



Review

An Overview: Polycyclic Aromatic Hydrocarbon Emissions from the Stationary and Mobile Sources and in the Ambient Air

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ABSTRACT

Polycyclic aromatic hydrocarbons are a class of semi-volatile organic carbons that are emitted from both natural and anthropogenic sources therefore are ubiquitous in nature. Their main sources are both fossil and biomass fuels as well as other feedstocks used in chemical and combustion processes. Mostly the combustion processes are PAH depletion processes rather than PAH generating processes. PAHs are emitted from both stationary and mobile sources at varying levels depending on the operation conditions such as fuels, feedstock, and control devices in use as well as process parameters for example combustion temperatures.

After emission from sources, the fates of PAHs in the atmosphere include partitioning between gas and particulate phases, particle size distribution, long range transport, dry and wet deposition on to water bodies, soil, vegetation and other receptor surfaces as well as resuspension from receptor surfaces back to the atmosphere. These processes are controlled by their physiochemical properties. Additionally, it is through these processes that human beings are exposed to PAHs via inhalation, ingestion and dermal contact.

Dry deposition is the major process through which PAHs from the atmosphere are made available to receptor surfaces including the human respiratory system. From studies with cumulative fractions of dry deposition and size distribution for particulate PAHs, it is evident that the coarse particles are majorly responsible for the highest fraction of deposition fluxes. This is especially true for the high molecular weight PAHs, since the low molecular weight PAHs are majorly in the gas phase, which have lower dry deposition velocities. On the other hand, the highest risk for human being comes in the form of fine particles, whose mean aerodynamic diameter is below 2.5 μm . This is because the particle bound content results and particle size distributions of PAHs indicate that the fine particles have the most PAH content owing to their large surface areas and high organic carbon content. For the wet deposition of PAHs, more research is recommended for measurement of scavenging ratios of individual PAHs, since there is a scarcity of studies focusing on this issue.

PAH mutagenic activity and exposure risk of humans can be estimated using the deposition rates, toxicity levels based on benzo(a)pyrene, or biomarkers such as urinary 1-hydroxypyrene. Other parameters that have been used to evaluate the risks of various exposure groups include inhalation exposure levels (IEL), incremental lifetime cancer risk (ILCR), and estimation of maximum consumption time (t_{max}). Highway toll workers, back carbon workers and food vendors in night markets are among susceptible groups identified using these biomarkers and exposure parameters.

To reduce exposure to human beings, PAH emissions need to be controlled at the sources. Control and reduction of PAH emissions from various sources involves largely altering the fuel and feedstock characteristics, using air pollution control devices and/or adjusting the operating parameter's such as temperatures and air-fuel ratios or turbulence in combustion processes.

Unfortunately, albeit all the studies done on PAHs, they still remain a concern in our environment and more attention and research should be dedicated to this group of compounds.

Keywords: PAHs; Emission sources; Atmospheric deposition; Particle size distribution; Artifacts; Biomarkers; Cancer risk.

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INTRODUCTION

Overview

One class of semi volatile organic compounds (SVOCs) that has received immense attention among the scientific community due to its ubiquitous nature in the environment is the polycyclic aromatic hydrocarbons (PAHs) (Skupinska *et al.*, 2004). They are also known as polyarenes or polynuclear aromatic hydrocarbons (Amodu *et al.*, 2013). These compounds majorly exist in the fossil fuels such as coal and crude oil. Additionally, the PAHs are found in the gasoline, diesel, heavy fuel oil and asphalt obtained from crude oil via petro refinery processes. Due to the survival mechanism, the PAHs in the fuels are not destroyed during the combustion process and they exist in the stack flue gas or engine exhaust (Li *et al.*, 1995; Mi *et al.*, 1998; Mi *et al.*, 2000; Lee *et al.*, 2011). Emission of PAHs is majorly due to unburnt PAHs present in the fossil fuels and depends on the aromatic content in the fuel especially fossil fuels and additives (Mi *et al.*, 1998; Mi *et al.*, 2000; Lin *et al.*, 2006a; Lee *et al.*, 2011). There exists a direct correlation between the PAH content in the fuel and PAH emission and formation from the exhaust streams (Mi *et al.*, 2000; Lin *et al.*, 2008b; Lee *et al.*, 2011). Another mechanism of PAH emission is the formation as products of incomplete combustion (PICs) of both biomass and fossil fuels that contain carbon and hydrogen (Khalili *et al.*, 1995; Wang *et al.*, 2009) during incineration, industrial production, transportation activities (Yang *et al.*, 2002) principally due to existence of cold spots and inefficient air/fuel mixing (Zevenhoven and Kilpinen, 2001). Generally, PAHs usually exist as complex mixture of various individual compounds (Guo *et al.*, 2011).

PAHs belong to larger group of aromatic carbons consisting of 2 to 13 cyclic rings that are fused together (Skupinska *et al.*, 2004; Lee and Dong, 2010). According to Wang *et al.* (2015) the arrangement of fused rings is usually linear, angular or clustered. Table 1 shows the commonly studied 21 PAHs with their IUPAC names/common names, chemical formulas, molecular weights, number of rings as well as the chemical structure. The PAHs with 2 to 3 fused benzene rings are classified as low molecular weight PAHs (LMW-PAHs), while the 4 ringed PAHs are classified as middle molecular weight (MMW-PAHs) and the rest (5 to 7 rings) are classified as higher molecular weight PAHs (HMW-PAHs) (Lee *et al.*, 2002; Amodu *et al.*, 2013). They may have equal numbers of rings, but the configurations and arrangements of the rings bring about differences in properties such as chemical and physical properties (Skupinska *et al.*, 2004).

Table 1. Molecular structure and chemical formula of priority toxic 21 PAHs (sourced: (Henner *et al.*, 1997; IARC, 2010)).

Compound	Abbreviation	Chemical Formula	Molecular Weight	No of Rings	Chemical Structure	Carcinogenicity *a
Naphthalene	Nap	C ₁₀ H ₈	128	2		NC
Acenaphthylene	AcPy	C ₁₂ H ₈	152	3		NC
Acenaphthene	Acp	C ₁₂ H ₁₀	154	3		NC
Fluorene	Flu	C ₁₃ H ₁₀	165	4		NC
Phenanthrene	PA	C ₁₄ H ₁₀	178	3		NC
Anthracene	Ant	C ₁₄ H ₁₀	178	3		NC
Fluoranthene	FL	C ₁₆ H ₁₀	202	4		NC
Pyrene	Pyr	C ₁₆ H ₁₀	202	4		NC
Cyclopenta[c,d]pyrene	CYC	C ₁₈ H ₁₂	228	5		
Benz[a]anthracene	BaA	C ₁₈ H ₁₂	228	4		SC
Chrysene	CHR	C ₁₈ H ₁₂	228	4		
Benzo[b]fluoranthene	BbF	C ₂₀ H ₁₂	252	5		C
Benzo[k]fluoranthene	BkF	C ₂₀ H ₁₂	252	5		
Benz[e]pyrene	BeP	C ₂₀ H ₁₂	252	5		
Benzo[a]pyrene	BaP	C ₂₀ H ₁₂	252	5		SC
Perylene	PER	C ₂₀ H ₁₂	252	5		NC
Indeno[1,2,3-cd]pyrene	IND	C ₂₂ H ₁₂	276	6		C
Dibenzo[a,h]anthracene	DBA	C ₂₂ H ₁₄	278	5		C
Benzo[b]chrycene	BbC	C ₂₂ H ₁₄	278	5		
Benzo[ghi]perylene	BghiP	C ₂₂ H ₁₂	276	6		NC
Coronene	COR	C ₂₄ H ₁₂	300	7		NC

*a – sourced from <http://www.env.gov.bc.ca/wat/wq/BCguidelines/pahs/pahs-01.htm> where NC = non-carcinogenic; WC = weakly carcinogenic; C = carcinogenic; SC = strongly carcinogenic.

Properties of PAHs

The physicochemical properties are also important as they indicate the bioavailability of PAHs in the environment in addition to determining the fate and effects in the environmental matrices in terms of risk assessment (De Maagd *et al.*, 1998; Dimitriou-Christidis, 2006). As mentioned before, PAHs are large group of compounds with many possible different structures and a wide range of physical and chemical properties, which may vary by several orders of magnitude (Mackay and Calcott, 1998; Dimitriou-Christidis, 2006). Some physicochemical properties of PAHs are tabulated in Table 2. PAHs are SVOCs with low volatility which is attributed to their chemical structure and number of aromatic rings (Dimitriou-Christidis, 2006). According to Skupinska *et al.* (2004), PAHs are solids with high melting points and boiling points in addition to being thermodynamically and chemically stable (Dimitriou-Christidis, 2006). The color of PAHs ranges from colorless to white to pale yellow (Haritash and Kaushik, 2009). There are hydrophobic hence highly lipophilic, therefore they are highly soluble in organic solvents (Henner *et al.*, 1997) and easily adsorbed onto solid phases (Dimitriou-Christidis, 2006). On the other hand, their solubility in water is low and decreases with an increase in molecular weights (Skupinska *et al.*, 2004). The lipophilicity nature of PAHs makes them easy to be attached to soils with high organic content (Amodu *et al.*, 2013; Włóka *et al.*, 2014). In the atmosphere and environment in general, the PAHs are destroyed via photochemical process under strong ultra violet light and sunlight (Lee and Dong, 2010).

PAHS SAMPLING, ANALYSIS AND QUALITY ASSURANCE AND CONTROL

Determination of PAH levels in the environment involves sampling and collection, then extraction from collection

equipment, which is followed by cleanup and analysis. Most studies reviewed in this study use the Modified Method 5 (MM5; Code of Federal Regulation, Title 40, Part 60, US EPA, 1996) that was developed by Graseby for sampling semi-volatile organics (Lee *et al.*, 2002; Chen *et al.*, 2003a, b; Park *et al.*, 2009). The various processes are described in detail in the subsequent parts.

Sampling of PAHs

Collection of PAH samples from stacks of stationary sources requires sampling equipment for both gaseous and particulate phases. Mostly the low molecular PAHs, that exist in the gaseous phase, are sampled using adsorbents such as XAD resins and polyurethane foams, while the filters are used to capture the heavy molecular PAHs attached to particles (IARC, 2010). Some of the filters used to collect the particulate phases include glass fiber filters, quartz fiber filters, cellulose filters or Teflon filters (Pandey *et al.*, 2011). PAHs are semi volatile and are mostly partitioned between particle and gas phases. In both the stacks and ambient air the PAH sampling train includes a PS-1 sampler equipped with glass cartridges containing mixed sorbents (Pandey *et al.*, 2011) mostly XAD resin sandwiched between two polyurethane foam (PUF) plugs. The cartridges usually collect the gaseous PAHs, while the particulate PAHs are collected using glass fiber filters, which are weighed prior and after sampling to determine the particulate weight.

Additionally, the filters and the cartridges are pre-cleaned and pre dried and wrapped with aluminum foil before sampling to minimize any interferences and contamination. This process involves using distilled water, methanol, dichloromethane and a mixture of acetone plus normal hexane.

The cartridges are placed in a sampling system composed of a pump, and a recorder whereby sufficient amount of flue gas is drawn through the filters and cartridges allowing

Table 2. Physico-Chemical properties of priority 16 PAHs (sourced from: (Lee and Dong, 2010; Skupinska *et al.*, 2004)).

