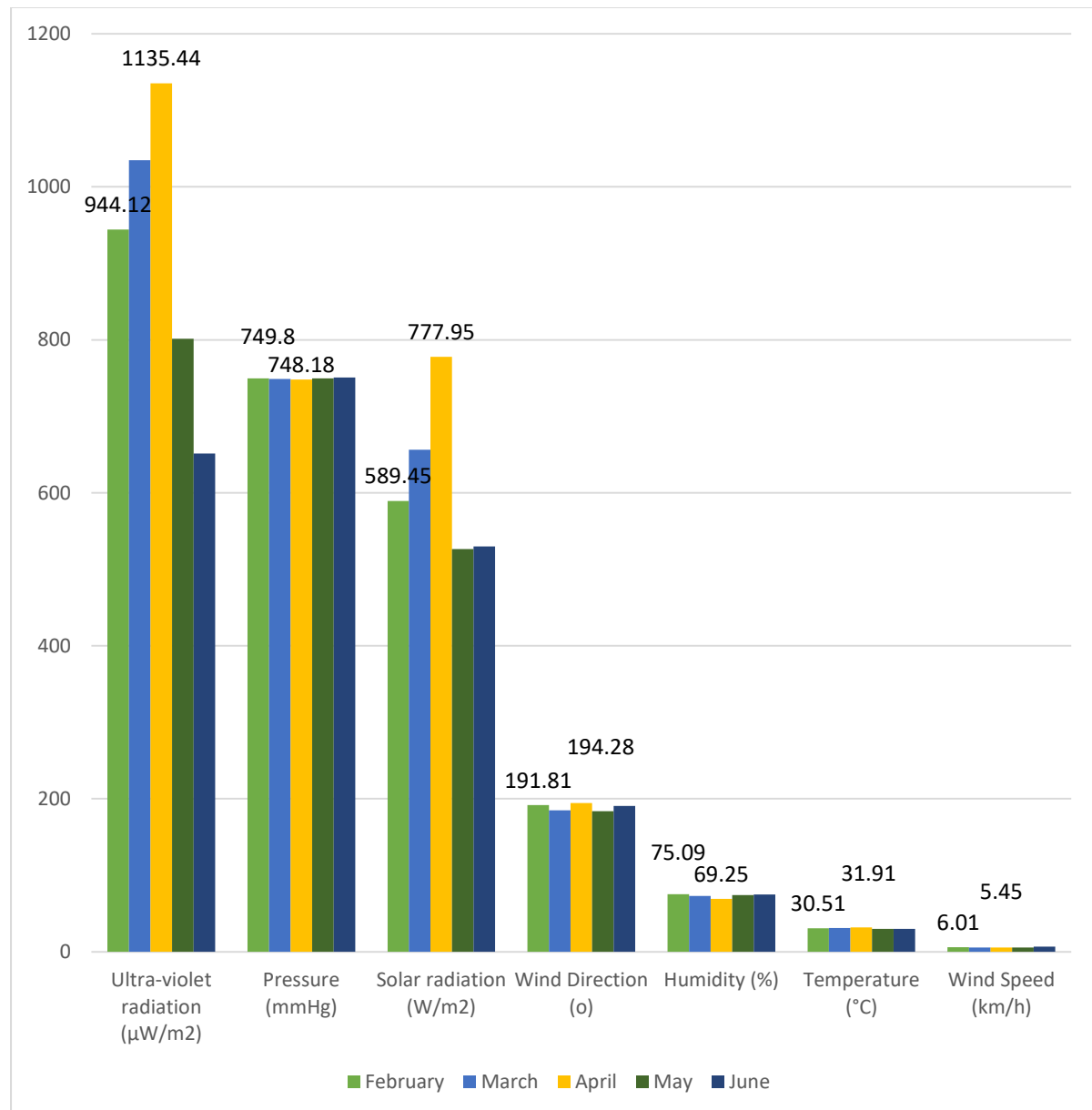
Figure 3.3: Bar chart showing Ultra-violet radiation, Solar radiation and Pressure for the month of February, March, May and June.

3.3.2 Correlation between the Total PM$_{2.5}$, PAHs and meteorological parameters for the total sampling period

Correlation is used to describe how data sets are related to one another. Correlation could be positive or negative or no correlation at all. Positive correlation means as one data is increasing, the other data is also increasing. Negative correlation means as one data is increasing, the other data is decreasing and no correlation means that the sets of data are not related. Correlation can be described by its strength. Data set can also have perfect correlation, strong correlation, or weak correlation. Correlation can be seen when two sets of data are graphed on scattered plots which is a graph of X and Y axis and dots representing the data points. The closer the data points are together and the more the form a straight line, the stronger the correlation.

Correlation can be calculated as a number called the correlation coefficients (r). The correlation coefficient can help identify what type of relationship the data sets and how strong or weak the relationship is. The correlation coefficient falls between -1.0 and 1.0

A correlation analysis carried out to determine the relationship between the meteorological parameters, total PAH and PM$_{2.5}$ for the total sampling period.

Table 3.3.2 Correlation Matrix between the meteorological parameters and PM$_{2.5}$ for the total sampling period

Variables	PM$_{2.5}$(µg /m³)	Total PAH(ng/ m³)	Ultra-violet radiation (µW/ m²)	Pressure (mmHg)	Solar radiation (W/m²)	Wind Direction (o)	Humidity (%)	Temperature (°C)	Wind Speed (km/ h)
PM$_{2.5}$(µg /m³)	**1.00**								
Total PAH(ng/ m³)	0.16	**1.00**							
Ultra-violet radiation (µW/m²)	0.45	**0.92**	**1.00**						
Pressure (mmHg)	-0.18	**-0.93**	**-0.95**	**1.00**					
Solar radiation (W/m²)	0.15	**0.97**	**0.91**	**-0.90**	**1.00**				
Wind Direction (o)	0.18	0.45	0.25	-0.11	0.49	**1.00**			
Humidity (%)	0.20	**-0.93**	-0.76	0.87	**-0.92**	-0.36	**1.00**		
Temperature (°C)	0.21	**0.97**	**0.95**	**-0.95**	**0.99**	0.36	**-0.90**	**1.00**	
Wind Speed (km/h)	-0.21	-0.74	**-0.84**	0.92	-0.66	0.23	0.67	-0.76	**1.00**

Values in red are different from 0 with a significance level alpha=0.01
Values in blue are different from 0 with a significance level alpha=0.05
Values in purple are different from 0 with a significance level alpha=0.1

The result of the correlation showed that there was no correlation between PM$_{2.5}$ and any other parameter. There was a correlation between the total PAHs concentration and solar radiation, Ultra-Violet radiation, pressure, humidity and temperature. PAH had a positive correlation with Ultra-violet ($p<0.05$, R= 0.92), Solar radiation ($p<0.01$, R= 0.97) and temperature ($p<0.01$, R= 0.97) while it correlated negatively with Pressure ($p< 0.05$, R= -0.93) and Humidity ($p<0.05$. R= -0.932).Within the meteorological parameters there was a correlation between solar radiation, Ultraviolet radiation, Pressure, Temperature, Wind speed and Humidity. A positive correlation exists between Ultra-violet radiation and Solar radiation at $p<0.05$, r = 0.91. It also