Compound	Melting point (°C)	Boiling point (°C)	Vapor Pressure Pa (25°C)	Log K _{OW} (n-octanol/water partition coefficient)	Water Solubility μg L ⁻¹ (25°C)	Henry's Constant Kpa m ³ mol ⁻¹ (25°C)
Naphthalene	81	217.9	1.4	3.4	3.17 × 10 ⁴	4.89 × 10 ⁻²
Acenaphthylene	92–93	265–275	8.8 × 10 ⁻¹	4.07	–	1.14 × 10 ⁻³
Acenaphthene	85	279	2.9 × 10 ⁻¹	3.92	3.93 × 10 ³	1.48 × 10 ⁻²
Fluorene	115–116	293–295	8 × 10 ⁻²	4.18	1.98 × 10 ³	1.01 × 10 ⁻²
Phenanthrene	216.4	342	1.6 × 10 ⁻²	4.6	1.29 × 10 ³	3.98 × 10 ⁻³
Anthracene	100.5	340	8 × 10 ⁻⁴	4.5	73	7.3 × 10 ⁻³
Fluoranthene	108.8	375	1.2 × 10 ⁻³	5.22	260	6.5 × 10 ⁻⁴
Pyrene	150.4	393	6 × 10 ⁻⁴	5.18	135	1.1 × 10 ⁻³
Benz[a]anthracene	160.7	400	2.8 × 10 ⁻⁵	5.16	14	–
Chrysene	253.8	448	8.4 × 10 ⁻⁵	5.91	2	–
Benzo[b]fluoranthene	168.3	481	6.7 × 10 ⁻⁵	6.12	1.2	5.1 × 10 ⁻⁵
Benzo[k]fluoranthene	215.7	280	1.3 × 10 ⁻⁵	6.84	2.5	4.4 × 10 ⁻⁵
Benzo[a]pyrene	178.1	496	7.3 × 10 ⁻⁷	6.5	3.8	3.4 × 10 ⁻⁵
Indeno[1,2,3-cd]pyrene	266.6	524	1.3 × 10 ⁻⁸	6.58	62	2.9 × 10 ⁻⁵
Dibenzo[a,h]anthracene	278.3	545	1.3 × 10 ⁻⁸	6.5	0.5 (27°C)	7 × 10 ⁻⁶
Benzo[ghi]perylene	163.6	536	1.4 × 10 ⁻⁸	7.1	0.26	2.7 × 10 ⁻⁵

the filters to capture the particle-adsorbed PAHs, while the resin and PUF in the cartridges adsorb the gaseous PAHs. The recorder measures the volume of air passing through the sampling system. Prior to weighing, the filters are placed in dehumidifiers or desiccators for some period usually 24 hrs to attain temperature and humidity equilibrium.

Analysis of PAHs

Mostly the PAHs analyzed are the 16 priority PAHs identified by the US EPA (IARC, 2010). The analysis of PAHs include extraction from filters and adsorbents used in sample collection followed by clean up and concentration processes. Then they are quantified using liquid chromatography, gas chromatography (GC) or high performance liquid chromatography (HPLC), which are usually coupled with mass spectroscopy (IARC, 2010). Prior to the actual analytical process, a preliminary analysis is important to ensure that the samples are within the calibration range of the quantification instrument (Ravindra *et al.*, 2008).

For extraction process, the method choices include conventional solvent extraction under reflux, Soxhlet extraction, microwave extraction, accelerated extraction and ultrasonic extraction (Pandey *et al.*, 2011). The most common method is the Soxhlet extraction, where the cartridges and filters are placed in a Soxhlet extractor with a mixture of n-hexane and dichloromethane in a 1:1 v/v ratio. The extraction process takes about 24 hours. Following the extraction process is the concentration process, whereby the extract is purged to about 2 mL using pure nitrogen then undergoes cleanup process. On the other hand, extraction under reflux utilizes toluene, microwave extraction uses hexane:acetone (1:1), while accelerated extraction makes uses of toluene, dichloromethane or a 1:1 mixture of hexane:dichloromethane and ultrasonic extraction uses toluene and dichloromethane as the solvents (Pandey *et al.*, 2011). Additionally, thermal desorption and other solvent free techniques have previously been considered (Pandey *et al.*, 2011).

The cleanup process involves removal of pollutants, which might co-elute with PAHs. About 15–17 grams of deactivated silica are placed in the cleanup column with glass wool placed at the bottom to hold it in place. Usually the silica is wet using deionized water then topped up with a few grams of anhydrous sodium sulfate. The elution solvent in this case is hexane. The eluate is then concentrated using nitrogen.

Determination and Quantification of PAHs

Various methods can be used for quantification of PAHs in different matrices. Some of these quantification methods include: thin layer chromatography (TLC), gel permeation chromatography (GPC), gas chromatography (GC), gas chromatography coupled with mass spectrometry (GC/MS), liquid chromatography (LC) or high performance liquid chromatography (HPLC). Detectors used with these methods include fluorescence, ultra violet (UV), flame ionization detector (FID), or mass spectroscopy detectors (MSD) (Liu *et al.*, 2007a).

In most studies, PAHs are detected and quantified using gas chromatography coupled with mass spectrometer (GC/MS). Scan mode is employed to determine the primary

and secondary ions for PAHs, while the actual quantification is done using selective ion monitoring mode. The GC/MS is usually preferred over other quantification methods, because the interferences from co-eluting compounds are greatly minimized. Additionally, the selective ion monitoring mode offers discrete monitoring and lower detection limits compared to full scan modes (Poster *et al.*, 2006).

Generally, in most studies, only about 16 priority PAHs are considered. On the other hand, some studies also include an extra five (cyclopenta[c,d]pyrene, benzo[e]pyrene, perylene, benzo[b]chrysene, coronene) to make it a total of 21 criteria PAHs. The 21 PAHs considered are naphthalene (Nap), acenaphthylene (AcPy), acenaphthene (Acp), fluorene (Flu), phenanthrene (PA), anthracene (Ant), fluoranthene (FL), pyrene (Pyr), Cyclopenta[c,d]pyrene (CYC), Benz[a]anthracene (BaA), Chrysene (CHR), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[e]pyrene (BeP), benzo[a]pyrene (BaP), perylene (PER), indeno(1,2,3-cd)pyrene (IND), dibenzo(a,h)anthracene (DBA), benzo[b]chrysene, benzo(ghi)perylene (BghiP), and coronene (COR). The GC/MS is routinely calibrated using serially diluted standard solutions to determine the limits of detection as well as obtain the calibration line for the quantification of samples.

Of these 21 or 16 PAHs, seven of them including, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene and dibenzo[a,h]anthracene, are considered to be potential carcinogenic compounds (Table 2). These PAHs are considered more important because they are more harmful or pose high health risks, occur in high concentrations in the environment hence higher exposure risk and there is more information on them compared to the rest of the PAHs (Ravindra *et al.*, 2008).

Quality Control and Quality Assurance (QA/QC)

To minimize errors and maintain the credibility of the PAH analysis process, recovery efficiencies of all the PAHs considered in a study are done by using surrogate standards added to the samples, as well as evaluating the detection limits (DL). In essence, the recoveries show the efficiency of the extraction process, since it is paramount that all the PAHs sampled and collected in sampling exercise be accounted for (Guo *et al.*, 2011). Determination of limit of detection (LOD) is useful considering that the levels of PAHs in various matrices are present in low concentrations. LOD is basically the lowest concentration level that can be determined (by a single analysis and with a defined level of confidence) to be statistically different from a blank and is calculated as the standard deviation of blanks multiplied by three (See and Balasubramanian, 2008).

For the various matrices, the limit of quantification (LOQ) is also used, which is a measure of the concentration of an analyte in a particular matrix for which the probability of producing analytical values above the method detection limit is 99% (See and Balasubramanian, 2008). According to Sheu *et al.* (1996a) and Sheu *et al.* (1996c), the LOQ can be obtained by dividing the detection limit by the sampling volume of the PS-1 sampler in stacks or the

exposed time for deposition samplers.

The LOQ for the PS-1 and deposition plates samples can range between 10 to 221 pg m^{-3} and 46–339 $\text{pg m}^{-2} \text{day}^{-1}$, respectively, for individual PAHs (Sheu *et al.*, 1996a, c), while the corresponding detection limits range between 23 to 524 pg. On the other hand, the surrogate standards help to correct the losses that occur during extraction and preparation processes. In addition, limit of quantification which are detection limits divided by the sampling volumes, are also determined. Laboratory blanks and field blanks are considered to quantify and determine the interferences and contamination (Ruwei *et al.*, 2013).

The cartridges and especially the XAD-2 resin are tested for breakthrough by testing the rear end section of the XAD-2 resin for presence of PAHs. Absence or little amount of PAHs in this section signifies no breakthrough in the apparatus (Sheu *et al.*, 1996a). Also to avoid breakthrough two consecutive cartridges are used in sequence (Wang *et al.*, 2015).

PAH Sampling Artifacts

Artifacts from sampling and measurements of PAHs in the atmosphere can result in overestimation or underestimation of PAHs and are dependent on the sampling equipment, season, atmospheric conditions, carbon content of total suspended particles (TSP) and physiochemical properties of compounds (Coutant *et al.*, 1988). Earlier on Bidleman *et al.* (1986) pointed out that the ratio between vapor phase and particle phase (V/P) of SVOCs in the ambient air is very important in determining their transport, phase distribution and deposition from the atmosphere. Since PAHs partition between particle and gas phases, their respective phase estimation during atmospheric measurements are based on the ratio of adsorbent-retained and filter-retained proportions (A/F) in terms of ng m^{-3} . According to Bidleman *et al.* (1986), this strategy of estimating V/P using experimental A/F is uncertain because it may overestimate the gaseous phase due to blow off effect of PAHs from particulate surfaces or underestimate the gaseous phase fraction as a result of adsorption of gaseous phase PAHs on the collected particle surfaces or on the particulate filters (Oliveira *et al.*, 2011; Wu *et al.*, 2014). The above uncertainties of V/P are controlled primarily by temperature, carbon content of total suspended particles (TSP) and sampling flow rate such that when these conditions change the A/F ratio is affected. Additionally, losses from PAH degradation and volatilization might occur, thus affecting the results of the measurements (Venkataraman *et al.*, 1999; Liu *et al.*, 2006).

Other artifacts commonly encountered include low PUF results owing to breakthrough problems (Billings and Bidleman, 1983; Wu *et al.*, 2014) and presence of interferences in sampling adsorbents as a result of contamination due to poor clean up, storage and handling procedures of sampling equipment in addition to detection methods applied (Bidleman, 1985). Further observed artifacts occur due to application of different extracting solvents from those used during cleaning or occurrence of surface reactions and oxidation of XAD surfaces by atmospheric oxidants to produce pollutant like compounds (Bidleman, 1985;

Possanzini *et al.*, 2006). Additional errors in measurement arise from non-equilibrium state in the atmosphere and biases during chemical analysis and analytical procedures (Shimmo *et al.*, 2004).

SOURCES OF PAHS

As mentioned earlier, mostly PAHs are originally present in the fossil fuels and are mainly emitted from both anthropogenic activities (stationary or mobile) as well as the natural sources, into the atmosphere, where they get partitioned into particulate and gaseous phase then transported and deposited back to the water bodies, vegetation, animal bodies and soil as the ultimate sinks (Wang *et al.*, 2009; Lee and Dong, 2010; Guo *et al.*, 2011). The LMW-PAHs are mainly in the gaseous phase, while the HMW-PAHs are attached to the particles, on the other hand the MMW-PAHs are partitioned between both gaseous and particulate phases (Wang *et al.*, 2009).

Partitioning of PAHs between the gaseous and particulate phases depends on the liquid vapor pressure, temperatures and particulate parameters such as size, surface area and chemical composition (Liu *et al.*, 2007a). In the environment, a large fraction of the PAHs is found in the soils and sediments, which are the ultimate sinks, but they are also the most significant contaminants in marine environment as well as reaching the pristine areas like Arctic and Antarctica via long range transport (Yunker and Macdonald, 1995; Wang *et al.*, 2009). This results into soil and water contamination leading to bioaccumulation in the food and animal tissues (Włóka *et al.*, 2014). Additionally, in the soils, PAHs may be introduced via sewage fertilizers (Oleszczuk, 2007). Other exposure sources for PAHs include tobacco smoking, indoor dusts, and indoor products such as air conditioning filters, printing machines, and pharmaceuticals (IARC, 2010; Chou *et al.*, 2015).

Natural sources include volcanoes, oil seeps, bitumen, wild forest fires, while anthropogenic sources are majorly combustion processes (Zhao *et al.*, 2008) especially those utilizing bio and waste fuels and fossil fuels such as coal, oil, shale oil and fracking, tars, residual heavy oil, used lubricating oil, peat and wood, which is treated with creosote as a preservative (Neilson and Hutzinger, 1998; Lundstedt *et al.*, 2007) and biomass (Yunker and Macdonald, 1995; Chuesaard *et al.*, 2014) as well as opening burning of solid wastes (Park *et al.*, 2013). The major sources include transport, chemical manufacturing and heat generation processes. Dai *et al.* (2008) also identifies oils spill, domestic and industrial waste water as sources of PAHs.

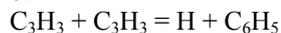
Formation Mechanism of PAHs

In combustion and chemical processes, PAHs are mostly present in the fuels and the feedstocks. Besides this, PAHs can be formed at the right conditions from chemical reactions of some hydrocarbons that act as precursors. The formation mechanisms of PAHs from these sources are complex and include precursors based homogeneous phase reactions supported by radicals and stable compounds such as single ring aromatics.

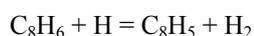
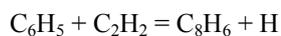
Cherchneff *et al.* (1992) in their study presents an overview scheme of ring closure, which includes combination of acetylene and 1-buten-3-ynyl radical to or combination of two propargyl radicals to form a phenyl ring as below:



or

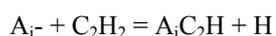


After ring closure the second ring closure is formed by reaction of phenyl with an acetylene molecule to form phenylacetylene, which reacts loses one hydrogen radical to form an aryl. The aryl radical reacts with an additional acetylene molecule to form naphthyl free radical.

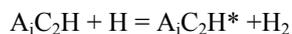


Additional growth of aromatic follows a similar mechanism, which can be summarized as follows:

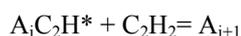
(a) addition of acetylene to an aromatic radical



(b) abstraction of hydrogen to make the stable aromatic molecule reactive



(c) addition of another acetylene group to close the ring



PAH Emissions from Stationary Sources

Different combustion sources emit varying levels of PAHs. For example, Kong *et al.* (2011) reports total-PAHs content in the ashes analyzed for coke production plant, coal fired power plant, heating station and iron smelting plant to be about 3090, 709, 620, and 290 $\mu\text{g g}^{-1}$, respectively. The following sections discuss the PAHs emissions from various sources in depth.

Formation of PAHs in stationary sources occurs mainly via pyrolysis and pyrosynthesis under oxygen deficient conditions (Ravindra *et al.*, 2008). Formation of PAHs depends on the fuel and feed composition in terms of carbon/hydrogen ratios and also the presence of PAHs in the fuel or process feedstock (Dyke, 2002). In addition to the fuel and feedstock, other factors that affect the formation of PAHs in combustion sources are the operation conditions such as temperatures, residence time, turbulence and air fuel ratios as well as the mode of feed introduction. The common three formation mechanisms of PAH formation include *de novo* synthesis of rings from chain of carbons, ring reformation via fragmentation and precursor pathways at temperature of 700°C and release and survival of PAHs present in fuels and feed materials (Dyke, 2002).

PAH Emissions from Boilers

Boilers mostly use petroleum derived heavy fuel for operation. Formation of PAHs from boilers emanates from incomplete combustion as well as the aromatic content in the heavy fuel oil. Lin *et al.* (2011b) reported emission of 434 $\mu\text{g Nm}^{-3}$ and 5.82 $\mu\text{g Nm}^{-3}$ from a 10 ton boiler operated by heavy fuel oil in terms of total-PAHs and total BaP_{eq} for 21 priority PAHs. In the same study, reductions in PAHs emissions were achieved by operating the same boiler with emulsified heavy fuel oil. The resulting emissions were 270 and 2.22 $\mu\text{g Nm}^{-3}$ for total-PAHs and total-BaP_{eq}, respectively, accounting for 38% and 62% reductions.

Similarly, different fuels used in boilers will result in varying emission factors. Li *et al.* (1999) reported total PAH emission factors to be 13300, 2920, 2880 and 208 $\mu\text{g total-PAHs kg-fuel}^{-1}$ for heavy fuel, diesel, co-combustion with heavy oil and natural gas, and co-combustion with coke oven gas and blast furnace gas, respectively.

In addition to different types of fuels used, combustion conditions and operating conditions are key factors affecting the emission levels of PAHs from boilers (Pongpiachan, 2014).

To reduce PAHs from boilers, Pongpiachan (2014) suggested optimization of fuel feeding loads, which are positively-correlated with PAH emissions. In addition, use of green fuel such as biodiesel instead of petroleum derived fuels and operating at full flame modes in place of “slumber” were also proposed as measures to reduce PAH emissions from boilers.

In another study, Chen and Lee (2007) pointed out that apart from using air pollution control devices to reduce pollutants, the use of alternative fuels and changing fuel characteristics is much novel way of controlling pollutants from boilers. Chen and Lee (2007) reported 38% and 30% reductions in total PAHs emission from a boiler by using oily waste water emulsified and water-emulsified heavy fuel oil compared to neat heavy fuel oil. The reductions were attributed to micro-explosion phenomena and dilution effect, which is achieved by water-oil emulsions.

PAH Emissions from Incinerators

PAH emissions from the incinerators depend mainly on the waste feed and also the operating conditions including turbulence, temperatures and residence times (Li *et al.*, 1995; Wheatley and Sadhra, 2004). Wastes such as high volume plastics, sludge, medical wastes are major sources of PAHs in incinerators (Davies *et al.*, 1976; Eiceman and Vandiver, 1983; Wheatley *et al.*, 1993; Li *et al.*, 1995; Durlak *et al.*, 1998; Li *et al.*, 2001; Lee *et al.*, 2002; Park *et al.*, 2009).

For example in a study by Li *et al.* (1995), the PAH contents in the feed waste sludge oil and plastics were averaging at 3600 and 13.8 $\mu\text{g g}^{-1}$, respectively, while in the liquid diesel used as auxiliary fuel it was 6970 mg L^{-1} . In the same study, the PAH contents in the solid ash residues are higher than those in the fly ash from the stacks by an order of magnitude (Li *et al.*, 1995).

According to Park *et al.* (2009) and Chen *et al.* (2003b), the PAH emissions from the incinerators depend on the

source and type of waste being incinerated, the type of facility, incineration process procedures and/or incineration conditions, the type air pollution control devices as well as the feeding load. Increasing incineration temperatures leads to lower PAH emissions, while higher feeding loads lead to higher PAHs emissions from an incinerator (Durlak *et al.*, 1998).

A distinct difference was observed by Li *et al.* (2001), whereby the emission factors for three kinds of plastics were different. The emission factors from the stack flue gases were 320, 315, and 462 mg kg-plastics⁻¹ and from the bottom ashes 195, 45.2 and 71.4 mg kg⁻¹ for polyvinyl chloride, polypropylene plastics and high density polyethylene, respectively.

PAH emissions can be enhanced by using air pollution control devices as shown by Chen *et al.* (2003a), whereby the emission factors for a livestock waste incinerator were 285 and 2.86 mg kg⁻¹, when operated with and without a wet scrubber, respectively. This was attributed to the low temperature operation conditions for the incineration with an air pollution control devices (APCDs), which favors PAH formations from incomplete combustion (Chen *et al.*, 2003a).

When considering difference in type of facility and difference in plant operations, Lee *et al.* (2002) reported the emission factors for a mechanical grate incinerator and a fixed grate incinerator to be 252000 µg kg-waste⁻¹ and 856000 µg kg-waste⁻¹, respectively, which were three order of magnitude higher than those of a municipal waste incinerator (871 µg kg-waste⁻¹). This mechanical grate incinerator had more efficient combustion conditions than the fixed grate incinerator, which accounted for the comparatively lower PAH emission factors, while medical incinerators emit more PAHs than municipal waste incinerators.

Similarly, Zhao *et al.* (2008) discusses differences in PAH emission from various hospital waste incinerators (HWI-I, II, III and IV) in China. The HWI-I was a medium scale incinerator with APCDs, HWI-II was small scale incinerator found in a hospital without APCDs, HWI-III was medium scale incinerator for a large city, while HWI-IV was large scale incinerator with optimum operation conditions and well maintained APCDs. The HWI-II was operated on diesel and natural gas, while the rest were run on diesel oil. Owing to the differences in operations, fuel type and waste feeds the corresponding PAH concentrations for 16 priority PAHs, where 22.5 and 16.4 mg kg⁻¹ in bottom ashes of HW-I and HW-II and 199 and 4.16 mg kg⁻¹ in fly ashes of HWI-III and HWI-IV, respectively.

PAH emissions from incinerators by far impact the atmospheric PAH levels in their surrounding areas. Mi *et al.* (2001a) reported ambient PAH levels for 21 criteria PAHs to be in a range of about 128–1350 ng m⁻³ for a municipal waste incinerator emitting PAHs at a rate of 245000 mg hr⁻¹ with a total-PAH emission factor of 871 mg per ton of waste being incinerated.

Not only the do the stack emissions from incinerators contribute to environmental PAHs, but also other waste streams such as the fly ashes and waste scrubber effluents as well as bottom ashes have been shown to pathways through which PAHs get into environment sites like landfills and

waste water plants (Li *et al.*, 1995; Lee *et al.*, 2002; Chen *et al.*, 2003a, b; Wheatley and Sadhra, 2004; Li *et al.*, 2014) as seen in Table 3.

PAH Emission from Coking, Steel and Iron Industries

It has been reported that in the steel and iron ore industries, PAHs are usually released during coke manufacturing, sintering, iron making, molding, casting and steel making processes (Yang *et al.*, 2002). In coking industries, PAHs are produced during coal charging, coke pushing and coke oven gas combustion stages. In a study done by Mu *et al.* (2013) for various coke plants in China, the emission factors ranged between 7.81–222 and 57.1–799 µg kg⁻¹ coal, for coal charging and pushing coke processes, respectively.