correlated positively with temperature ($p<0.05$, $r = 0.95$). It correlated negatively with Pressure ($p<0.05$, $r = -0.95$) and wind speed ($p<0.1$, $r = -0.84$). Solar radiation correlated negatively with Pressure ($r = -0.92$, $p<0.05$), and correlated positively with Temperature ($r = 0.99$, $p<0.01$). Humidity correlated negatively with temperature ($r = -0.90$, $p<0.05$). Pressure correlated negatively with Temperature ($r = -0.95$, $p<0.05$), and with solar radiation ($r = -0.90$, $p<0.05$).
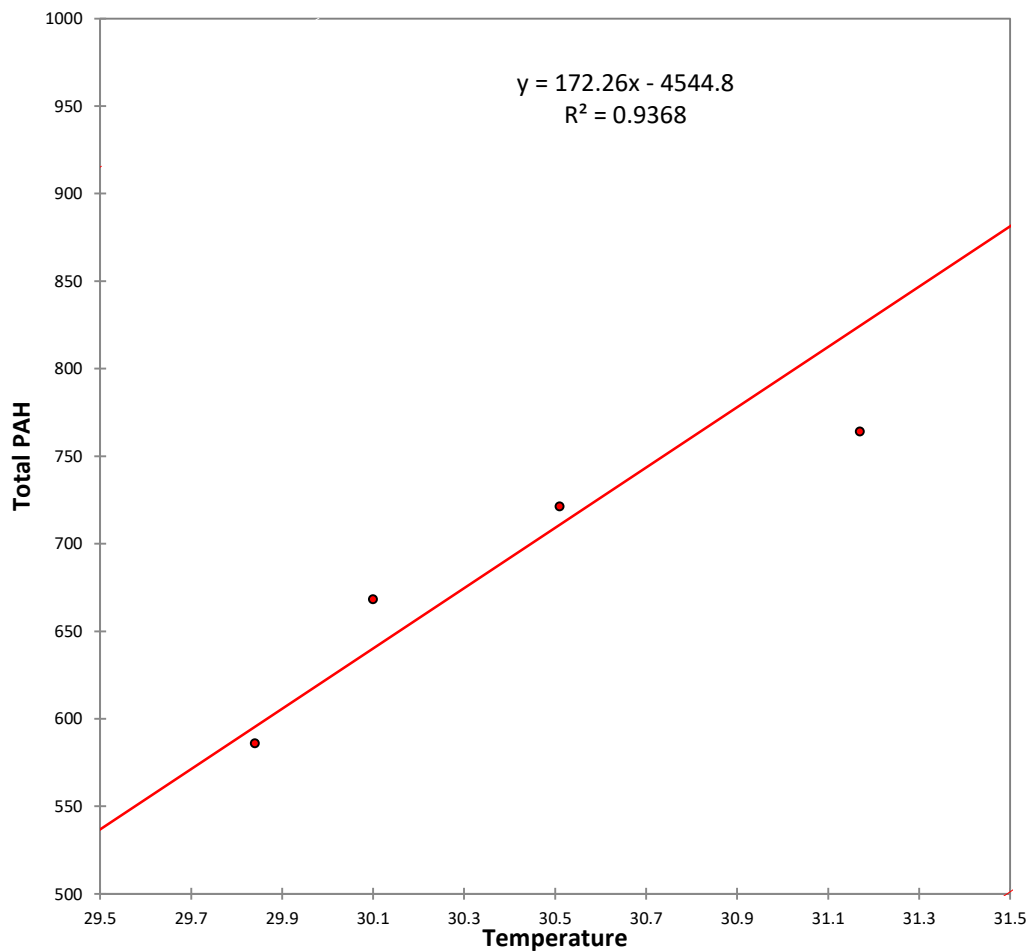
Fig 3.4a   Scatterplot showing positive correlation between Total PAH(ng/m^3) and Temperature (^{o}C)
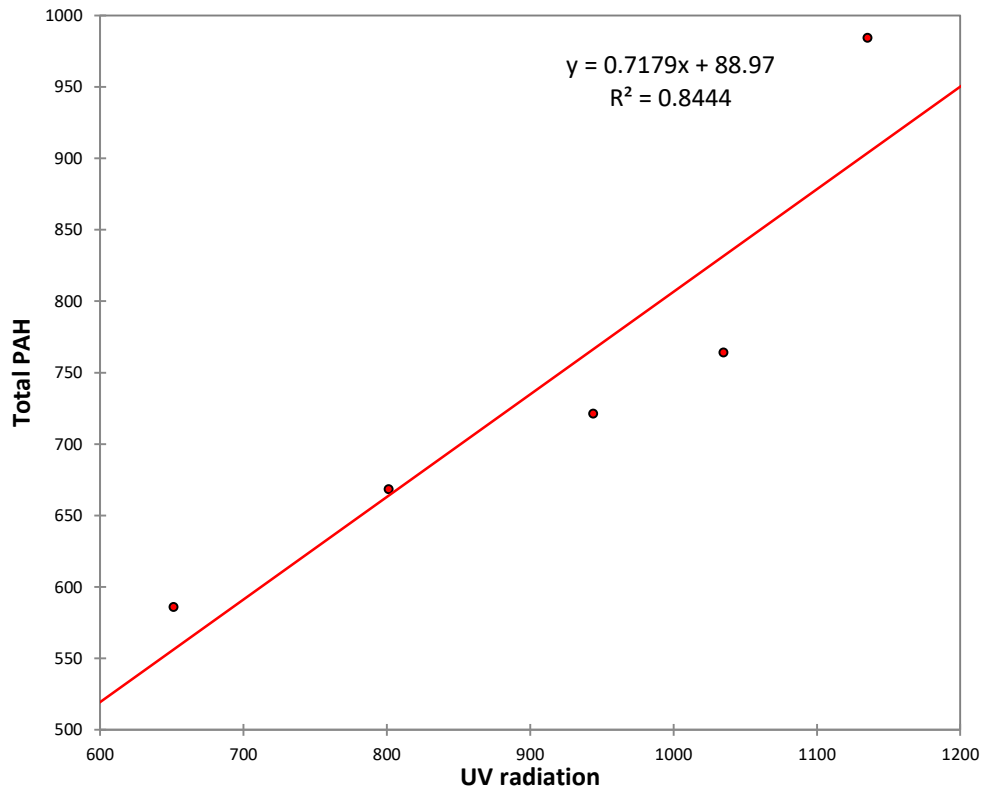
Fig 3.4b   Scatterplot showing positive correlation between Total PAH(ng/m^3) and Ultra-violet radiation (μW/m^2)
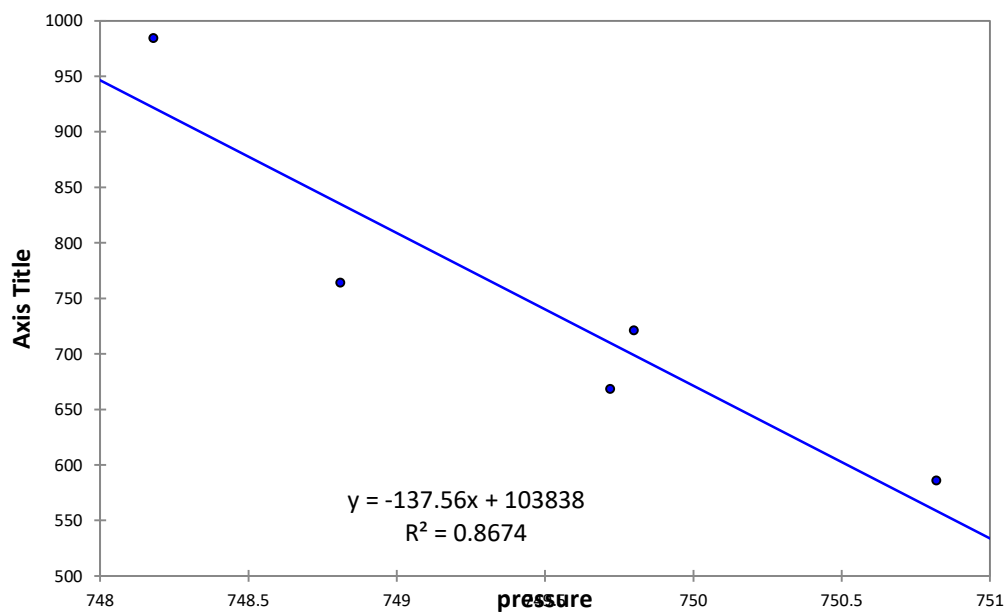
Fig 3.4c   Scatterplot showing negative correlation between Total PAH(ng/m^3) and Pressure (mmHg)
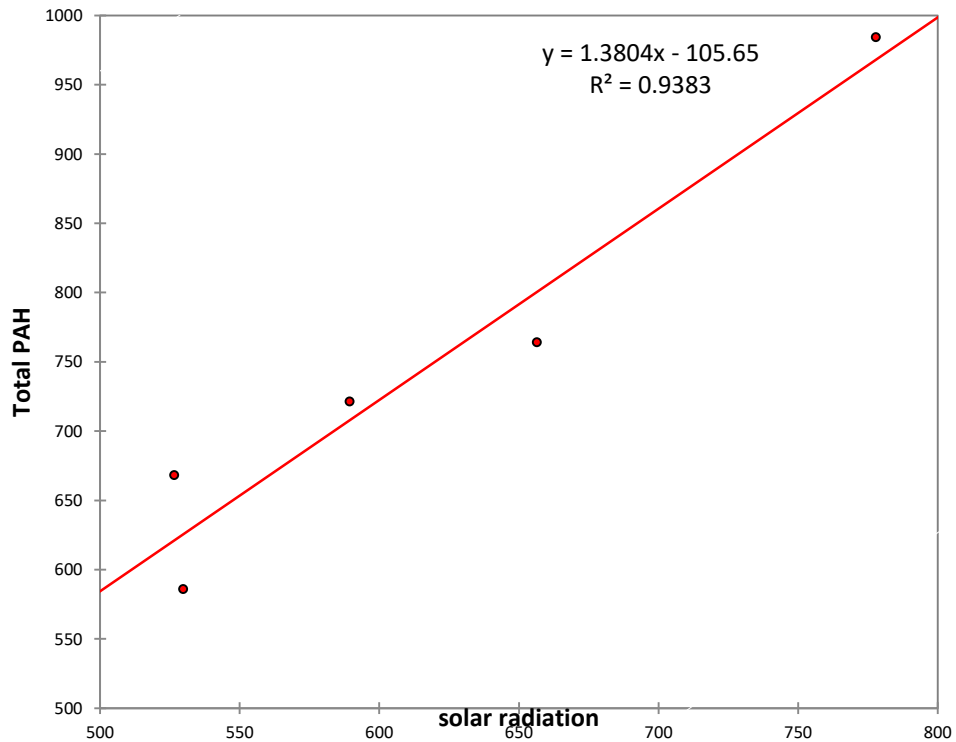
Fig 3.4d   Scatterplot showing positive correlation between Total PAH(ng/m^3) and Solar Radiation (W/m^2)
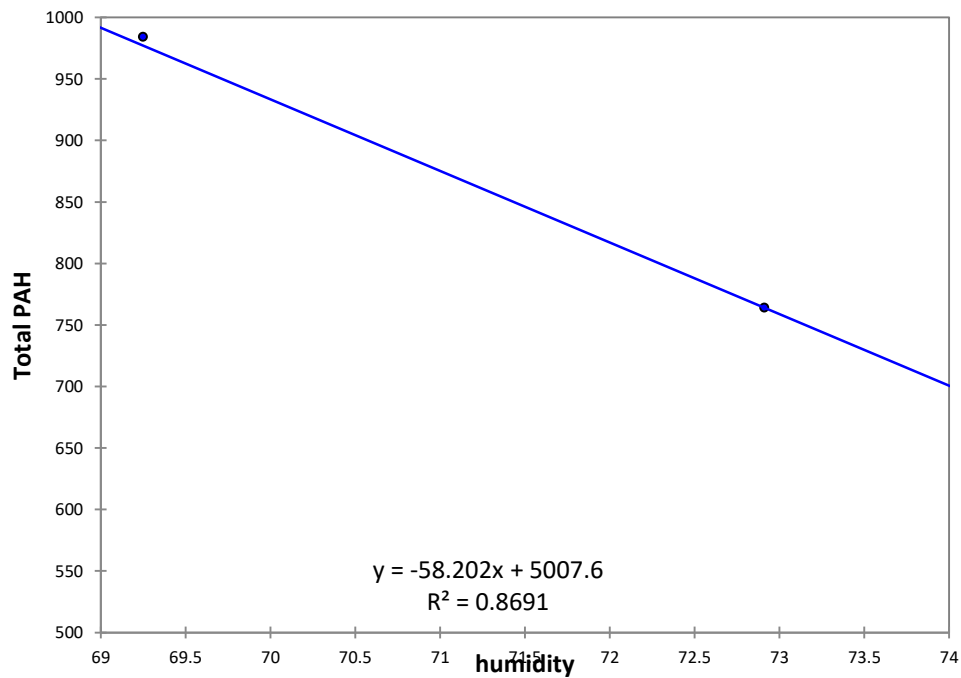
Fig 3.4e   Scatterplot showing negative correlation between Total PAH(ng/m^3) and Humidity(%)

3.4   Source Identification Analysis

In order to ascertain the possible sources of pollutants emission to the environment, principal component analysis (PCA), cluster analysis (CA), PAH diagnostic ratio were carried out. PCA and CA were performed using XLSTAT 2005 add-in for Microsoft Excel

3.4.1   Principal Component Analysis

A principal component analysis is used in explanatory data analysis to

1. Study the correlation among a large number of interrelated variables by grouping the variables into a few factors

2. Interpret each factor according to the meaning of the variable

3. Summarize variables by few factors.

PCA is the oldest and most widely used multivariate statistical technique in atmospheric sciences. It simplifies the interpretation of complex systems and transforms the original set of variables into a smaller set of linear combinations that accounts for most of the variance of the original set. The primary function of this analysis is the reduction of the number of variables while retaining the original information as much as possible. Variables with similar characteristics are grouped into factors. These factors can be interpreted either as an emission source, or a chemical interaction. In practice many of these factors, however, indicate more than one possible cause. In general, each factor from PCA is associated with a source characterized by its most representative chemical marker, PAH compound(s) in this case.

In most applications, mathematical and statistical software are used for source grouping by using PCA with vari-max rotation and the retention of principal components having eigen value >1 of complete data set of PAH concentrations. The principal components that show the

maximum percentage of total variance of the data set are used as factors. Loading determines the most representative PAHs compounds in each factor and generally a value >0.5 is selected. The following conclusions have been drawn from various studies, which have used PCA methods to enhance the accuracy of emission source identification:

1. A high factor loading of fluoranthene, pyrene, and especially of benzo[g,h,i]perylene and coronene, benzo[a]anthracene, B[a]P, benzo[b]fluoranthene, and indeno[1,2,3-cd]pyrene as source markers for gasoline emission.

2. Diesel emission has a high factor loading for fluoranthene, phenanthrene, anthracene, and pyrene (Ravindra *et al.*, 2006). Other studies also suggest that fluoranthene, pyrene with high factor loading of benzo[b]fluoranthene and benzo[k]fluoranthene indicates diesel-powered vehicles.

3. Volatile compounds such as fluoranthene and species of high molecular weight such as indeno[1,2,3-cd] pyrene, are probably generated together by the combustion of lubricating oil and also might be emitted by industrial sources.

4. A high factor loading of acenaphthylene, acenaphthene, chrysene, benzo[b]fluoranthene, and benzo(e)pyrene, points to stationary emission sources (Ravindra *et al.*, 2006a).

5. A high level of anthracene, phenanthrene, Benzo[a]Pyrene, benzo[ghi]perylene, and chrysene has been suggested for steel industry emissions(Ravindra *et al.*, 2006a).

The PAHs were used as variables in the PCA analysis of the monthly mean for the samples collected for both dry and wet season. The data was subjected to factor analysis with varimax rotation and only factors with Eigen value > 1 were considered significant. The PCA plot obtained is presented in figure 3.4 below.