PAH Emissions from Joss Paper Burning

Furnaces associated with religious ceremonies for Taoism and Buddhism have been linked to PAH emissions in Taiwan (Yang *et al.*, 2005c; Rau *et al.*, 2008). Yang *et al.* (2005c) investigated the PAH emission from joss paper furnaces placed near temples in Taiwan, the emission factors were 74.6 mg kg-joss⁻¹ paper and 67.3 mg kg-joss⁻¹ paper for furnaces operating without and with air pollution devices, respectively. In the same study, it was shown that bamboo made joss paper had lower PAH emission compared to that made from recycled waste paper. Later, Rau *et al.* (2008) investigated contribution of joss paper burning during massive open burning event and the total PAH concentration for 16 criteria PAHs at the open burning site and a downwind site were 2330 and 794 ng m⁻³, respectively.

PAH Emissions from Coal Fired Power Plants

According to Revuelta *et al.* (1999), the operating conditions especially combustion efficiencies and excess oxygen, are the key factors controlling PAH emissions from coal fired power plants. Secondary with lesser influence and related to the operating conditions, are the type of coal and plant design. PAH emissions from coal fired power plants are characterized by lower molecular weight PAHs with 4 rings or less, found primarily in the gaseous phase, but very few high molecular ring PAHs (Revuelta *et al.*, 1999). Operations of coal fired power plants poses threat to immediate environment as confirmed by a study by Donahue *et al.* (2006), who showed that contribution by local coal power plants to the total-PAHs flux to surface sediments in Alberta lakes were in the range of 140 to 1100 µg m⁻² year⁻¹. In the same study, the total PAH content in the fly ashes were in the range of 770 to 2760 ng g⁻¹ (Donahue *et al.*, 2006).

PAH Emissions from Asphalt Plants

Lee *et al.* (2004) evaluated the PAH emission from batch hot mix asphalt plants. Asphalt generally contain a mixture of paraffinic and aromatic hydrocarbons and the total-PAH concentrations from these plants averaged at 354, 83.7, and 107 µg Nm⁻³, for batch mixer, preheating boiler and discharging chute, respectively. In the same study, the PAH content in the cyclone fly ash and bag filter fly ash averaged at 2800 and 4900 ng g⁻¹, respectively. The

Table 3. Averaged total PAHs emissions from stationary sources from literature.

Source	Number of routine PAHs considered	Categories of PAH contents	PAH contents	Dominant PAHs	Reference
PAHs concentration in liquid fuels					
Oily sludge and waste plastics incinerator	21 PAHs	Diesel auxiliary fuel (mg L^{-1})	6970		(Li et al., 1995)
Animal carcass and medical waste incinerators	21 PAHs	Liquid diesel auxiliary fuel (mg L^{-1})	7300	AcP, AcPy, Flu, Nap, PA, Ant	(Chen et al., 2003b)
PAH content in solid fuel and solid feed stocks					
Oily sludge and waste plastics incinerator	21 PAHs	Waste oily sludge ($\mu\text{g g}^{-1}$)	3600		(Li et al., 1995)
5 Sewage sludge incinerators	16 PAHs	Polyethylene plastics ($\mu\text{g g}^{-1}$)	13.8		(Park et al., 2009)
Integrated iron and steel plants	17 PAHs	Sewage sludge (mg kg^{-1})	1.84–12.2	BkF, BpF, CHR, Pyr, Phe	(Park et al., 2009)
Coal fired power plant	16 PAHs	Ashes from coke coking storage piles ($\mu\text{g g}^{-1}$)	300–989	BpF, Flu, IND, BkF, Ant, Phe	(Kong et al., 2011)
PAHs concentration in bottom ashes and fly ashes					
Oily sludge and waste plastics incinerator	21 PAHs	Coal ($\mu\text{g g}^{-1}$)	37.6	Chry, Pyr, BbF, BaP	(Ruwei et al., 2013)
Mechanical grate medical waste incinerators	21 PAHs	Flue gas particulate ($\mu\text{g g}^{-1}$)	139		(Li et al., 1995)
Fixed grate medical waste incinerator	21 PAHs	Ash ($\mu\text{g g}^{-1}$)	3.03		(Li et al., 1995)
Livestock incinerator	21 PAHs	Electrostatic precipitator fly ash (ng g^{-1})	13800	BaA, FL, BeP, BbF	(Lee et al., 2002)
		Front bottom ash (ng g^{-1})	3170	BaA, NaP, BeP, PA	(Lee et al., 2002)
Animal carcass and medical waste incinerators	21 PAHs	Bottom ash (ng g^{-1})	162	Nap, FL, Pyr	(Lee et al., 2002)
		Electrostatic precipitator fly ash (ng g^{-1})	47000	COR, IND, BbF, BaA	(Lee et al., 2002)
4 Swedish municipal waste incinerators	16 PAHs	Bottom ash	3480	BaA, Ant, Flu	(Lee et al., 2002)
		Bottom ash (with wet scrubber) ($\mu\text{g g}^{-1}$)	731	COR, Nap, PA, CHR, DBA, IND	(Lee et al., 2002)
4 Swedish municipal waste incinerators	16 PAHs	Bottom ash (without wet scrubber) ($\mu\text{g g}^{-1}$)	470	Nap, PA, COR, FL, BghiP	(Chen et al., 2003b)
		Bottom ashes of hog farm waste incinerator (ng g^{-1})	737	COR, Nap	(Chen et al., 2003b)
5 Korean sewage sludge incinerators	16 PAHs	Bottom ashes of livestock disease control incinerator (ng g^{-1})	470	CO _r , Nap, PA, FL	(Chen et al., 2003b)
		Bottom ashes of medical waste incinerator (ng g^{-1})	421	PA, FL, Pyr, Nap, COR	(Chen et al., 2003b)
10 Japanese waste incinerator	16 PAHs	Four year old weathered bottom ash ($\mu\text{g kg}^{-1}$)	479–3590		(Johansson and van Bavel, 2003a)
		Mixed ash (50% fresh fly ash and 50% 2 year old bottom ash) ($\mu\text{g kg}^{-1}$)	57800–77100		(Johansson and van Bavel, 2003a)
5 Swedish municipal waste incinerators	16 PAHs	Circulated fluid bed fly ash ($\mu\text{g kg}^{-1}$)	141–45000		(Johansson and van Bavel, 2003b)
		Weathered bottom shes ($\mu\text{g g}^{-1}$)	479–3590		(Johansson and van Bavel, 2003b)
10 Japanese waste incinerator	16 PAHs	Bottom ashes (mg kg^{-1})	0.002–0.345	-	(Park et al., 2009)
		Fly ashes (mg kg^{-1})	0.011–0.228	-	(Park et al., 2009)
10 Japanese waste incinerator	16 PAHs	Bottom ashes ($\mu\text{g kg}^{-1}$)	65–1580		(Sato et al., 2011)

Table 3. (continued).

Source	Number of routine PAHs considered	Categories of PAH contents	PAH contents	Dominant PAHs	Reference
Integrated iron and steel plants	17 PAHs	Stack ashes before electrostatic precipitator at coking process ($\mu\text{g g}^{-1}$)	7060	Flu, Pyr., IND, BpF,	(Kong et al., 2011)
		Electrostatic precipitator bottom ashes at coking process ($\mu\text{g g}^{-1}$)	1780–5320	Flu, BpF, IND, Pyr, Ant, Phe	
		Electrostatic precipitator bottom ashes at iron making process ($\mu\text{g g}^{-1}$)	290	BpF, Flu, Chr, BaA, Pyr	
Heating station	17 PAHs	Bottom ashes of electrostatic precipitator ($\mu\text{g g}^{-1}$)	620	Flu, Ant, Pyr, BpF, Phe	(Kong et al., 2011)
Coal fired-combined heat and power plant	16 PAHs	Fly ash ($\mu\text{g g}^{-1}$)	3470–4800		(Li et al., 2014)
Coal fired power plant	17 PAHs	Bottom ash ($\mu\text{g g}^{-1}$)	709	Flu, Ant, Phe, Pyr, BaA	(Kong et al., 2011)
Coal fired power plant	16 PAHs	Fly ash ($\mu\text{g g}^{-1}$)	0.93–2.08	Flan, Nap, Phen, Flu	(Ruwei et al., 2013)
		Bottom ash ($\mu\text{g g}^{-1}$)	2.83–5.32	BaP, BaF, Flan, Nap,	
PAH concentration in stack flue gases					
Oily sludge and waste plastics incinerator	21 PAHs	Stack flue gas ($\mu\text{g m}^{-3}$)	648		(Li et al., 1995)
Mechanical grate medical waste incinerators	21 PAHs	Ambient air (ng m^{-3})	1530		(Lee et al., 2002)
Fixed grate medical waste incinerator	21 PAHs	Stack flue gases ($\mu\text{g Nm}^{-3}$)	1290	Nap, AcPy, PA, Ant	
Livestock incinerator	21 PAHs	Stack flue gases ($\mu\text{g Nm}^{-3}$)	587	Nap, PA, Ant	(Lee et al., 2002)
		Stack flue gases with wet scrubber ($\mu\text{g m}^{-3}$)	636	Nap, PA, AcPy, FL, Pyr	(Chen et al., 2003a)
		Stack flue gases without wet scrubber ($\mu\text{g m}^{-3}$)	571	Nap, PA, AcPy, FL, Pyr	
Animal carcass and medical waste incinerators	21 PAHs	Stack flue gases with fuel only ($\mu\text{g m}^{-3}$)	5.70	Nap, PA, BpF, IND	(Chen et al., 2003b)
		Stack flue gases for hog farm waste incinerator ($\mu\text{g m}^{-3}$)	592		
		Stack flue gases for livestock disease control incinerator ($\mu\text{g m}^{-3}$)	527		
5 Korean sewage sludge incinerators	16 PAHs	Stack flue gases for medical waste incinerator ($\mu\text{g m}^{-3}$)	391		(Park et al., 2009)
		Inlet of stack ($\mu\text{g m}^{-3}$)	3.93–925	Nap	
		Outlet of stacks ($\mu\text{g m}^{-3}$)	1.15–189	Nap	
Tire pyrolysis plant	21 PAHs	Exhaust of flare ($\mu\text{g Nm}^{-3}$)	215	Nap	(Chen et al., 2007a)
4 Coke fired - steel and iron plants	21 PAHs	Stack ($\mu\text{g Nm}^{-3}$)	778	Nap, Ant, AcPy	(Yang et al., 2002)
4 heavy oil fired-steel and iron plants	21 PAHs	Stack ($\mu\text{g Nm}^{-3}$)	1360	Nap, Ant, AcPy	(Yang et al., 2002)
4 electricity- fired -steel and iron plants	21 PAHs	Stack ($\mu\text{g Nm}^{-3}$)	910	Nap, Ant, AcPy	(Yang et al., 2002)

Table 3. (continued).

Source	Number of routine PAHs considered	Categories of PAH contents	PAH contents	Dominant PAHs	Reference
25 industrial boilers	21 PAHs	Stack flue gases ($\mu\text{g m}^{-3}$)	488		(Li et al., 1999)
Single boiler	21 PAHs	Heavy oil operated- Stack flue gases ($\mu\text{g m}^{-3}$)	451		(Chen and Lee, 2007)
		Heavy oil/waste water emulsion operated- Stack flue gases ($\mu\text{g m}^{-3}$)	278		
		Heavy oil/waste water emulsion operated- Stack flue gases ($\mu\text{g m}^{-3}$)	317		
6 utility boilers for coal fired power plants	16 PAHs	flue gases ($\mu\text{g m}^{-3}$)	8.84–22.6		(Wang et al., 2015)
Coking plants	16 PAHs	Coal charging stack ($\mu\text{g m}^{-3}$)	360		(Mu et al., 2013)
		Pushing coke stack ($\mu\text{g m}^{-3}$)	124		
		Coke oven gas combustion stack ($\mu\text{g m}^{-3}$)	227		
PAH concentration in wet scrubber effluents					
Mechanical grate medical waste incinerators	21 PAHs	Waste scrubber effluent ($\mu\text{g L}^{-1}$)	124	BaA, BaP, Nap	(Lee et al., 2002)
Fixed grate medical waste incinerator	21 PAHs	Waste scrubber effluent ($\mu\text{g L}^{-1}$)	62	BghiP, IND, Nap	(Lee et al., 2002)
Livestock incinerator	21 PAHs	Wet scrubber effluent ($\mu\text{g L}^{-1}$)	45.6	Nap, DBA, PA, Pyr	(Chen et al., 2003a)
Animal carcass and medical waste incinerators	21 PAHs	Waste scrubber effluent for hog farm waste incinerator ($\mu\text{g L}^{-1}$)	45.3	Nap	(Chen et al., 2003b)
		Waste scrubber effluent for medical waste incinerator ($\mu\text{g L}^{-1}$)	10.5	Nap, COR	
Tire pyrolysis plant	21 PAHs	Waste scrubber effluent ($\mu\text{g L}^{-1}$)	104	Nap, IND	(Chen et al., 2007a)

corresponding emission rates (mg min^{-1}) and emission factors ($\text{mg ton-products}^{-1}$) for total-PAHs in this study were 125, 0.837, and 7.77 mg min^{-1} and 128, 0.860 and $9.90 \text{ mg ton-products}^{-1}$ for batch mixer, preheating boiler and discharging chute, respectively.

PAH Emissions from Restaurants

Several studies have identified restaurants as major sources of PAHs (See and Balasubramanian, 2008; Pan *et al.*, 2011; Chen *et al.*, 2012) as well as trans, trans-2,4-decadienal (Yang *et al.*, 2007), alkanes, alkanolic acids, alkenolic acids, dicarboxylic acids, alkanals, alkenals, alkanones, amides, and particulate organic matter (Chang *et al.*, 2011). PAH emission from the restaurants depend on the kind of fuel and/or food oil used, cooking styles and methods, ingredients and dishes made, cooking equipment used, ventilation hoods and stacks operation (Roe *et al.*, 2004; Abdullahi *et al.*, 2013).

To exemplify the influence of the cooking method on PAH emissions, a study done by See and Balasubramanian (2008) reported the total-PAH emission, for 16 criteria PAHs, to be 36.5, 25.0, 21.5, 14.3 and 10.5 ng m^{-3} for deep-frying, panfrying, stir-frying, boiling, and steaming, respectively. The high emission from deep frying is as a result of high amount of oil used and the high temperatures involved. Results from another study by Chen *et al.* (2012) show that the average total-PAH concentration in the stack flue gases for 16 priority PAHs to be about 21.0, 21.5 and $58.8 \mu\text{g m}^{-3}$ for 9 Chinese, 7 western and 4 barbeque restaurants, respectively. In another study, Chen *et al.* (2007b) evaluated 8 gaseous and 22 particulate PAHs from Chinese, Western and Western-fast food restaurants. The average total-PAH concentrations in the stack flue gases were 3310, 4490, and 2100 ng m^{-3} for 2 Chinese, 2 Western and Western-fast food restaurants, respectively. In the same study, while evaluating different cooking styles, the total-PAH emissions were 690, 4060 and 3120 ng m^{-3} for steaming, deep frying and mixed styles, respectively (Chen *et al.*, 2007b).

In a similar study by Li *et al.* (2003), the average total-PAH concentrations for 21 PAHs were 80.1, 92.9, 63.3 and $55.5 \mu\text{g m}^{-3}$ for 4 Chinese, 2 Western, 2 fast food and 2 Japanese style restaurants. The corresponding total-PAH emission factors were 281, 259, 156, 37.8 milligram per liter of food oil consumed, while the emission factor in terms of total BaP_{eq} were 21.2, 20.5, 0.518, 0.106 milligram per liter of food oil consumed, for 4 Chinese, 2 Western, 2 fast food and 2 Japanese style restaurants, respectively. Based on the data by Li *et al.* (2003), and considering, the food oil consumption per lunch or dinner and the number of each kind of restaurant, the corresponding total PAH emission factors were 3765, 4015, 2153, 620 milligram per lunch or dinner and for total BaP_{eq} 284, 318, 7.15, 1.74 milligram per lunch or dinner, for the Chinese, western, fast food and Japanese restaurants, respectively. Additionally, the evaluated emission rates for the investigated 4 Chinese, 2 Western, 2 fast food and 2 Japanese style restaurants 2038, 258, 31.4, and 5.11 kilograms per annum for total-PAHs and 154, 20.4, 0.104, and 0.014 kg per annum for total-BaP_{eq}, respectively. From the data presented by Li *et al.* (2003), this study evaluated the emission factors of total-PAHs and

total-BaP_{eq} from home kitchens to be about 16.5 and 1.24 milligram per person per day, respectively. The observed differences were attributed to the difference in cooking method and the kinds of food oils used (Li *et al.*, 2003). The influence of type of cooking equipment and ingredients, was evaluated by Jørgensen *et al.* (2013), whereby the emission concentration levels for total-PAHs from fresh bacon cooked by electric stove, fresh bacon cooked by gas stove and smoked bacon cooked by gas stove was 296, 267, and 302 ng m^{-3} , respectively.

As mentioned earlier restaurants are also sources of other compounds like trans, trans-2,4-decadienal (*tt*-DDE), which are more toxic than PAHs but fortunately emitted in lower concentrations. Yang *et al.* (2007) reported the emission factors in terms of $\mu\text{g customer}^{-1}$ to be 1990, 570 and 63.8 for barbeque, Chinese and western restaurants respectively. The toxicological effects of *tt*-DDE are very similar to those of PAHs and includes formation of DNA adducts and promotes cancer in human beings (Yang *et al.*, 2007).

Control Strategies and Technologies of PAH Emissions from Stationary Sources

As mentioned earlier the main factors affecting the PAH emission from stationary sources are fuel and feed composition and operation control conditions such as temperature, turbulence and also air pollution control devices. Therefore to control PAHs, mostly requires higher temperatures, sufficient excess air or better turbulence and scaling up (Zevenhoven and Kilpinen, 2001). Li *et al.* (2001) shows that the waste feed consisting of three different plastics resulting in different levels of PAHs in the waste streams. The study by Chen *et al.* (2003a) shows the impact of operation conditions, whereby the total-PAH emission from a livestock incinerator with a wet scrubber was higher than those from a livestock incinerator operated without a wet scrubber as a result of lower operating temperatures when using wet scrubber. In another study, Wang *et al.* (2002) proposed use of terephthalic acid (TPA) as co-combustion fuel for a waste biological sludge incinerator. Wang *et al.* (2002) reported approximately 74%, 78%, 86% and 85% reduction in total PAHs output rates for cyclone fly ash, wet scrubber effluent, stack flue gases and overall emission, respectively, when comparing co-combustion of biological sludge with TPA and without TPA. A study done by Chen *et al.* (2013), achieved reduction efficiencies of about 46% and 58% in terms total PAHs and total BaP_{eq}, respectively, when co-combusting municipal solid sludge and coal at a ratio of 30/70 in a drop tube furnace.

Since fuel composition is one of the major factor affecting PAHs emissions from stationary sources, some studies have shown that altering the fuel composition can ultimately lead to reduced PAH levels from waste streams. By co-combusting municipal solid sludge and coal in a 30/70 blending ratio (Chen *et al.*, 2013) achieved 23–46% reduction in total-PAHs at temperatures ranging from 950–1250°C in a laboratory scale furnace. For an industrial boiler, reduction efficiencies of about 38% and 62% for total-PAHs and total-BaP_{eq}, respectively, were achieved when the fuel was changed from commercial heavy fuel to heavy fuel oil emulsified with

10% solvent containing waste water (Lin *et al.*, 2011b).

Adsorption technologies are some of the most used methods to control PAHs from sources. The efficiency depends on the textural and surface chemical properties of the sorbent materials (Zhou *et al.*, 2010). Liu (2006) evaluated removal efficiency of PAHs using activated carbon fibers (ACFs), whereby the removal efficiencies of particulate PAHs using ACFs were higher than those of gaseous PAHs. The removal of solid phase PAHs depend on the pores sizes, where by the lower the pore size, the higher the removal rate. Additionally, the ACFs efficiencies increased with increasing adsorption temperatures. In the same study to improve the removal efficiency of gaseous PAHs (Liu, 2006) increased the weight of ACFs. The increasing removal efficiency with increasing temperatures had earlier on been observed by Liljelind *et al.* (2001), when using titanium/vanadium catalyst to remove PAHs.

To improve on the removal efficiency, Lin *et al.* (2011a) and Tseng *et al.* (2011) used metal catalysts such as palladium, copper, cobalt, nickel, which enhances PAH removal via catalysis and adsorption mechanisms. The metal catalysts encourage the oxidation of PAHs especially the HMW-PAHs (Lin *et al.*, 2011a). In addition to activated carbon fibers, granular activated carbon has been shown through experimental studies to successfully remove PAHs of 2 to 4 rings (Valderrama *et al.*, 2007). Additionally, Zhou *et al.* (2005) reports that injecting activated carbon in the flue gases duct reduces the PAH emission concentration from the stack flue gases of MSWIs, but on the other hand it increases the amount of fly ash, but no apparent increase of PAH content in the fly ash. The action of the injected activated carbon is to allow the gaseous PAHs to adsorb on the surface and transfer to particulate phase via nucleation, condensation and adsorption (Zhou *et al.*, 2005).

When considering conventional air pollution devices such as electrostatic precipitator and wet scrubber (Lee *et al.*, 2002), the wet scrubber is more efficient in removing PAHs compared to electrostatic precipitator (ESP). The removal efficiencies for total-PAHs for wet scrubber and electrostatic precipitator were averaging at 14.4% and 1.18%, respectively, for two different municipal waste incinerators. These results show that these APCDs (wet scrubber and electrostatic precipitator) are not efficient for PAH removal. In the same study, the average overall removal efficiencies were 81.8%, 88.7% and 3.83% for HMW-, MMW-, and LMW-PAHs, respectively.

These results correspond to another study by the same group whereby the wet scrubber was more efficient in removing PAHs than the electrostatic precipitator, because PAHs are mostly in the gas phase and some parts of the gas phase PAHs can be removed by the effluent but not in the ESP. Similarly, a study by Chen *et al.* (2007a) investigating PAHs from tire pyrolysis, the removal efficiencies of total-PAHs by flare and wet scrubber to be 66.8% and 76.2%, respectively. In this study, the removal efficiencies for particulate LMW- and MMW-PAHs were higher than those of HMW-PAHs (Chen *et al.*, 2007a).

Apart from altering the feed and fuel composition, operating condition and using adsorption technique, other

studies have investigated different ways of removing and reducing PAH emissions from stationary sources. As for other removal techniques, Chmielewski *et al.* (2003) studied the use of electron beam irradiation to remove PAHs and found out that the method reduces the LMW-PAHs, while encouraging formation of the MMW- and HMW-PAHs, which are more toxic. Chang *et al.* (2011) used atmospheric plasma reactor to remove PAHs from restaurant exhausts and obtained removal efficiencies above 50%. In the study, it was demonstrated that the removal efficiencies increased with increasing plasma output power (Chang *et al.*, 2011).