Table 3.4 Factor scores for Principal Components:

Observation	F1	F2	sum
Naphthylene	-1.120	6.721	5.601
Acenaphthylene	-1.120	6.721	5.601
Acenaphthene	-1.120	6.721	5.601
Fluorene	-1.120	6.721	5.601
Anthracene	-0.853	-1.237	-2.090
Phenanthrene	-0.079	-3.853	-3.932
Fluoranthene	**2.241**	-16.786	-14.545
Pyrene	-0.174	-5.187	-5.361
Benz (a) anthracene	-2.270	1.465	-0.805
Chrysene	-0.715	**1.513**	0.798
Benzo (k)fluoranthene	-0.021	**-0.183**	-0.204
Benzo (b) fluoranthene	**0.428**	**-0.619**	-0.190
Benzo (a) pyrene	**1.254**	**-1.773**	-0.520
Indeno (1,2,3 –c,d) pyrene	**1.359**	-0.395	0.964
Dibenz (a,h) anthracene	**0.408**	**-1.911**	-1.503
Benzo (g,h,i) perylene	**2.903**	2.082	4.985
Eigen value	12.490	1.104	
Variability (%)	78.062	6.898	

From the plot we have F1 which accounts for 78.06% and F2 which accounts for 6.9%,

summing up to 85.5% of the total factors.
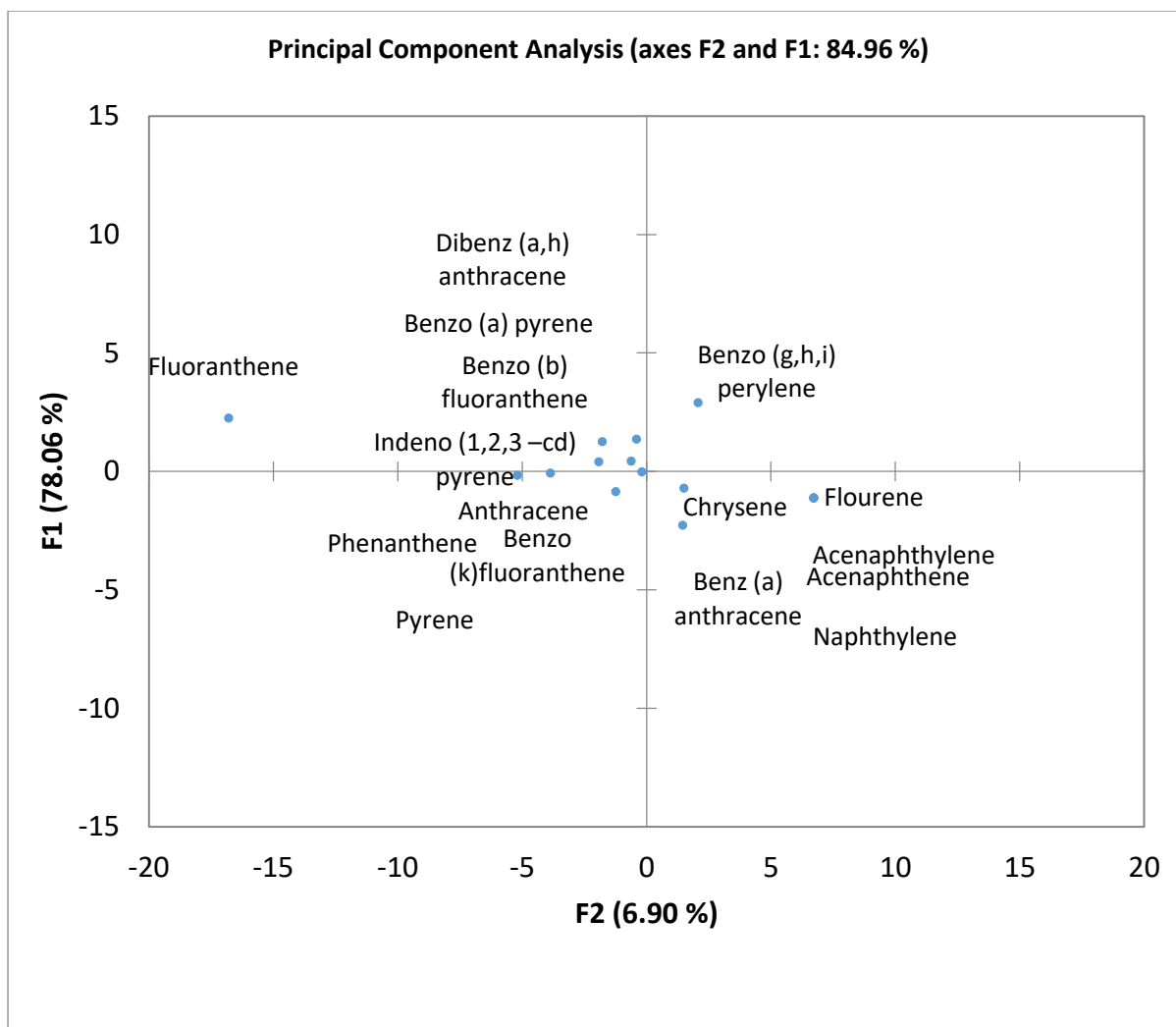
Figure 3.5   PCA plot

F1 was positive for Benzo(a) pyrene, Indeno(1,2,3-c,d)pyrene, Benzo(b) fluoranthene, Dibenz(a, h)anthracene and Benzo(g,h,i)perylene. These are source markers for gasoline emissions (Guo *et al*, 2003) while F2 had positive loading for Benzo(a) anthracene, Chrysene, Fluorene, Naphthylene, Acenaphthylene and Acenaphthene which are source markers for stationery emissions (Ravindra *et al*, 2006)

3.4.2 Cluster analysis (CA)

Cluster analysis (CA) is used to divide a data set into smaller sets. The task of cluster analysis is to assign a set of variables into groups (also called clusters) so that the variables in the same cluster are more similar (in some sense or another) to each other than to those in other clusters. Hierarchical clustering, also known as connectivitybased clustering, is based on the core idea of objects being more related to nearby objects than to objects farther away.The result of characterization of PM$_{2.5}$were subjected to HCA with the aid of cluster package using Euclidean distance and complete linkage farthest neighbours as a measure of correlation.

Table 3.5: Results of HCA presented by class

Class	1	2	3	4	5
Objects	11	1	1	2	1
Sum of weights	11	1	1	2	1
Within-class variance	1085.4701	0.0000	0.0000	479792.0633	0.0000
Minimum distance to centroid	11.1369	0.0000	0.0000	489.7918	0.0000
Average distance to centroid	24.9517	0.0000	0.0000	489.7918	0.0000
Maximum distance to centroid	75.3528	0.0000	0.0000	489.7918	0.0000
	Naphthylene	Benzo (b) fluoranthene	Benzo (a) pyrene	Indeno (1,2,3 – cd)pyrene	Dibenz (a,h) anthracene
	Acenaphthylene			Benzo (g,h,i) perylene	
	Acenaphthene				
	Flourene				
	Anthracene				
	Phenanthene				
	Fluoranthene				
	Pyrene				
	Benz (a) anthracene				
	Chrysene				
	Benzo (k)fluoranthene				

The cluster analysis showed five clusters. Cluster 1 having Naphthylene, Acenaphthylene, Acenaphthene, Fluorene, Anthracene, Phenanthrene, Fluoranthene, Pyrene, Benzo(a)anthracene, Chrysene, and Benzo(k)fluoranthene. This cluster is made up of mainly the low molecular weight PAHs with the exception of Pyrene, Chrysene and benzo(k)fluoranthene. Cluster 2 showed Benzo(b)fluoranthene , cluster 3 showed Benzo(a)pyrene, cluster 4 had Indeno(1,2,3-cd)pyrene and benzo(g,h,i,) perylene, while cluster 5 had only Dibenz(a,h)anthracene.
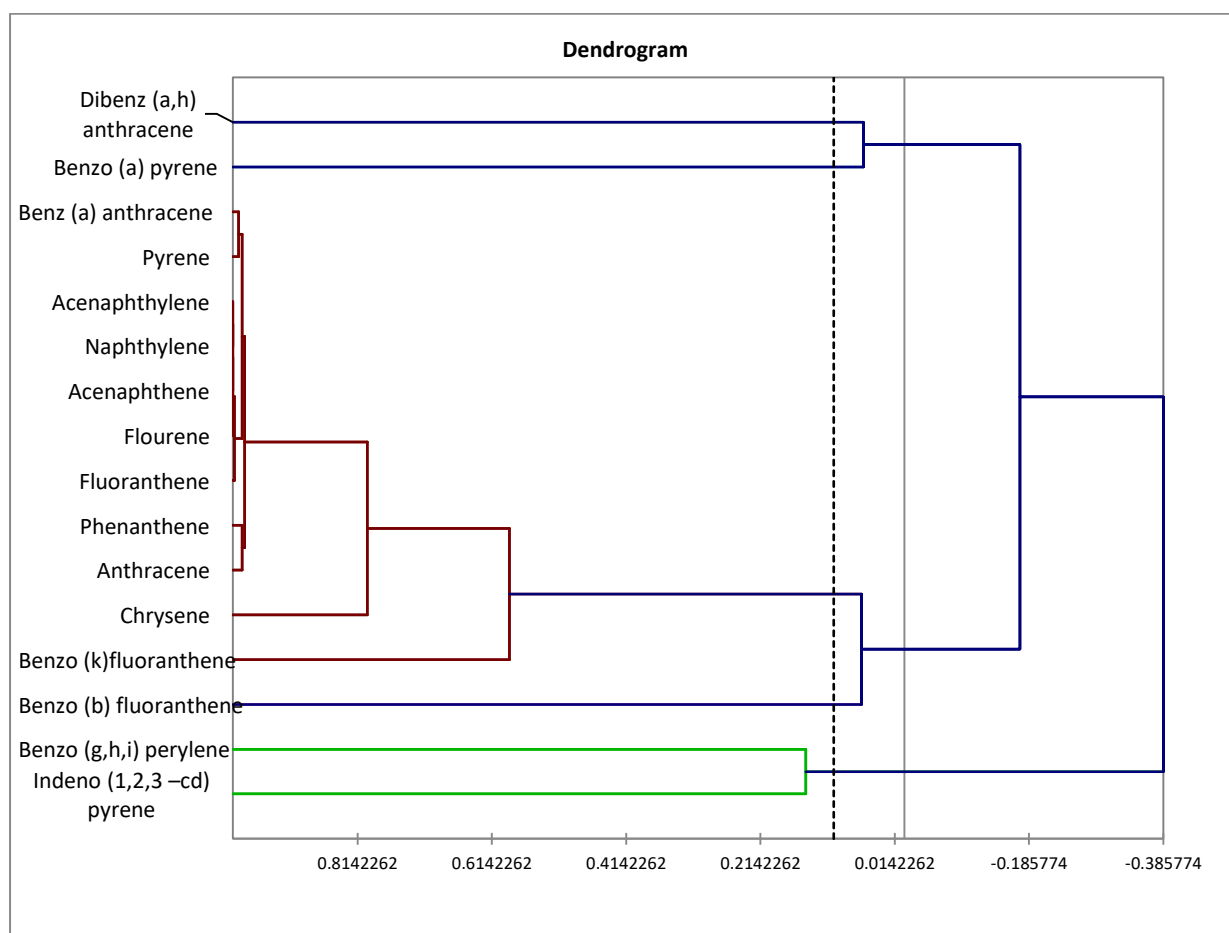
Figure 3.6 **Hierarchical Clustering Analysis plot showing objects in the clusters**

3.4.3 PAH Diagnostic Ratio

Table 3.6: Characteristic values of selected molecular ratio for pyrolytic/petrogenic and diesel/gasoline origin of PAHs for the month of February, March, May and June

PAH		Result from this work				Standard	Possible
	February	March	April	May	June	Value range	sources
B(b)F/B(k)F	3.48	3.54	4.88	5.27	4.39	**>0.5**	**Diesel**
Anth/(Anth + Phen)	0.68	0.47	0.69	0.50	0.55	< 0.1	Petrogenic
						>0.1	**Pyrolytic**
B(a)P/{B(a)P+Chry}	0.92	0.91	0.83	0.90	0.92	0.5	Diesel
						0.73	**Gasoline**
B(a)P/B(ghi)P	0.46	0.46	0.25	0.77	0.56	**0.5–06**	**Traffic emission**
						>1.25	Brown coal
Ind(1,2,3-cd)P/{Ind(1,2,3-cd)P+B(ghi)P	0.30	0.37	0.22	0.40	0.38	0.18	Cars
						0.37	**Diesel**
						0.56	Coal
						0.62	Wood burning
Ind(1,2,3-cd)P/B(ghi)P	0.41	0.59	0.27	0.67	0.61	**<0.4**	**Gasoline**
						~1	Diesel
						0.35–0.70	**Diesel emissions**
Fluo/Pyr	0.34	0.44	0.64	0.48	0.56	**0.6**	**Vehicular**