PAH Emissions from Mobile Sources

The mobile sources in this section include emissions from automobiles, helicopters, and ships which are equipped with either a compression or spark-ignition internal combustion engine. Several studies (Khalili *et al.*, 1995; Marr *et al.*, 1999) have identified these vehicles as major sources of PAH emissions in the environment. These aromatic compounds' formation mechanisms in the mobile sources are either through pyrosynthesis or survival mechanism and the emissions depends on several factors including the engine type, fuel composition, load and age, mileage, PAH content in lubricant oil, lubricant oil combustion, driving mode and emission control devices such as air filters (Ravindra *et al.*, 2008; Katsoyiannis, 2014). These factors are addressed in more detail in the subsequent sections.

PAH Emissions from Gasoline Automobile Engines

Though the gasoline engines produce less PAH emissions compared to diesel engines, the overall number of gasoline vehicles are much higher than the diesel vehicles (Marr *et al.*, 1999). Also, gasoline engines generate ten times more carcinogenic PAH compounds that diesel ones during cold engine start-up (Devos *et al.*, 2005). However, more research work and resultant technology advancement have been carried out on diesel engines, which have significantly reduced their pollutant emissions (Kokko *et al.*, 2000). According to Elghawi *et al.* (2010), two mechanisms of PAH formation in the gasoline engines are possible i.e., survival and pyrosynthesis. Westerholm *et al.* (1988) found that approximately 95% of the PAH content in the gasoline fuel was decomposed and over 50% of the PAH emitted were formed during the combustion process. The studied factors that influence PAH emissions in the gasoline automobile engines include the, driving mode (cold or hot start-up) fuel, fuel-air equivalence ratio, engine load and speed, and compression ratio.

The environmental concern for lead emissions led to the adoption of lead-free gasoline fuels in spark-ignition engines. However, the mean total-PAH and total-BaP_{eq} concentrations in these fuels have been reported to be higher than that from premium gasoline (Mi *et al.*, 1996; Mi *et al.*, 2001b). Mi *et al.* (1996) studied the PAH concentrations from 95-lead-free gasoline (95-LFG) and premium gasoline (PLG) at different cruising speeds; idle, 40, 80, and 110 km hr⁻¹. The researchers found the mean total-PAH concentrations for the four different cruising speeds to be between 258 and 385 µg m⁻³ and between 190 and 263 µg m⁻³ for 95-

LFG and PLG, respectively. The mean total-PAH emission factors were 374 and 322 $\mu\text{g km}^{-1}$ for 95-LFG and PLG, respectively, while total-BaP_{eq} were 2.92 and 2.47 $\mu\text{g km}^{-1}$ for 95-LFG and PLG fueled engines, respectively. They also concluded that the total-PAH emission rates increased with increasing cruising speed for both fuel in the engine. Mi *et al.* (2001b) compared the total-PAH and total-BaP_{eq} emission factors between premium gasoline (PLG), 92-lead-free gasoline (92-LFG) and 95-lead-free gasoline (95-LFG). The average total-PAH and total-BaP_{eq} emission factors were 3800 $\mu\text{g L}^{-1}$ and 63.7 $\mu\text{g L}^{-1}$ for PLG, 2710 $\mu\text{g L}^{-1}$ and 14.3 $\mu\text{g L}^{-1}$ for 92-LFG and 6380 $\mu\text{g L}^{-1}$ and 101 $\mu\text{g L}^{-1}$ for 95-LFG, respectively. It can therefore be concluded that the lower the lead concentration the higher the total-PAH and total-BaP_{eq} emission.

PAH emissions from gasoline engines depend on the air/fuel ratio. The PAH exhaust emissions are found to decrease with a leaner mixture. Pedersen *et al.* (1980) showed that PAH emissions were high in both rich and very lean operating conditions. When the fuel-air equivalence ratio (ϕ) is increased, the hydrocarbon concentrations in the cylinder increase due to lower oxygen concentrations which later become PAH formation precursors (Baral *et al.*, 2011). Baral *et al.* (2011) showed that the total-PAH emitted at $\phi = 1$ and $\phi = 1.2$ were higher by approximately 4 and 7 times respectively than at $\phi = 0.8$. The difference being more pronounced in LMW-PAHs and HMW-PAHs. MMW-PAHs were similar in the three different fuel-air equivalence ratio conditions.

Generally, increasing the engine load results in PAH emissions increase in gasoline fueled engines (Elghawi *et al.*, 2010; Baral *et al.*, 2011). This has been attributed to the higher intake flow rate and decrease in the intake temperature when the engine load is raised and as a result, increases the amount of liquid gasoline in the cylinder and increasing the likelihood of diffusion burning in the cylinder (Baral *et al.*, 2011). Elghawi *et al.* (2010) found that the total-PAHs concentration increased from 850 $\mu\text{g m}^{-3}$ at low load to 1276 $\mu\text{g m}^{-3}$ at high engine load. Also, Baral *et al.* (2011) showed that the PAH emissions are higher, when the engine load is changed from 20% to 50% than when the load was increased from 50% to 100%. The explanation given was due to higher exhaust temperature, which may have led to the oxidation of PAHs.

When the engine speed increases, the ignition timing is advanced causing an increase of PAH emissions from gasoline engines. This is because an increase in engine speeds reduces the time for gases to move into and out of the crevices within the cylinders of the engine. This lowers the adsorption or desorption of the fuel components in the oil film leading to an increase of PAH emission (Kayes and Hochgreb, 1999). However, Baral *et al.* (2011) showed that PAH emissions decreased when the engine speed was increased from 1000 to 1500 rpm and slightly increased when the engine speed was increased from 1500 to 2000 rpm. Since the increase in the speed also leads to an increase in the in-cylinder temperature, the PAH formation and oxidation rates increase, which are limited by the residence time (Kayes and Hochgreb, 1999). These competing factors could be

used to explain the increase and decrease of PAH emission.

The compression ratio, which is the ratio of the displacement and clearance ratio, can be used as a guide for the power the engine can generate, the higher the ratio the higher the power. PAH emissions have been shown to slightly increase with increasing compression ratio (Baral *et al.*, 2011). The slight increase in PAH is because a higher compression ratio increases the peak temperatures, which favor both the competing factors of PAH formation as well as their oxidation (Baral *et al.*, 2011).

Control Strategies for PAH Reduction in Gasoline Automobile Engines

Emission control technologies have been developed and implemented with the aim of achieving or surpassing the stiffer regulations imposed on PAH emissions among other pollutants. Some of the emission control strategies employed in gasoline fueled engines include the use of emission control devices e.g., catalytic converters and use of reformulated gasoline (RFG). In this section, the results of major control strategies in previous studies will be presented and discussed.

PAH emissions are known to be significantly affected by the ambient temperatures, especially for cold start emissions (Erlandsson and Abrahamsson, 1995). Ludykar *et al.* (1999) showed the mean total-PAH and BaP emissions generated from a car equipped with a three-way catalyst (TWC) ran in accordance with the European driving cycle (EDC) at -20°C ambient temperatures were 4662 and 116 $\mu\text{g km}^{-1}$, respectively. This was significantly higher than the emissions at -7°C and 22°C , with the latter recording the least total-PAH and BaP emissions of 141 and 0.16 $\mu\text{g km}^{-1}$, respectively. Stoichiometric TWC is a superior emission control technology of reducing the amount of PAH emissions among other pollutants than direct injection and carburetor (Kokko *et al.*, 2000).

RFG was introduced to ensure that the fuel burns more cleanly than pure gasoline fuel. Several additives have been added to RFG e.g., oxygenates such as ethanol and methyl-tert-butyl-ether (MTBE) and surfactant additives (Harley *et al.*, 2006). The aromatic compounds content in RFG is usually lower than 35.0% with benzene volume below 1.0%, sulfur below 100 ppm, oxygen mass added to a minimum of 2.0% and a maximum of 2.7% and the vapor pressure decreased from 80 kPa to 70 kPa (Kokko *et al.*, 2000). With so many properties different from pure gasoline fuel, it has not been possible to conclude which one of the properties is most important in the observed reduction of PAH emissions from RFG fuels.

The addition of ethanol to gasoline has been widely adopted, especially in Brazil and US, driven mostly by the need to reduce the overdependence on fossil fuels and the associated environmental concerns. Kokko *et al.* (2000) found that PAH emissions from ethanol blended gasoline (E85) were much lower than gasoline. Schramm (2004) showed the engine using E85 had lower total-PAH emissions of 21 ng km^{-1} and 26 ng km^{-1} under federal test procedure (FTP) and EU test cycles, respectively. This is because of the leaning effect of ethanol which allows more fuel to oxidize. However, the use of ethanol in gasoline engine has

resulted in an increase of carbonyl emissions (Magnusson *et al.*, 2002). Pang *et al.* (2008) showed that total carbonyl emissions from a gasoline engine-out emission factor was 3.1–8.2% higher at 66.7–99.4 mg kW⁻¹ h⁻¹ when fueled by ethanol blended gasoline containing 10 vol% ethanol than only from a fossil gasoline fueled engine. The tailpipe emissions were also 3.0–61.7% higher at 9.2–20.7 mg kW⁻¹ h⁻¹. Acetaldehyde was the dominant carbonyl in the engine emission fueled by 10 vol% ethanol blend.

Schramm (2004) also found that biodegradable lubricant (from vegetable oil) emitted more PAH than mineral oil based lubricant in two flexible fuel vehicles (FFV's). Although the biodegradable lubricant did not have any PAH content, its use in the gasoline engine resulted into more PAH emissions. This observation is attributed to the high fuel consumption that resulted in engines that used biodegradable lubricant. The amount of PAH emitted were 15 ng km⁻¹ and 30 ng km⁻¹ for the engine using gasoline fuel under FTP and EU test cycles respectively.

PAH Emissions from Gasoline Motorcycles

Motorcycles are a convenient means of transport for many individuals around the world. However, they are regarded as one of the major PAH emitters, since their small engines and general sizes limit the number and magnitude of emission control devices e.g., catalytic-converters that can be installed. PAH emissions from older, non-catalyzed motorcycles are comparable or higher than other light-duty gasoline and diesel vehicles (Spezzano *et al.*, 2007). The factors that affect the PAH emission levels from the gasoline motorcycle include engine type, engine temperature, service age, mileage, and maintenance.

Yang *et al.* (2005b) studied PAH emissions from three different types of motorcycle engines: 2-stroke carburetor, 4-stroke carburetor and 4-stroke with fuel injection. Their results showed that 4-stroke with fuel injection had the least total-PAH and total-BaP_{eq} emission factors with 3390 µg km⁻¹ and 3.52 µg km⁻¹, respectively while 2-stroke carburetor had the highest with 8320 µg km⁻¹ and 10.8 µg km⁻¹, respectively. Engines with a higher mileage were also shown to have significantly higher PAH emissions than newer ones e.g., emission factor of a new 4-stroke with fuel injection was 1120 µg km⁻¹ compared to 3390 µg km⁻¹ for an in-use one. The high PAH emissions from a 2-stroke motorcycle engine results from the use of lubricant with the gasoline in the engine system, where the mixture might escape and become PAH precursors (Spezzano *et al.*, 2008). LMW-PAHs were also shown to dominate in the exhaust gas in all of the engine types, Naphthalene being the highest (96–98%).