From table 3.4 above, diagnosis of the PAHs ratios showed that Ant/Ant+Phe in the months that are characteristic of the dry season ranged from 0.47 to 0.69 and it ranged from 0.50 - 0.55

during the wet season. This shows PAHs from here to be of pyrogenic origin. While the Fluo/Pyr ranged from 0.34 to 0.64 in the months that are characteristic of the dry season to 0.48 - 0.56 in the months that are characteristic of the wet season and; the values shown in this ratios are all below 0.6 which indicates vehicular emissions. The BaP/BaP+Chry ratio ranged from 0.83 - 0.92 for the months that are characteristic of both dry and wet seasons; this indicates that the major emission source is gasoline as Ravindra *et al* 2008 reported that values around 0.5 are diesel emissions while values around 0.73 are gasoline emissions. The Ind/Ind+BghiP ratio ranged from 0.22 to 0.37 during the months that are characteristic of the dry season and 0.38 to 0.40 during the months that are characteristic of the wet season. This shows emissions from diesel combustion. This also shows PAHs from the sampling locations to be of mixed sources which are petroleum sources and petroleum combustion sources. The B(b)F/B(k)F ratio ranged from 3.48- 4.88 during the months that are characteristic of dry season to 4.39- 5.27 for the months that are characteristic of the wet season; this indicates that PAHs are of petroleum origin and petroleum combustion, specifically from diesel combustion as reported by Ravindra *et al*, 2008 that values above 0.5 indicates diesel emissions . The B(a)P/B(g,h,I)P showed ratio 0.25 to 0.77 the sampling period with months that are characteristic of both wet and dry season; values between 0.5 to 0.6 indicate traffic emissions while values above 1.25 indicate brown coal. The Ind(1,2,3-cd)P/B(g,h,i)P ratio was within 0.27-0.67 for sampling period. This ratio tells us that ratios within 0.35-0.70 are of diesel emission source and this indicate that the PAHs in all locations are likely of petroleum sources.

From this analysis it could be said that PAHs in the PM$_{2.5}$ samples in the dry and wet majorly of combustion sources from mixed origin which is mainly petroleum (gasoline and diesel).

3.5   Estimation of Toxicity and Carcinogenicity

Table 3.7: BAP-TEQ calculation from TEQ value and PAH concentration

PAH congeners	TEQ value	[PAH] (ng/m^3)	(BaP-TEQ) (ng/m^3)
Benzo[a]anthracene	0.1	5.27	0.527
Chrysene	0.01	12.91	0.1291
Benzo[b]fluoranthene	0.1	72.2	7.22
Benzo[k]fluoranthene	0.1	16.77	1.677
Benzo[a]pyrene	1	122.63	122.63
Dibenz[a,h]anthracene	1	99.06	99.06
Indeno[1,2,3-cd]pyrene	0.1	130.51	13.051
Benzo[g,h,i]perylene	0.1	289.03	28.903
∑8PAH	2.42	748.36	273.1971

BaP-TEQ (carcinogenic equivalents, ng/m³) was calculated by multiplying the concentrations of each PAH compound with its TEF for cancer potency relative to BaP.

TEF of dibenz(ah)anthracene (DahA) is around 5 at low dose and close to 1 at higher dose based on local tumors induced by subcutaneous injection into mice (Kyung *et al*., 2010)

 BaP-TEQ levels for the sum of non-volatile PAH (∑8PAH) were calculated as follows:

- (BaP-TEQ)∑8PAH = [BaA] × 0.1 + [Chry] × 0.01 + [BbF] × 0.1 + [BkF] × 0.1 + [BaP] × 1 + [IP] × 0.1 + [DahA] × 1 + [BghiP] × 0.01.

- (BaP-TEQ)∑8PAH = 5.27 ×0.1 + 12.91×0.01 + 72.20 × 0.1 + 16.71 ×0.1 + 122.63×1 + 130.51× 0.1 + 99.06×1 + 289.03×0.01

- (BaP-TEQ)∑8PAH = 273.1971ng/m^3

- (BaP-TEQ)∑8PAH = 0.273 µg/m^3

Carcinogenic risk = $(\text{BaP} - \text{TEQ})\sum 8\text{PAH} \ \text{X} \ UR_{BaP}$

UR_{BaP} = Inhalation cancer unit risk factor of BaP $\Rightarrow$ (1 X $10^{-6}\mu g/m^3$)

UR_{BaP} is estimated from Cancer Potential Factor (CPF) From the relation

UR = CPF X $20m^3$/(70kg X CV)

This estimated value for UR is coined by relating the average weight of 70kg for human and $20m^3$ of average inhalation. (OEHHA, 2005)

Carcinogenic risk = 0.273 $\mu g/m^3 \times$ (1 X $10^{-6} \mu g/m^3$)

$$= 2.73 \times 10^{-7} \ \mu g/m^3$$

$$= 2.73 \times 10^{-4} \ ng/m^3$$

The cancer risk value obtained for this study at the sampling location is $2.51 \times 10^{-7} \ \mu g/m^3$ equivalent to $2.73 \times 10^{-4} \ ng/m^{3.}$

This is far above the USEPA acceptable standard for PAHs which is 1 x $10^{-6} \ ng/m^3$. This shows that the environment is highly polluted.

The (BaP-TEQ) $\sum 8$PAH levels observed in this study were considerably higher than those reported for other homes impacted heavily by industrial and traffic emissions in Ohura *et al.*. (BaP-TEQ)$\sum 8$PAH risk levels depend not only on concentrations of individual 8 PAH, but also the composition of PAH mixtures affected by varying emission sources. The largest contribution of individual PAH to (BaP-TEQ) $\sum 8$PAH was made by B(a)P, followed by D(ah)A, and IndP.

CONCLUSION

Polycyclic aromatic hydrocarbons (PAHs) are distributed ubiquitously in the ambient air environment, which lead to wide exposure in the general populations (ATSDR, 1995; Li *et al.* 2008). PAHs in the atmosphere can come from natural sources, such as forest fires and volcanic eruptions. However, their presence, especially in densely populated areas, is significantly caused by anthropogenic emissions, such as automobile exhaust, fossil fuel combustion, biomass burning, cigarette smoking, and industrial activities. PAHs have been reported to be carcinogenic and mutagenic, and possess toxicities towards a variety of target organs/systems, such as liver and immune system (ATSDR, 1995). Airborne PAHs, when bound to particulate matters especially the fine particles ($PM_{2.5}$), may increase potential health effects because particles carrying the toxic compounds can penetrate and deposit deep in the bronchioles and alveoli of the lungs

The results obtained from this study revealed that the ambient air in the selected auto-mechanic workshop around Uwelu motor spare parts market, Benin City were heavily polluted with $PM_{2.5.}$ The concentration of the particulate matter found were higher than the regulatory limit stated by the regulatory bodies, which is $25\mu g/m^3$. The $PM_{2.5.}$ The major source of this particulate are vehicular emissions, wear/tear of brake linings, automobile batteries, spilling of used oil/ lubricants. The PAH analysis for the $PM_{2.5}$filters revealed a high level of high molecular weight PAHs. The expected carcinogenicity was estimated using TEF and excess cancer risk calculations and they showed that the level of PAHs which are known human carcinogens were much higher than the USEPA acceptable standard.

Principal component analysis and PAH diagnostic ratio explained the emission sources as pyrogenic, vehicular emission such as gasoline/diesel emission, traffic as well as stationary

emissions. Cluster analysis was able to obtain the various clustering in the PAHs, further suggesting that the source of PAHs in the study location is.

FINDINGS

From all the work done in this study, the following findings were obtained

- Total $PM_{2.5}$ concentration around auto-mechanic environs was higher than values recorded in similar studies in Benin City and Lagos in other environs.

- Total PAH concentrations were also relatively high but were lower than the OSHA and NIOSH regulatory limit of occupational exposure for 8hour and 10 hour Time weight average respectively.

- Overall concentration of PAHs was also higher in the dry season than in the rainy season.

- PAHs in Auto-Mechanic environs are more from anthropogenic pyrogenic sources;

- These anthropogenic petrogenic sources are more due to point source diesel and gasoline combustion pollution

RECOMMENDATION

Based on the work done in this study, the following recommendations are given:

- Adequate environmental monitoring can help reduce environmental PAHs as well as other pollutant release, therefore, this should be well implemented by relevant bodies and the public as a whole;

- The general public should be well educated about the environment and how the little wrong thing done in the environment every moment has great negative implications on health and could last for several years;

- The public should be well enlightened on what PAHs, their source, health effects are and how to control their release into the environment.

- Automobile workshops should be assessed regularly to ensure compliance to environmental regulations relevant to this industry

- Use of available products that reduces environmental emissions due to petroleum combustion should also be encouraged.

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Appendix 1a: PAH concentrations for various sampling locations in the month of February

PAH Component	Location 1	Location 2	Location 3	Location 4	mean
Naphthylene	nd	nd	nd	nd	**nd**
Acenaphthylene	nd	nd	nd	nd	**Nd**
Acenaphthene	nd	nd	nd	nd	**Nd**
Flourene	nd	nd	nd	nd	**Nd**
Anthracene	nd	nd	6.42	nd	**6.42**
Phenanthene	3.14	nd	4.62	1.19	**2.98**
Fluoranthene	nd	1.53	1.44	1.98	**1.65**
Pyrene	nd	3.95	6.51	4.25	**4.90**
Benz (a) anthracene	3.98	4.09	8.12	7.99	**6.05**
Chrysene	6.83	15.96	20.57	4.01	**11.84**
Benzo (k)fluoranthene	15.71	30.78	10.39	10.19	**16.77**
Benzo (b) fluoranthene	31.27	71.56	85.38	45.90	**58.53**
Benzo (a) pyrene	60.45	200.18	135.58	nd	**132.07**
Indeno (1,2,3 –cd)	126.71	189.85	58.09	100.45	**118.78**
Dibenz (a,h) anthracene	nd	87.16	nd	56.05	**71.61**
Benzo (g,h,i) perylene	301.98	398.04	408.15	50.30	**289.62**
Total ng/m3	**550.07**	**1,003.10**	**745.27**	**282.31**	**721.21**

Appendix 1b: PAH concentrations for various sampling locations in the month of March

PAH Component	Location 5	Location 6	Location 7	Location 8	mean
Naphthylene	nd	nd	nd	nd	**nd**
Acenaphthylene	nd	nd	nd	nd	**nd**
Acenaphthene	nd	nd	nd	nd	**nd**
Fluorene	nd	nd	nd	nd	**nd**
Anthracene	nd	2.51	5.52	nd	**4.02**
Phenanthrene	5.09	nd	3.72	4.37	**4.39**
Fluoranthene	nd	2.03	1.55	2.43	**2.00**
Pyrene	nd	2.09	8.01	3.45	**4.52**
Benzo(a) anthracene	4.98	2.54	7.52	6.59	**5.41**
Chrysene	5.93	30.75	10.27	2.91	**12.47**
Benzo (k)fluoranthene	13.81	25.69	20.99	11.29	**17.95**
Benzo (b) fluoranthene	21.27	53.15	83.18	96.59	**63.55**
Benzo (a) pyrene	120.54	119.07	105.18	175.53	**130.08**
Indeno(1,2,3-cd)pylene	96.51	211.14	280.11	80.11	**166.97**
Dibenz(a,h)anthracene	92.15	nd	85.15	116.24	**97.85**
Benzo (g,h,i) perylene	214.56	470.73	300.25	150.78	**284.08**
Total ng/m3	**574.84**	**919.70**	**911.45**	**650.29**	**764.07**

Appendix 1c: PAH concentrations for various sampling locations in the month of April