As expected, the PAH emissions from the cold start are significantly higher than hot-start driving cycle. This is of great concern for motorcycles PAH emissions because they are mostly driven during the cold-start period especially in urban areas. Besides the poor air/fuel mixing and low fuel volatility experienced during cold temperatures, the emission control devices might also fail to attain their working temperature leading to the high PAH emissions (Yang *et al.*, 2005b; Spezzano *et al.*, 2008).

PAH Emissions from Helicopters

Not much research has been invested in the studying of PAH emissions from helicopters. However, the average total-PAH and total-BaP_{eq} emissions and emission factors from a helicopter UH-H1 turbo-shaft engine has been shown by Chen *et al.* (2006) to be significantly higher than those from heavy-duty diesel engines, motor vehicles and F101 aircraft turbine engine. LMW-PAHs dominated the total-PAHs emission (98%) in the UH-H1 engine. According to the study, the total emission levels of BaP during one landing and takeoff (LTO) cycle was higher than the European Commission standard (1.24 mg LTO⁻¹). The average total-PAH emission factor was found to be 63.5 mg L⁻¹ for JP-4 fuel, while the total-BaP_{eq} was 0.306 mg L⁻¹ for JP-4 fuel. The mean total-PAH concentration in the exhaust of the engine was 843 µg m⁻³. The PAH emissions could not be fully explained by the fuel composition and the power setting of the engine implying more research needs to be carried out.

PAH Emissions from Diesel Fueled Engines

Diesel engines are favored in the commercial transportation and agricultural machinery due to their advantage over gasoline engines which include higher fuel efficiency and higher power output (Marr *et al.*, 1999). Large low-speed 2-stroke diesel engines have been reported to achieve over 50% efficiency, while smaller 4-stroke direct injection turbocharged ones reach efficiencies of approximately 40% (Guzzella and Amstutz, 1998). However, one of their key drawbacks is the high particulate matter (PM) emissions. The fine and ultrafine size particles of the diesel PM have been known to pose the greatest health risk (USEPA, 2002). They have a large surface area and are composed of elemental carbon, which adsorbs organic compounds including PAHs (Wichmann, 2007). Hence, diesel engines are a significant source of PAH emissions in the atmosphere and more so in the urban areas (Borrás *et al.*, 2009; Vieira de Souza and Corrêa, 2015).

Studies have shown that PAHs emitted from diesel engines originate from pyrosynthesis of aromatic compounds, unburnt fuel and lubricating oil (Borrás *et al.*, 2009). The PM in the unburnt diesel fuel has been shown to be the primary contributor to particle-phase PAHs in the exhaust of a direct-injection and two direct-injection diesel engines. Also, the LMW-PAHs present in unburnt diesel fuel have been shown to be primary contributors to the exhaust emissions of PAHs in the direct injection diesel engine (Marr *et al.*, 1999), while MMW- and HMW-PAHs form during the combustion processes. Majority of the LWM-PAHs have been found to originate from unburnt fuel and from lubricating oil. The PAH emissions from diesel automobile engines depend on a number of factors including fuel composition, engine type, engine load, speed, mileage, presence of catalysts and working conditions such as temperature, pressure, and humidity.

Khalili *et al.* (1995) results showed that LMW-PAHs contributed the most to the total PAH mass in diesel engines with the predominant PAHs being fluorene, naphthalene, acenaphthylene, phenanthrene, and anthracene. The aromatics

present in diesel fuel are the major contributors of PAH emissions from the engine (Schramm, 2004). Mi *et al.* (2000) found that the addition of 3 vol% and 5 vol% fluorene in diesel fuel increased the amount of total-PAH emissions from a heavy-duty engine by 2.6 and 5.7 times, respectively. On the other hand, when considering desulfurization as a fuel reformulation technique, Borrás *et al.* (2009) showed that reduction of sulfur content had no significant change in the total PAH concentrations of light-duty diesel vehicles.

Control Strategies for Reduction of PAH Emissions from Diesel Engines

The ever growing concern of air pollution from vehicles and stricter regulations around the world have led researchers to study and develop control strategies to reduce the PAH emissions from diesel engines. These strategies have mainly focused on diesel fuel reformulation e.g., adding oxygenates and sulfur reduction, and control devices such as the diesel particulate filter (DPF) and diesel oxidation catalyst (DOC) (Marr *et al.*, 1999) including use of plasma combustion (Lin *et al.*, 2013).

Oxygenated fuels which include biodiesel, alcohols, ethers, and ketones have been added to diesel to promote better combustion, which decrease the chance of soot and PAH formation. For an oxygenate fuel to be considered a suitable additive, its miscibility in fossil diesel and cetane number should be high and volatility low (Chen, 2011). Emulsified biosolutions have been added to biodiesel-diesel blends in order to stabilize the fuel, reduce the emissions and save energy. These blends have also been shown to reduce the PAH emissions in diesel engines e.g., Lin *et al.* (2008b) showed that addition of 9.90 vol% of a biosolution and 29.70 vol% of soy-biodiesel and 0.99 vol% surfactant to premium diesel reduced the emissions of total-PAH and total-BaP_{eq} compared to premium diesel with 30% vol soy-biodiesel or premium diesel with 9.90 vol% water, 29.70 vol% soy-biodiesel and 0.990 vol% surfactant. The mean total-PAH emission factors in the exhaust were 349 $\mu\text{g L}^{-1}$ and 138 $\mu\text{g kWh}^{-1}$ while that of the mean total-BaP_{eq} were 0.442 $\mu\text{g L}^{-1}$ and 0.175 kWh^{-1} . The reduction is attributed to the close-to-zero PAH content in biodiesel and biosolution.

Another additive researched is paraffinic fuel. Yuan *et al.* (2007) studied the emissions of premium diesel fuel, palm oil biodiesel, fossil fuel diesel blended with 20 vol% palm-oil-biodiesel, paraffinic fuel blended with 5 vol% palm oil biodiesel and paraffinic fuel blended with 20 vol% palm oil diesel. Overall, paraffinic fuel with 5% palm oil biodiesel was the superior fuel for heavy duty diesel engines. The results showed that the use of that paraffinic fuel blend had lesser total-PAHs and total BaP_{eq} emissions than premium diesel fuel by 88.9% and 88.1%, respectively. The mean total-PAHs and total BaP_{eq} concentration were 25.8 $\mu\text{g m}^{-3}$ and 0.0818 $\mu\text{g m}^{-3}$, respectively.

DPFs have been preferred and employed in the reduction of PM in diesel engines. They differ with respect to substrate material, regeneration strategy, and use of catalysts (Cutler, 2004). In general, DPFs have been shown to reduce the PM mass emissions by over 90% (Matti Maricq, 2007)

thereby, reducing the available surface area for the condensation of PAHs and other semi-volatile compounds. The combination of DPF with DOC to oxidize the CO and gas-phase hydrocarbons and selective catalytic reduction (SCR) to oxidize the NO_x has been common practice for diesel engines.

PAH Emissions from Ships

Some studies have identified ships to be major PAH emission contributors to the environment and more specifically in the coastal regions (Soclo *et al.*, 2000; Contini *et al.*, 2011). The marine fuel used in engine ships tend to be of a lower grade with higher PAH and sulfur content than the premium diesel used on road vehicles and therefore their use leads to more PAH emissions. However, very few studies have quantitatively analyzed the PAH emissions from ship's main and auxiliary engines.

Cooper (2003) studied the PAH emissions from auxiliary engines of ferries and found out the total-PAH emission factors from engines that used either marine gasoil or marine diesel oil ranged between 0.15–2.0 mg kWh^{-1} . The ferries that used the heavier residual oil had much higher PAH emissions of 9.5 and 11 mg kWh^{-1} . This difference is attributed to higher PAH content in heavier residual oil than marine gasoil and diesel oil. HMW-PAHs such as BaP, DBA, IND and COR are more abundant in heavier residual oil than diesel fuel (Sippula *et al.*, 2014).

Since research on PAH emissions from ship's main and auxiliary engines is limited, few studies have been carried on the effect of emission control strategies on these pollutants. Efforts to replace heavier residual oil in marine vehicles with other fuels that result in less pollution has been underway with other studies looking at the possibility of using liquefied natural gas (Burel *et al.*, 2013; Anderson *et al.*, 2015). Though these studies did not include an analysis of PAH emissions, the significant reduction of PM in their studies could also suggest a decrease in PAH due to the slight correlation of the two (Baral *et al.*, 2011).

Because marine fuel is of low quality and cheaper, the illegal use of the fuel in heavy duty diesel vehicles has been reported. Lin *et al.* (2006b) studied the effect of using fishing boat fuel oil (FBFO) in heavy duty diesel vehicle versus premium diesel fuel and found that the PAH concentration was much higher when FBFO was used. The content of total-PAHs in FBFO was 25.3 wt%, which was 1.04 times higher in magnitude than premium diesel fuel. The total-PAH concentration for FBFO used was 4230 $\mu\text{g Nm}^{-3}$, while that from premium diesel fuel was 1320 $\mu\text{g Nm}^{-3}$. The mean total-BaP_{eq} concentration of FBFO was 19.3 $\mu\text{g Nm}^{-3}$ which was 5.47 times higher than premium diesel fuel. LMW-PAHs were the most dominant species in all the fuels followed by MMW-PAHs then HMW-PAHs. All these PAHs were higher in FBFO than in premium diesel fuel. The total-PAH emission factors were 51.5 mg L^{-1} of FBFO and 15.8 mg L^{-1} of premium diesel fuel, while that of total-BaP_{eq} emission factors were 0.235 mg L^{-1} of FBFO and 0.0404 mg L^{-1} of premium diesel fuel. Therefore, the illegal use of FBFO in heavy duty diesel engines of traveling vehicles could significantly increase the emissions of PAHs

both in terms of quantity and toxicity. The possible measures to reduce the illegal use of FBFO in Taiwan were studied by Wu *et al.* (2010). In their work, they added 0.5 vol% of the residue from the desulfurization unit (RDF) and pyrolysis fuel oil (PFO) to the FBFO to make the fuel distinguishable from premium diesel fuel and also damaging to heavy duty engines of traveling vehicles. The total-PAH and total-BaP_{eq} emission concentration of RDF0.5 and PFO0.5 fueled engines were 2062 $\mu\text{g m}^{-3}$ and 9.21 $\mu\text{g m}^{-3}$, and 2011 $\mu\text{g m}^{-3}$ and 12.5 $\mu\text{g m}^{-3}$, respectively. Both the total-PAH emissions from engines fueled by the blends were higher than from FBFO fueled engines, which was 1923 $\mu\text{g m}^{-3}$. However, the total-BaP_{eq} emission factor from the FBFO fueled engines were higher, 12.8 $\mu\text{g m}^{-3}$, than from emissions from the engines fueled by the two blends. They also found that the inclusions of these additives changed the color of FBFO to brown in test tube samples. These new blended FBFO, represented as RDF0.5 and PFO0.5 had higher viscosities which generally lead to high carbon formation, injector coking, piston ring sticking, lubrication oil dilution and oil degradation (Agarwal, 2007).