PAH Component	Location 9	Location 10	Location 11	Location 12	mean
Naphthylene	nd	nd	nd	nd	**Nd**
Acenaphthylene	nd	nd	nd	nd	**Nd**
Acenaphthene	nd	nd	nd	nd	**Nd**
Fluorene	nd	nd	nd	nd	**Nd**
Anthracene	7.15	4.94	4.54	nd	**5.54**
Phenanthrene	3.25	2.27	2.74	nd	**2.75**
Fluoranthene	1.1	2.31	nd	nd	**1.7**
Pyrene	5.05	nd	**5.05**	2.93	**2.66**
Benzo(a) anthracene	7.82	4.79	5.78	2.98	**5.34**
Chrysene	26.8	6.67	7.73	27.18	**16.93**
Benzo (k)fluoranthene	11.04	11.18	13.81	65.42	**25.36**
Benzo (b) fluoranthene	215.53	116.95	39.17	nd	**123.88**
Benzo (a) pyrene	105.55	97.32	140.04	129.1	**118.01**
Indeno (1,2,3 – cd)	110.73	79.79	136.01	241.11	**141.91**
Dibenz (a,h) anthracene	75.61	66.33	90.65	nd	**77.53**
Benzo (g,h,i) perylene	508.85	515.77	554.02	487.47	**516.53**
Total ng/m3	**1078.52**	**907.7**	**994.49**	**956.22**	**984.24**

Appendix 1d: PAH concentrations for various sampling locations in the month of May

PAH Component	Location 13	Location 14	Location 15	Location 16	mean
Naphthylene	nd	nd	nd	nd	**nd**
Acenaphthylene	nd	nd	nd	nd	**nd**
Acenaphthene	nd	nd	nd	nd	**nd**
Fluorene	nd	nd	nd	nd	**nd**
Anthracene	3.66	nd	4.91	7.10	**5.22**
Phenanthrene	2.21	nd	2.26	11.29	**5.25**
Fluoranthene	nd	nd	2.30	1.10	**1.70**
Pyrene	nd	2.14	nd	5.01	**3.57**
Benz(a)anthracene	4.66	2.08	4.76	7.76	**4.81**
Chrysene	6.23	13.84	5.96	26.60	**13.16**
Benzo(k)fluoranthene	11.13	11.73	11.11	10.96	**11.23**
Benzo(b)fluoranthene	31.56	0.00	90.29	114.65	**59.13**
Benzo (a) pyrene	137.02	128.12	104.07	104.75	**118.49**
Indeno(1,2,3cd)pyrene	109.60	158.93	71.12	70.25	**102.47**
Dibenz (a,h) anthracene	556.55	65.4735	57.7698	79.0839	**189.72**
Benzo (g,h,i) perylene	124.11	178.98	97.58	213.34	**153.50**
Total ng/m3	**986.73**	**561.29**	**452.12**	**651.89**	**668.26**

Appendix 1e: PAH concentrations for various sampling locations in the month of June

PAH Component	Location 17	Location 18	Location 19	Location 20	mean
Naphthylene	nd	nd	nd	nd	**nd**
Acenaphthylene	nd	nd	nd	nd	**nd**
Acenaphthene	nd	nd	nd	nd	**nd**
Fluorene	nd	nd	nd	nd	**nd**
Anthracene	0.85	nd	nd	nd	**0.85**
Phenanthrene	1.32	nd	0.09	nd	**0.71**
Fluoranthene	nd	nd	1.45	nd	**1.45**
Pyrene	1.10	0.47	nd	6.22	**2.60**
Benz(a)anthracene	1.76	1.67	5.91	9.63	**4.74**
Chrysene	4.21	17.18	7.39	11.87	**10.16**
Benzo(k)fluoranthene	9.44	14.56	nd	13.6	**12.53**
Benzo(b)fluoranthene	32.43	19.56	112.05	59.67	**55.93**
Benzo (a) pyrene	120.89	108.29	129.15	99.59	**114.48**
Indeno(1,2,3cd)pyrene	116.95	197.22	88.26	87.18	**122.40**
Dibenz (a,h) anthracene	nd	81.25	5.98	88.54	**58.59**
Benzo (g,h,i) perylene	85.38	300.76	95.35	324.21	**201.42**
Total ng/m3	**374.32**	**740.96**	**445.63**	**700.51**	**585.86**

APPENDIX 2

Chromatographs showing peak heights for various PAHs detected
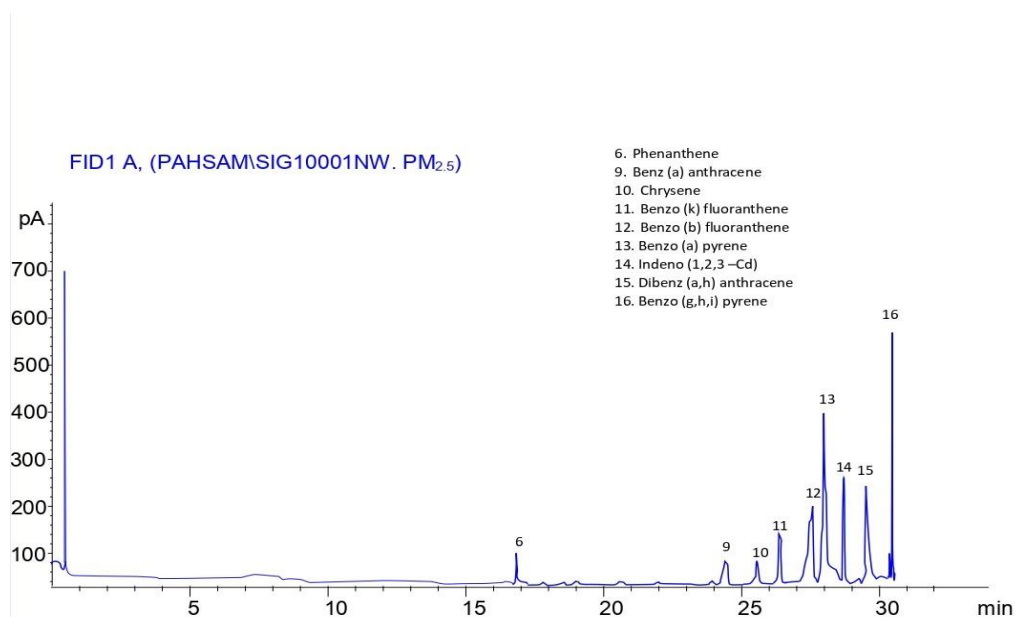
Appendix2a: Chromatographs showing peak heights for various PAHs detected in Location 13
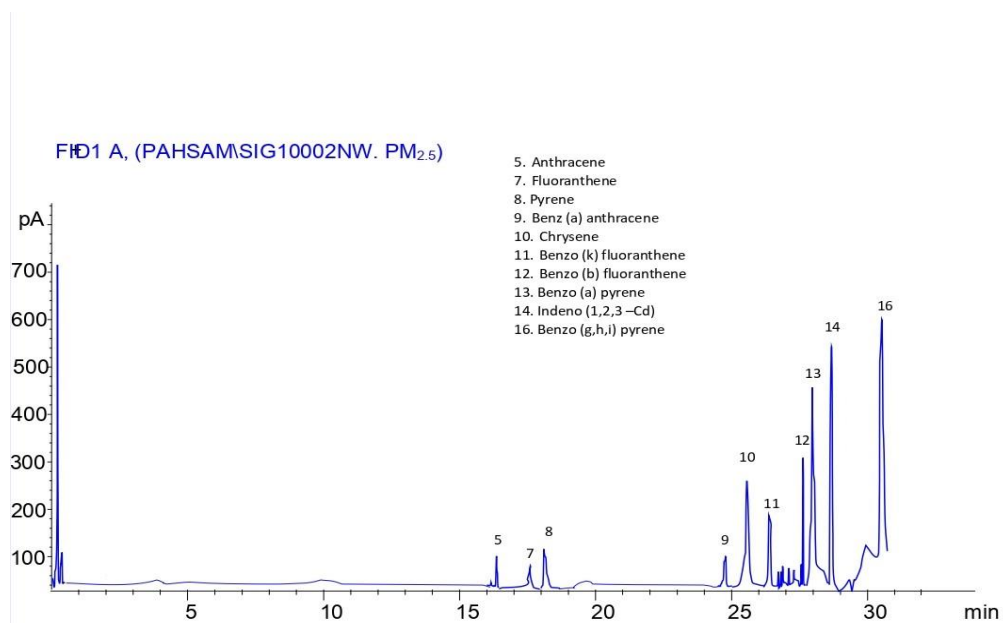
Appendix2b: Chromatographs showing peak heights for various PAHs detected in Location 14
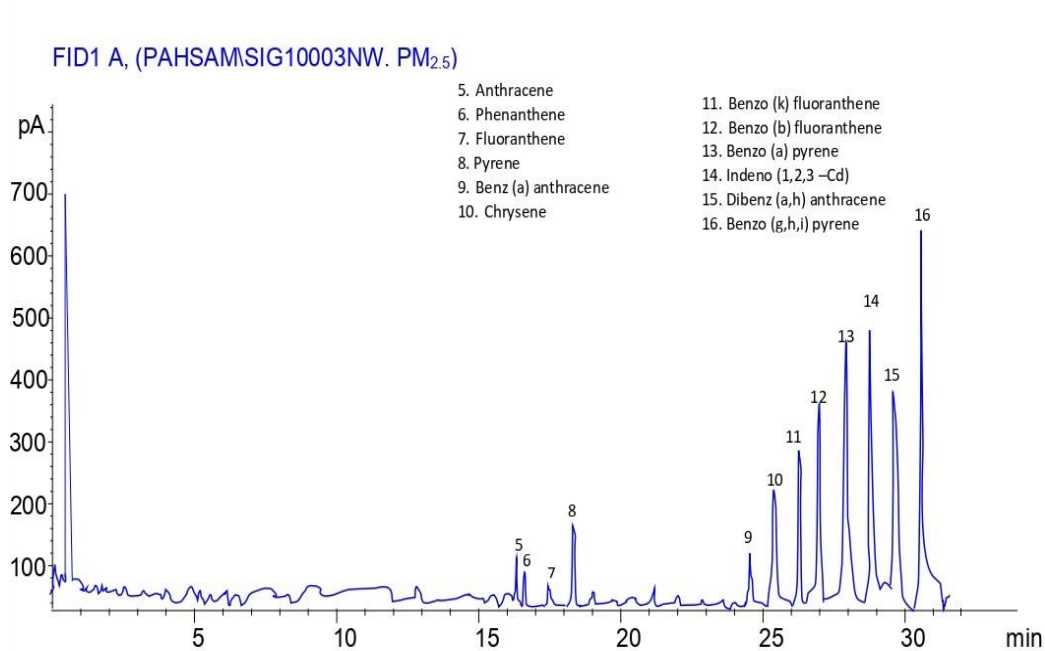
Appendix2c: Chromatographs showing peak heights for various PAHs detected in Location 9
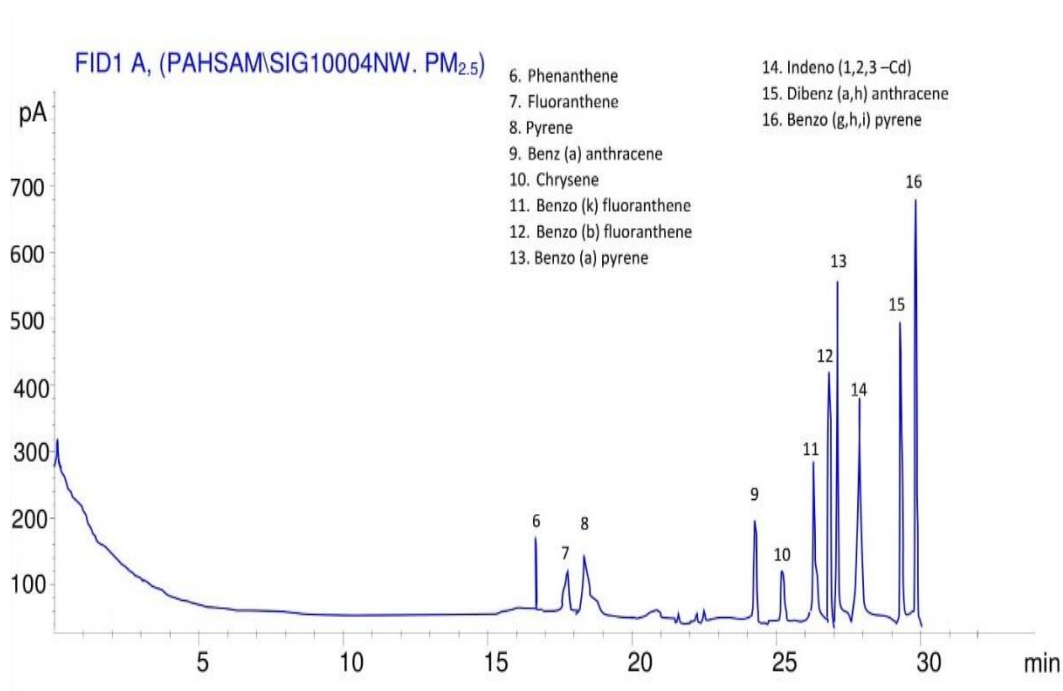
Appendix2d: Chromatographs showing peak heights for various PAHs detected in Location 10
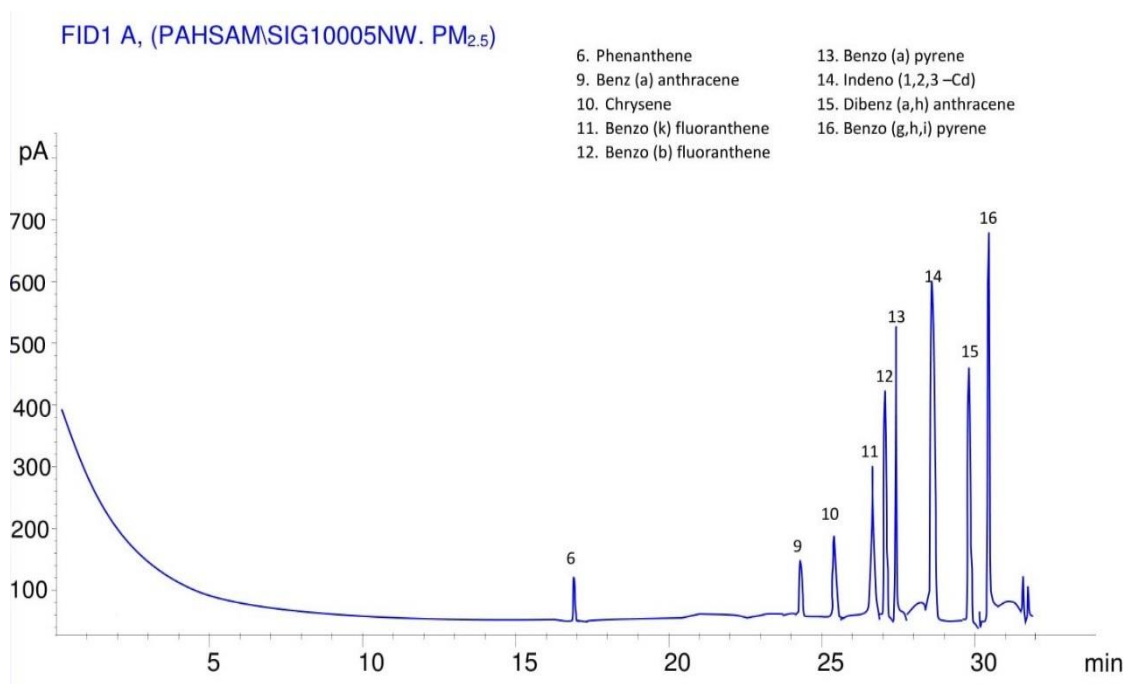
Appendix2e: Chromatographs showing peak heights for various PAHs detected in Location 11
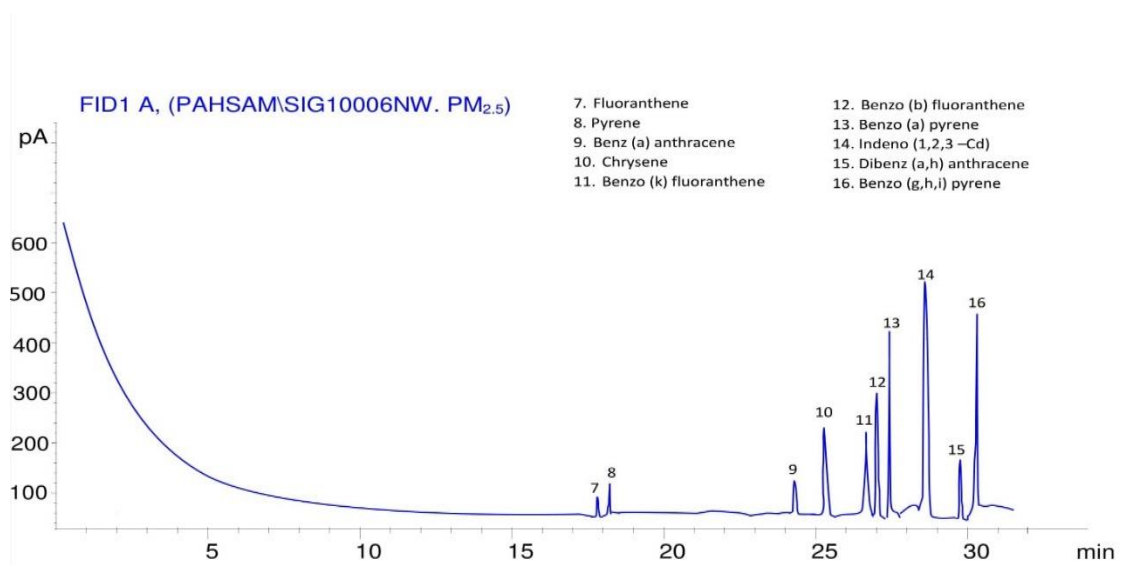
Appendix2f: Chromatographs showing peak heights for various PAHs detected in Location 17

FID1 A, (PAHSAM\SIG10007NW. PM$_{2.5}$)

5. Anthracene
6. Phenanthene
7. Fluoranthene
8. Pyrene
9. Benz (a) anthracene
10. Chrysene
11. Benzo (k) fluoranthene
12. Benzo (b) fluoranthene
13. Benzo (a) pyrene
14. Indeno (1,2,3 –Cd)
15. Dibenz (a,h) anthracene
16. Benzo (g,h,i) pyrene
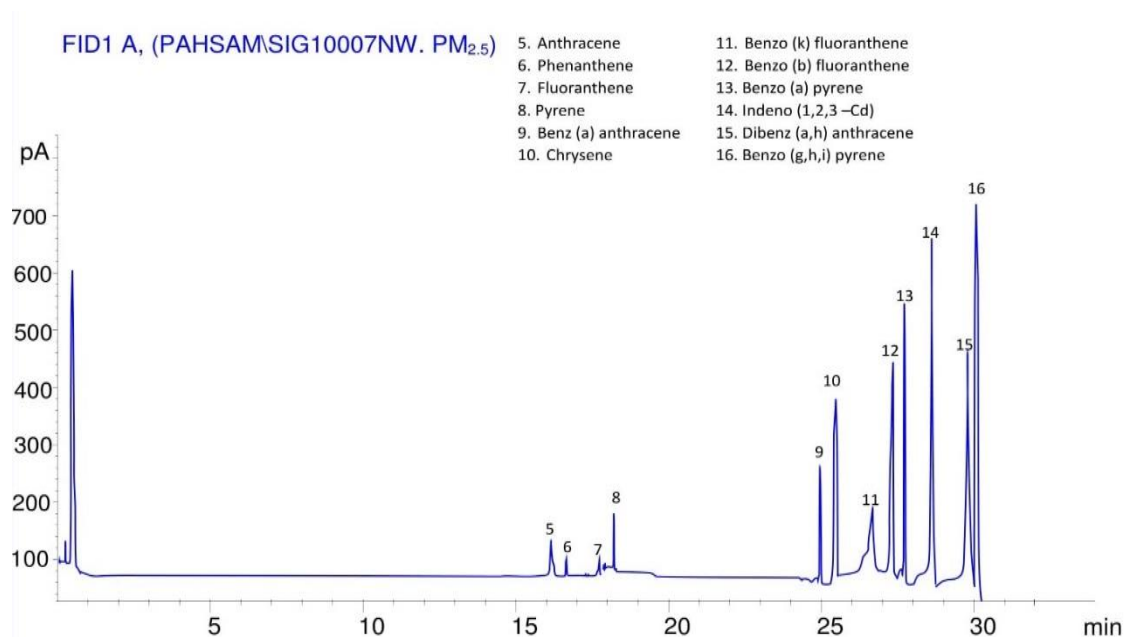
Appendix2g: Chromatographs showing peak heights for various PAHs detected in Location 18

FID1 A, (PAHSAM\SIG10008NW. PM$_{2.5}$)

6. Phenanthene
7. Fluoranthene
8. Pyrene
9. Benz (a) anthracene
10. Chrysene
11. Benzo (k) fluoranthene
12. Benzo (b) fluoranthene
13. Benzo (a) pyrene
14. Indeno (1,2,3 –Cd)
15. Dibenz (a,h) anthracene
16. Benzo (g,h,i) pyrene
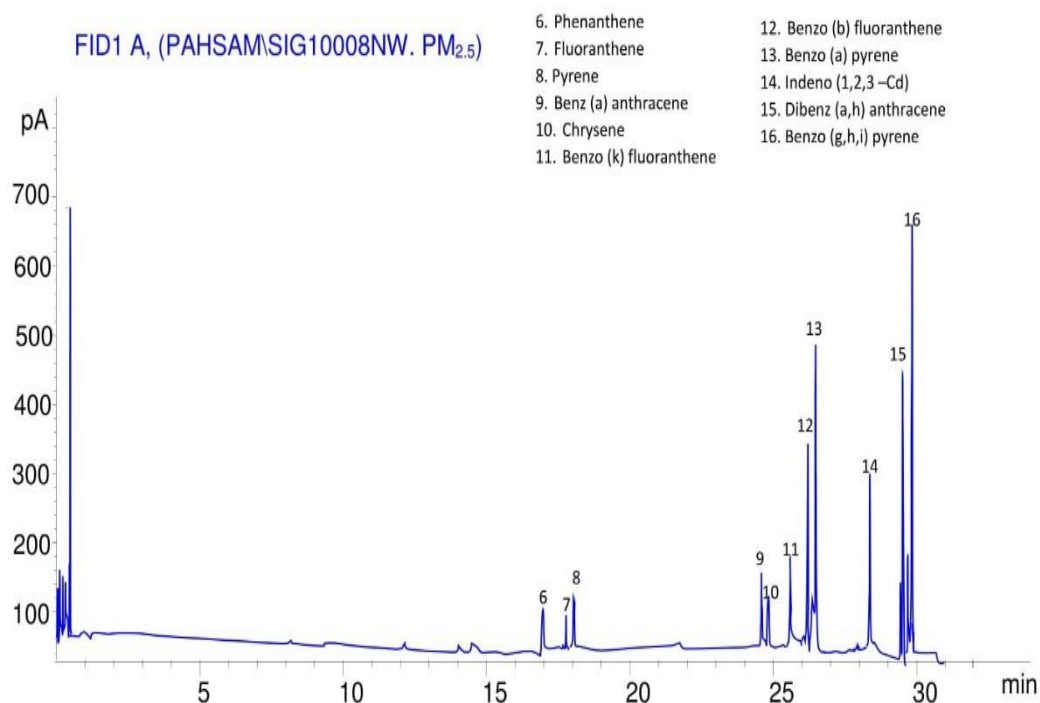
Appendix2h: Chromatographs showing peak heights for various PAHs detected in Location 19

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APPENDIX 3

Meteorological Data for the sampling period

FEBRUARY

LOCATION 1

Times (hr.)	Temperature (°C)	Humidity (%)	Pressure (mmHg)	Wind Speed (km/h)	Wind Direction (o)	Solar radiation (W/m2)	Ultra-violet radiation (µW/m2)
9am	26.45	89.00	750.80	2.10	130.00	280.48	286.00
10am	27.51	87.00	750.70	5.20	195.00	375.03	571.00
11am	28.35	85.00	750.50	8.40	276.00	485.65	1,002.00
12am	32.15	68.00	749.50	6.50	30.00	575.85	1,258.00
1pm	32.61	67.00	750.80	5.50	250.00	565.25	1,152.00
2pm	31.52	72.00	750.10	5.40	277.00	455.15	985.00
3pm	31.24	75.00	750.10	10.30	301.00	301.45	1,025.00
4pm	30.01	77.00	750.20	4.80	267.00	200.78	625.00
Min	**26.45**	**67.00**	**749.50**	**2.10**	**30.00**	**200.78**	**286.00**
Max	**32.61**	**89.00**	**750.80**	**10.30**	**301.00**	**575.85**	**1,285.00**
Mean	**29.98**	**77.50**	**750.83**	**6.02**	**215.75**	**404.95**	**863.00**

FEBRUARY

LOCATION 2

Times (hr.)	Temperature (°C)	Humidity (%)	Pressure (mmHg)	Wind Speed (km/h)	Wind Direction (o)	Solar radiation (W/m2)	Ultra-violet radiation (μW/m2)
9am	27.15	88.00	750.80	9.20	140.00	380.24	295.00
10am	28.21	86.00	750.60	6.10	190.00	475.08	611.00
11am	29.52	79.00	750.30	7.20	286.00	685.65	1,102.00
12am	32.25	65.00	748.50	6.50	235.00	975.85	1,458.00
1pm	32.65	64.00	748.10	5.50	90.00	865.20	1,252.00
2pm	31.61	69.00	749.50	7.50	77.00	450.25	985.00
3pm	31.52	71.00	750.10	6.30	130.00	351.15	1,005.00
4pm	30.21	76.00	750.20	4.90	260.00	250.28	655.00
Min	**27.15**	**64.00**	**748.10**	**4.90**	**77.00**	**250.28**	**295.00**
Max	**32.65**	**88.00**	**750.80**	**9.20**	**286.00**	**975.85**	**1,458.00**
Mean	**30.39**	**74.75**	**749.76**	**6.65**	**176.00**	**554.21**	**920.37**

FEBRUARY

LOCATION 3

Times (hr.)	Temperature (°C)	Humidity (%)	Pressure (mmHg)	Wind Speed (km/h)	Wind Direction (o)	Solar radiation (W/m2)	Ultra-violet radiation (µW/m2)
9am	27.45	87.00	749.70	5.10	302.00	280.82	333.00
10am	28.51	85.00	749.60	5.60	158.00	385.03	672.00
11am	29.35	84.00	749.50	5.70	268.00	485.50	1,102.00
12am	33.15	65.00	747.80	8.50	205.00	1,575.15	1,458.00
1pm	33.61	66.00	748.40	6.10	202.00	1,665.25	1,542.00
2pm	32.52	71.00	748.80	4.40	111.00	551.58	1,085.00
3pm	30.24	75.00	749.10	5.30	95.00	371.45	1,125.00
4pm	30.01	76.00	749.20	4.90	260.00	310.78	725.00
Min	**27.45**	**65.00**	**474.80**	**4.40**	**95.00**	**280.82**	**333.00**
Max	**33.61**	**87.00**	**479.70**	**8.50**	**302.00**	**1,665.25**	**1,542.00**
Mean	**30.61**	**76.13**	**749.01**	**5.70**	**200.13**	**703.20**	**1,005.25**

FEBRUARY

LOCATION 4

Times (hr.)	Temperature (°C)	Humidity (%)	Pressure (mmHg)	Wind Speed (km/h)	Wind Direction (o)	Solar radiation (W/m2)	Ultra-violet radiation (μW/m2)
9am	28.10	86.00	750.50	5.20	145.00	390.25	375.00
10am	29.20	83.00	750.20	4.20	195.00	485.08	681.00
11am	30.20	75.00	750.90	3.20	186.00	695.55	1,202.00
12am	33.00	62.00	748.10	5.50	205.00	1,075.85	1,498.00
1pm	33.40	54.00	747.80	5.70	190.00	1,165.20	1,352.00
2pm	32.40	69.00	748.50	6.20	97.00	850.25	1,085.00
3pm	31.70	71.00	750.10	5.80	120.00	551.15	955.00
4pm	30.40	76.00	750.70	9.50	265.00	350.28	755.00
Min	**28.10**	**54.00**	**747.80**	**3.20**	**97.00**	**350.28**	**375.00**
Max	**33.40**	**86.00**	**750.90**	**9.50**	**265.00**	**1,165.20**	**1,498.00**
Mean	**31.05**	**72.00**	**749.60**	**5.66**	**175.38**	**695.45**	**987.88**

MARCH

LOCATION 5

Times (hr.)	Temperature (°C)	Humidity (%)	Pressure (mmHg)	Wind Speed (km/h)	Wind Direction (o)	Solar radiation (W/m2)	Ultra-violet radiation (µW/m2)
9am	26.90	89.00	750.50	4.20	230.00	270.50	296.00
10am	27.80	86.00	750.30	5.20	190.00	395.05	591.00
11am	29.45	83.00	750.00	4.40	76.00	505.95	1,102.00
12am	33.20	60.00	747.80	7.50	30.00	775.85	1,258.00
1pm	33.60	56.00	747.10	6.50	250.00	665.55	1,350.00
2pm	32.50	68.00	748.20	5.40	117.00	555.25	1,005.00
3pm	31.90	72.00	748.50	5.80	305.00	351.45	1,025.00
4pm	30.80	76.00	749.20	4.80	265.00	220.28	645.00
Min	**26.90**	**60.00**	**747.10**	**4.20**	**30.00**	**220.28**	**296.00**
Max	**33.60**	**89.00**	**750.50**	**7.50**	**305.00**	**775.85**	**1,350.00**
Mean	**30.81**	**73.75**	**748.95**	**5.48**	**182.88**	**467.49**	**909.00**

MARCH

LOCATION 6

Times (hr.)	Temperature (°C)	Humidity (%)	Pressure (mmHg)	Wind Speed (km/h)	Wind Direction (o)	Solar radiation (W/m2)	Ultra-violet radiation (µW/m2)
9am	26.20	89.00	750.90	5.00	148.00	350.25	285.00
10am	28.90	85.00	750.40	5.50	180.00	505.28	621.00
11am	30.40	77.00	749.80	7.00	280.00	785.60	1,201.00
12am	32.90	64.00	748.10	6.50	230.00	1,075.15	1,508.00
1pm	33.70	62.00	748.10	5.50	190.00	965.20	1,362.00
2pm	33.90	63.00	748.30	6.50	77.00	650.25	1,385.00
3pm	32.50	70.00	748.20	5.50	130.00	351.15	1,105.00
4pm	31.20	74.00	749.20	4.90	260.00	250.28	755.00
Min	**26.20**	**64.00**	**748.10**	**4.90**	**77.00**	**250.28**	**285.00**
Max	**33.90**	**89.00**	**750.90**	**7.00**	**280.00**	**1,075.15**	**1,385.00**
Mean	**31.24**	**73.00**	**749.13**	**5.80**	**186.88**	**616.65**	**1,027.75**

MARCH

LOCATION 7

Times (hr.)	Temperature (°C)	Humidity (%)	Pressure (mmHg)	Wind Speed (km/h)	Wind Direction (o)	Solar radiation (W/m2)	Ultra-violet radiation (μW/m2)
9am	28.30	85.00	749.90	2.50	225.00	300.12	433.00
10am	28.90	84.00	748.40	4.60	50.00	405.05	702.00
11am	30.40	80.00	748.50	5.70	268.00	485.50	1,102.00
12am	34.10	63.00	747.00	3.50	185.00	1,875.25	1,868.00
1pm	33.90	61.00	748.60	9.60	215.00	1,665.20	1,542.00
2pm	32.80	70.00	748.10	4.40	15.00	591.65	1,385.00
3pm	31.10	75.00	748.10	5.50	195.00	471.15	1,325.00
4pm	30.20	74.00	748.20	5.90	265.00	410.78	775.00
Min	**28.30**	**61.00**	**747.00**	**2.50**	**15.00**	**300.12**	**433.00**
Max	**34.10**	**85.00**	**749.90**	**9.60**	**268.00**	**1,665.20**	**1,868.00**
Mean	**31.21**	**74.00**	**748.35**	**5.21**	**177.25**	**775.59**	**1,141.50**

MARCH

LOCATION 8

Times (hr.)	Temperature (°C)	Humidity (%)	Pressure (mmHg)	Wind Speed (km/h)	Wind Direction (o)	Solar radiation (W/m2)	Ultra-violet radiation (μW/m2)
9am	28.30	81.00	750.10	6.20	95.00	395.15	385.00
10am	28.90	83.00	749.20	4.50	295.00	515.01	701.00
11am	30.80	73.00	749.00	3.20	186.00	695.55	1,202.00
12am	33.70	61.00	747.70	5.80	105.00	1,175.85	1,518.00
1pm	33.80	56.00	747.50	5.90	110.00	1,265.20	1,652.00
2pm	32.80	68.00	748.30	6.50	205.00	880.15	1,185.00
3pm	32.00	70.00	749.10	6.80	320.00	751.25	1,055.00
4pm	30.80	75.00	749.70	5.20	225.00	450.28	795.00
Min	**28.30**	**56.00**	**747.50**	**3.20**	**95.00**	**395.15**	**385.00**
Max	**33.80**	**81.00**	**750.10**	**6.80**	**320.00**	**1,265.20**	**1,652.00**
Mean	**31.42**	**70.88**	**748.83**	**5.51**	**192.63**	**766.06**	**1,061.63**

APRIL

Location9

Times (hr.)	Temperature (°C)	Humidity (%)	Pressure (mmHg)	Wind Speed (km/h)	Wind Direction (o)	Solar radiation (W/m2)	Ultra-violet radiation (µW/m2)
9am	27.85	85	749.5	5.2	330	290.81	316
10am	28.7	83	749.5	5.8	195	415.05	611
11am	30.15	81	748	4.5	176	605.95	1202
12am	34.15	56	747.1	7.2	130	995.95	1758
1pm	33.65	58	747.2	9.8	55	865.55	1350
2pm	33.52	64	747.2	5.9	205	755.25	1105
3pm	32.95	70	748.1	6.8	105	551.45	1125
4pm	31.85	74	748.8	4.1	205	210.28	675
Min	**27.85**	**56**	**747.1**	**4.1**	**55**	**210.28**	**316**
Max	**34.15**	**85**	**749.5**	**9.8**	**330**	**995.95**	**1758**
Mean	**31.60875**	**71.375**	**748.175**	**6.1625**	**175.125**	**586.2863**	**1017.75**

APRIL

location 10

Times (hr.)	Temperature (°C)	Humidity (%)	Pressure (mmHg)	Wind Speed (km/h)	Wind Direction (o)	Solar radiation (W/m2)	Ultra-violet radiation (μW/m2)
9am	26.9	86	749.1	2.2	95	390.15	380
10am	28.9	81	749.1	5.7	190	595.25	721
11am	31.8	75	748.3	7	180	885.65	1301
12am	33.8	56	747.5	6.1	130	1375.15	1628
1pm	34.7	52	747.1	5.5	290	1565.2	1762
2pm	33.9	61	747.4	4.5	277	750.25	1525
3pm	33.5	65	748.2	6.5	35	451.25	1205
4pm	32.2	72	748.3	4	160	350.25	855
Min	**26.9**	**52**	**747.1**	**2.2**	**95**	**350.25**	**380**
Max	**34.7**	**86**	**749.1**	**7**	**190**	**1565.2**	**1762**
Mean	**32.00375**	**67.875**	**748.125**	**5.1875**	**181.5**	**795.3938**	**1172.125**

APRIL

LOCATION 11

Times (hr.)	Temperature (°C)	Humidity (%)	Pressure (mmHg)	Wind Speed (km/h)	Wind Direction (o)	Solar radiation (W/m2)	Ultra-violet radiation (μW/m2)
9am	27.9	80	749.1	4	280	380.62	595
10am	29.6	79	748.1	5.9	250	655.16	795
11am	32.9	72	747.9	6.1	268	515.15	1208
12am	35.5	51	746.5	3.5	185	1885.55	1668
1pm	34.9	52	747.6	5.1	215	1795.12	1649
2pm	32.6	69	748.1	4.7	215	541.95	1485
3pm	31.5	73	748.6	5.7	295	479.25	1385
4pm	31.2	74	748.9	4.9	65	440.56	795
Min	**27.9**	**51**	**746.5**	**3.5**	**65**	**380.62**	**595**
Max	**35.5**	**80**	**749.1**	**6.1**	**280**	**1885.55**	**1668**
Mean	**32.0125**	**69.125**	**748.1**	**4.9875**	**221.625**	**836.67**	**1197.5**

APRIL

LOCATION 12

Times (hr.)	Temperature (°C)	Humidity (%)	Pressure (mmHg)	Wind Speed (km/h)	Wind Direction (o)	Solar radiation (W/m2)	Ultra-violet radiation (µW/m2)
9am	28.9	79	749	6.8	195	405.55	397
10am	29.4	76	748.5	5.5	25	715.21	791
11am	31.9	72	748	1.2	286	605.55	1302
12am	34.1	60	747.3	5.8	125	1575.15	1628
1pm	34.8	56	747.1	5.2	210	1765.2	1872
2pm	33.9	61	748.3	6.5	205	890.65	1385
3pm	32.2	70	748.7	6.8	320	750.15	1055
4pm	30.9	75	749.7	5.8	225	440.28	805
Min	**28.9**	**56**	**747.1**	**1.2**	**25**	**405.55**	**397**
Max	**34.8**	**79**	**749.7**	**6.8**	**320**	**1765.2**	**1872**
Mean	**32.0125**	**68.625**	**748.325**	**5.45**	**198.875**	**893.4675**	**1154.375**

MAY

LOCATION 14

Times (hr.)	Temperature (°C)	Humidity (%)	Pressure (mmHg)	Wind Speed (km/h)	Wind Direction (o)	Solar radiation (W/m2)	Ultra-violet radiation (μW/m2)
9am	27.90	83.00	751.70	4.20	210.00	350.64	275.00
10am	27.90	82.00	750.90	9.20	150.00	455.58	311.00
11am	28.90	76.00	750.10	7.60	186.00	685.65	902.00
12am	32.30	65.00	748.50	6.50	135.00	815.25	1,228.00
1pm	32.70	64.00	748.10	5.50	90.00	965.20	1,392.00
2pm	31.70	69.00	749.50	7.50	77.00	450.25	1,005.00
3pm	31.50	71.00	750.10	6.50	130.00	351.15	965.00
4pm	30.20	76.00	750.20	1.50	260.00	250.28	655.00
Min	**27.90**	**64.00**	**748.10**	**1.50**	**77.00**	**250.28**	**275.00**
Max	**32.70**	**83.00**	**751.70**	**9.20**	**260.00**	**965.20**	**1,392.00**
Mean	**30.37**	**73.25**	**749.89**	**6.06**	**154.75**	**540.50**	**841.63**

MAY

LOCATION 13

Times (hr.)	Temperature (°C)	Humidity (%)	Pressure (mmHg)	Wind Speed (km/h)	Wind Direction (o)	Solar radiation (W/m2)	Ultra-violet radiation (μW/m2)
9am	25.90	87.00	751.90	4.50	230.00	260.45	266.00
10am	26.90	85.00	750.50	5.60	295.00	365.03	371.00
11am	28.70	80.00	750.10	5.80	96.00	395.95	985.00
12am	33.20	65.00	748.50	6.90	30.00	575.85	1,258.00
1pm	32.60	67.00	750.80	5.50	250.00	505.95	1,152.00
2pm	31.60	72.00	750.10	5.40	277.00	455.15	885.00
3pm	31.20	75.00	750.10	5.30	301.00	301.45	1,025.00
4pm	30.10	77.00	750.20	4.80	267.00	200.78	625.00
Min	**25.90**	**65.00**	**748.50**	**4.50**	**30.00**	**200.78**	**266.00**
Max	**33.20**	**87.00**	**751.90**	**6.90**	**301.00**	**575.85**	**1,258.00**
Mean	**30.03**	**76.00**	**750.28**	**5.48**	**218.25**	**382.58**	**820.88**

MAY

LOCATION 15

Times (hr.)	Temperature (°C)	Humidity (%)	Pressure (mmHg)	Wind Speed (km/h)	Wind Direction (o)	Solar radiation (W/m2)	Ultra-violet radiation (µW/m2)
9am	27.20	86.00	750.80	6.10	152.00	280.82	332.00
10am	28.10	83.00	749.60	5.60	85.00	305.10	572.00
11am	29.10	77.00	748.00	5.80	116.00	385.50	702.00
12am	32.90	62.00	747.90	6.80	215.00	1,275.15	1,258.00
1pm	31.60	68.00	748.20	6.60	262.00	1,165.25	1,142.00
2pm	31.50	71.00	748.80	4.40	111.00	551.58	1,085.00
3pm	30.70	74.00	749.30	5.80	95.00	389.45	625.00
4pm	30.50	76.00	749.40	6.90	260.00	150.58	425.00
Min	**27.20**	**62.00**	**747.90**	**4.40**	**85.00**	**150.58**	**332.00**
Max	**32.90**	**88.00**	**750.80**	**6.90**	**260.00**	**1,275.15**	**1,258.00**
Mean	**30.20**	**74.88**	**749.00**	**6.00**	**162.00**	**562.93**	**767.75**

MAY

LOCATION 16

Times (hr.)	Temperature (°C)	Humidity (%)	Pressure (mmHg)	Wind Speed (km/h)	Wind Direction (o)	Solar radiation (W/m2)	Ultra-violet radiation (µW/m2)
9am	26.30	87.00	750.50	5.90	345.00	290.15	275.00
10am	27.30	83.00	750.20	4.20	195.00	485.08	681.00
11am	30.20	75.00	750.10	3.20	186.00	695.55	902.00
12am	31.10	62.00	749.10	4.50	305.00	975.15	1,198.00
1pm	32.40	54.00	747.80	5.70	190.00	1,165.20	1,352.00
2pm	31.40	69.00	748.50	6.20	97.00	850.25	1,085.00
3pm	30.10	71.00	750.10	5.80	120.00	351.15	455.00
4pm	29.50	76.00	750.70	5.80	165.00	250.28	255.00
Min	**26.30**	**54.00**	**747.80**	**3.20**	**97.00**	**250.28**	**255.00**
Max	**32.40**	**87.00**	**750.70**	**6.20**	**345.00**	**1,165.20**	**1,352.00**
Mean	**29.79**	**72.13**	**749.73**	**5.16**	**200.38**	**620.35**	**775.38**

JUNE

LOCATION 17

Times (hr.)	Temperature (°C)	Humidity (%)	Pressure (mmHg)	Wind Speed (km/h)	Wind Direction (o)	Solar radiation (W/m2)	Ultra-violet radiation (µW/m2)
9am	24.20	89.00	753.90	9.50	330.00	158.15	166.00
10am	26.80	85.00	752.50	5.60	205.00	165.05	375.00
11am	27.10	83.00	751.10	7.80	96.00	345.95	785.00
12am	31.30	69.00	750.50	6.90	30.00	705.85	958.00
1pm	32.60	67.00	749.80	6.50	250.00	935.95	1,152.00
2pm	31.50	72.00	750.10	5.40	277.00	455.15	885.00
3pm	31.20	75.00	750.10	2.30	301.00	301.45	825.00
4pm	30.10	77.00	750.20	4.80	267.00	200.78	625.00
Min	**24.20**	**67.00**	**749.80**	**2.30**	**30.00**	**200.15**	**166.00**
Max	**32.60**	**89.00**	**753.90**	**9.50**	**330.00**	**965.95**	**1,152.00**
Mean	**29.35**	**77.13**	**751.03**	**6.10**	**219.50**	**408.54**	**721.38**

JUNE

LOCATION 18

Times (hr.)	Temperature (°C)	Humidity (%)	Pressure (mmHg)	Wind Speed (km/h)	Wind Direction (o)	Solar radiation (W/m2)	Ultra-violet radiation (µW/m2)
9am	26.10	88.00	752.90	8.20	105.00	345.55	205.00
10am	27.20	86.00	751.70	6.50	155.00	455.58	301.00
11am	28.60	75.00	751.30	7.60	18.00	685.05	805.00
12am	32.10	66.00	750.50	6.50	135.00	815.15	798.00
1pm	32.60	64.00	750.10	9.50	90.00	1,095.20	1,055.00
2pm	31.60	69.00	750.20	7.50	75.00	690.55	985.00
3pm	30.50	71.00	751.10	6.50	130.00	351.15	585.00
4pm	30.20	76.00	751.20	5.50	225.00	250.28	555.00
Min	**26.10**	**64.00**	**750.10**	**5.50**	**18.00**	**250.28**	**205.00**
Max	**32.60**	**88.00**	**752.90**	**9.50**	**225.00**	**1,095.20**	**1,055.00**
Mean	**29.86**	**74.38**	**751.13**	**7.23**	**116.63**	**586.06**	**661.13**

JUNE

LOCATION 19

Times (hr.)	Temperature (°C)	Humidity (%)	Pressure (mmHg)	Wind Speed (km/h)	Wind Direction (o)	Solar radiation (W/m2)	Ultra-violet radiation (µW/m2)
9am	27.10	86.00	752.60	6.10	352.00	370.82	293.00
10am	28.10	84.00	751.10	9.60	185.00	405.10	572.00
11am	28.70	75.00	751.10	5.80	116.00	475.50	702.00
12am	32.90	60.00	749.10	7.80	215.00	1,305.25	1,250.00
1pm	32.60	68.00	749.20	6.60	262.00	1,115.25	1,100.00
2pm	31.50	71.00	749.90	4.40	165.00	671.55	785.00
3pm	30.70	72.00	751.00	10.80	195.00	379.45	525.00
4pm	29.50	76.00	751.30	6.90	265.00	150.58	320.00
Min	**27.10**	**60.00**	**749.10**	**4.40**	**116.00**	**150.58**	**293.00**
Max	**32.90**	**86.00**	**752.60**	**10.80**	**352.00**	**1,365.25**	**1,250.00**
Mean	**30.14**	**74.00**	**750.66**	**7.25**	**219.38**	**609.19**	**693.38**

JUNE

LOCATION 20

Times (hr.)	Temperature (°C)	Humidity (%)	Pressure (mmHg)	Wind Speed (km/h)	Wind Direction (o)	Solar radiation (W/m2)	Ultra-violet radiation (μW/m2)
9am	26.20	85.00	752.10	5.90	145.00	290.15	275.00
10am	27.20	83.00	751.95	7.50	195.00	485.08	681.00
11am	30.20	75.00	750.90	3.20	346.00	695.55	902.00
12am	32.90	60.00	748.50	4.50	305.00	965.55	998.00
1pm	31.40	63.00	750.10	5.70	190.00	605.25	452.00
2pm	31.40	69.00	749.50	6.20	195.00	580.15	385.00
3pm	30.80	78.00	750.10	10.80	120.00	351.15	285.00
4pm	30.00	80.00	750.70	5.80	165.00	150.28	255.00
Min	**26.20**	**60.00**	**748.50**	**3.20**	**120.00**	**150.28**	**255.00**
Max	**32.90**	**85.00**	**752.10**	**10.80**	**346.00**	**965.55**	**998.00**
Mean	**30.01**	**74.13**	**750.48**	**6.20**	**207.63**	**515.40**	**529.13**