PAH Emissions from Diesel Fueled Generator

Diesel fueled generators have been widely used as an emergency electricity power source in commercial and residential areas especially in countries that experience rampant power outages (Rajput and Lakhani, 2009). Most of the studies on PAH emissions from these generators have also focused on the effect of using diesel fuel blends like with biodiesels, diselholts (blends of diesels, biodiesels, and alcohols), and acetone-butanol-ethanol (ABE) solution on the emissions (Lin *et al.*, 2010; Tsai *et al.*, 2010; Tsai *et al.*, 2014).

Tsai *et al.* (2011) found that mean total-PAH and total BaP_{eq} concentrations from a diesel generator to be 114 and 2.97 $\mu\text{g Nm}^{-3}$, respectively. The emission factors of the total-PAHs were 31.6 and 0.82 mg L^{-1} fuel for total-BaP_{eq}. LMW-PAHs were the most dominant in the exhaust of the diesel generator. The study also compared the PAH concentrations and emission factors when diesel fuel blended with waste-edible-oil biodiesel was used instead. The blend with 20% waste-edible-oil biodiesel had the least total-PAH and total-BaP_{eq} concentrations and emission factors. A different study by Lin *et al.* (2006a) showed the mean total-PAH and total-BaP_{eq} emission factors from the exhaust of pure fossil diesel fueled generator were 1110 and 1.65 $\mu\text{g L}^{-1}$, respectively. In the same study, the diesel blends with higher palm-biodiesel composition had lower PAH emissions. This was attributed to the less PAH content present in the palm-biodiesel fuel than diesel. Tsai *et al.* (2010) presented a similar result using soy-biodiesel and diesel blends. However, total-PAH emissions were found to be higher when the ratio of soy-biodiesel diesel blend was 50/50 which may be due to incomplete burning of the fuel blend. Therefore, biodiesel blends can be used in generators to reduce the PAH emissions and also reduce the amount of fossil diesel used.

However, the use of biodiesel blends could increase emissions of carbonyls such as formaldehyde, acetaldehyde, acrolein, acetone, propionaldehyde, butyraldehyde, and

benzaldehyde (Turrio-Baldassarri *et al.*, 2004; Correa and Arbilla, 2008). Also, because biodiesels have a lower heat value than petroleum diesel, more fuel gets consumed by the generator. The ratio of biodiesel to pure fossil diesel is a critical factor in total-PAH emission, energy efficiency, the brake specific fuel consumption (BSFC) and brake specific energy consumption (BSEC). The engine efficiency correlates negatively with this ratio while BSFC and BSEC correlates positively (Tsai *et al.*, 2011).

Some researchers have also studied the reduction of PAHs in diselholts fueled generators (Lin *et al.*, 2010) and ABE solution (Lin *et al.*, 2012). However, another major drawback of these fuel reformulation strategies is the increased NO_x emissions which have led to the research on water-addition in the diesel blends. Tsai *et al.* (2014) showed that the addition of water and water containing acetone or pure acetone in waste-edible-oil-biodiesel diesel blend significantly reduced the total-PAH and total-BaP_{eq} concentrations in the exhaust emissions of generators. For example, adding 1 vol% of water and 1–3 vol% of water containing acetone or pure acetone to diesel decreased the total-PAH and total-BaP_{eq} concentrations by 3.98–16.1% and 0.69–17.5%, respectively.

Output/Input Ratios of PAHs

This study would like to point out that PAHs are to a greater extent, destroyed in combustion processes rather than being formed during combustion process. The mechanisms of formation and destruction of PAHs in combustion processes are very complex and thus mass balance studies that use output and input ratios (O/I) to explain the fate of PAHs are confirmatory of this observation (Wang *et al.*, 2012). If an O/I ratio is greater than one it implies that PAHs are formed in the process, while an O/I ratio less than unity shows that the PAHs in the input material are destroyed in the combustion process. For example, Van Caneghem and Vandecasteele (2014) reported that the input/output ratio ranging between 100 to 2600 for a fluidized bed combustor dealing with various types of industrial wastes, which had a destruction-efficiency greater than 99%. Vitrification of incinerator ash in coke bed furnace produced output/input ratios of about 0.063, 0.002 and < 0.001 for LMW-, MMW-, and HMW-PAHs, respectively correspond to a destruction efficiency of 99% (Kuo *et al.*, 2003).

Furthermore, Wang *et al.* (2002), reports that O/I ratios for an incinerator dealing with biological sludge were 0.12 and 0.085 for total PAHs and total BaP_{eq}, respectively while the corresponding ratios for co-combustion of biological sludge and terephthalic acid were 0.041 and 0.0047, respectively. For a diesel engine operating on diesel and diesel fortified with various amounts of H₂/O₂, the O/I ratios ranged from 0.003 to 0.1 for total PAHs by mass basis and from 0.005 to 0.08 on a total BaP_{eq} basis (Wang *et al.*, 2012). In another study, Lin *et al.* (2006a) evaluated O/I ratios for an engine run with diesel and blends of diesel and palm biodiesel. In the study, the O/I ratios ranged at 0.025–0.049 and 0.0034–0.0071 for total-PAHs and total-BaP_{eq}, respectively. On the contrary, Rajput and Lakhani (2009) notes that even though the LMW-PAHs were depleted in diesel engine, the HMW-

PAHs were pyrosynthesized in the process leading to an O/I ratio greater than unity.

PAHs Homologues

More importantly the type of source of PAHs is indicative of the compositions of the PAH mixtures (Yang *et al.*, 1998; Dimitriou-Christidis, 2006) or rather normalized PAHs in the atmosphere and PAH profiles are indicative of their sources (Chen *et al.*, 2003a; Wheatley and Sadhra, 2004) especially due to the compositional differences owing to difference in fuels (Yang *et al.*, 1998). Usually principal component analysis and diagnostic ratios are employed to determine the relationship between the composition of PAHs in receptor sites and those from possible sources (Manoli *et al.*, 2004; Kong *et al.*, 2011; Amodio *et al.*, 2013). Other strategies used for source identification include positive matrix factorization and spatial distribution analysis (Larsen and Baker, 2003; Jang *et al.*, 2013).

For most stationary combustion sources, the LMW-PAHs are dominant in the stack flue gases especially in the gaseous phase due to high temperatures, while in the bottom ashes and fly ashes, the MMW-PAHs and HMW-PAHs that are major contributors (Lee *et al.*, 2002). The removal efficiencies from the wet scrubber are lower for the LMW-PAHs which exist majorly in the gaseous phase compared to the MMW- and HMW-PAHs that are attached to particulate matter (Lee *et al.*, 2002). Similarly, Chen *et al.* (2003a) points out that the LMW-PAHs were the majority in the gas phase, especially Nap, AcPy, PA, FL and Pyr, while the HMW-PAHs were dominant in the particulate phase of the stack flue gases as well as the wet scrubber effluent. (Yang *et al.*, 1998) reports that the contributions of Nap to the total emission factors of blast furnace, basic oxygen furnace, coke oven, electric arc furnace, heavy oil plant, power plant, cement processing were 90%, 92%, 79%, 72%, 68%, 78% and 60%, respectively with the contribution from the LMW-PAHs averaging at 75%. On the other hand, Nap is bicyclic, thus not really polycyclic (Yang *et al.*, 1998). In another study (Lin *et al.*, 2011b) showed that the main PAHs emitted from a boiler fueled with normal petroleum heavy oil and waste water emulsified heavy oil were Nap, PA, FL and Pyr. For the incineration of three plastics; polyvinylchloride, high-density polyethylene, and polypropylene, the main congeners were the Nap, AcPy, Acp, and Flu (Li *et al.*, 2001), while Li *et al.* (1999) reports Nap, FL, Pyr, and PA as the dominant congeners in boilers operated with different fuels. Combustion of joss paper during religious ceremonies emits Nap, PA, Flu, and AcPy as the highly contributing PAHs (Yang *et al.*, 2005c). For fly ashes from a hospital waste incinerator, the dominant congeners were Flu, BbF, IND, Pyr, PA (Zhao *et al.*, 2008).

Indicator PAHs

The composition differences of PAHs in the waste streams of various sources are dependent of the feedstock and fuels used in the various processes (Khalili *et al.*, 1995). These differences in PAH profiles or ratios of particular select PAHs can be used for source tracing and identifications purposes (Yang *et al.*, 1998). To define the indicator PAHs

from a particular source the following equation can be employed (Yang *et al.*, 1998):

$$\text{Ratio}_{ji} = \frac{(X_i / \sum X)_j}{(X_i / \sum X)_{\min}} \quad (1)$$

where:

X_i is the total gas and particle concentration of the i th individual PAH;

$(X_i / \sum X)_j$ is the ratio between the concentration of the i th individual and the total PAH concentration from an emission source j ;

and $(X_i / \sum X)_{\min}$ is the ratio between the concentration of the i th individual and the minimum of the total PAH concentration from all emission sources.

Using the same equation, Yang *et al.* (1998) evaluated the indicator PAHs for various sources and found out that for steel industry the indicator PAHs are 4- and 5-ringed PAHs, while for the cement industry they are the 3 ringed PAHs similar for the mobile sources. The detailed information is as follows: BaP and BaA (blast furnace), PER and BeP (basic oxygen furnace in the steel industry), BaP and COR (coke furnace in the steel industry), CYC and PER (electric arc furnace in the steel industry), AcPy, Acp and Ant (cement industry), CYC and DBA (coal fired power plant) and finally CYC and BaP (heavy oil burners) (Yang *et al.*, 1998). As for other sources the indicator PAHs include IND, and CHR for industrial waste incinerator, AcPy and FL for diesel vehicle and Flu and CHR for gasoline powered plant (Yang *et al.*, 1998). In their study, Khalili *et al.* (1995) identified Nap, AcPy, Flu, PA, FL and Pyr as indicator PAHs from traffic sources, diesel engines and gasoline engines, while in coke ovens the indicator PAHs were Nap, AcPy, PA, Flu, Ant, and FL. As for wood combustion, the indicator PAHs included AcPy, Nap, Ant, PA, BaP and BeP (Khalili *et al.*, 1995). The PAH profiles were studied for steel and iron industries operating on different fuels and the reported indicator PAHs were BaA, BkF, BghiP for coal fuel fired plants, BaP, Acp, AcPy for heavy fuel oil operated plants and COR, Pyr, BbC for electricity fueled plants (Yang *et al.*, 2002). A study by Kwon and Choi (2014) used diagnostic PAHs at many heavy industry sites, including a thermal power plant, carbon plant, calcium carbide factory, paper mill, pharmaceutical factory and industrial park which shared common diagnostic PAHs such as PA, FL, Pyr, and CHR, while the distinctive PAH emissions from a ferroalloy plant were BaA and BaP. Additional indicator PAHs from various sources are presented in Table 3.

Indicator PAHs can also be presented as the particle bound content obtained by dividing the dry deposition PAH mass by the total dry deposition mass of particles in terms of $\mu\text{g g}^{-1}$. Sheu *et al.* (1997) evaluated the indicator PAHs in terms of particle bound content from traffic, urban and petrochemical industrial sites. For the traffic site, the indicator PAHs for $\text{PM}_{1.0}$ were IND ($1450 \mu\text{g g}^{-1}$), PER ($1100 \mu\text{g g}^{-1}$), BeP ($711 \mu\text{g g}^{-1}$) similar to those in $\text{PM}_{2.5}$ whereby the indicator PAHs were IND ($1450 \mu\text{g g}^{-1}$), PER

(1180 $\mu\text{g g}^{-1}$), BeP (490 $\mu\text{g g}^{-1}$), while for PM_{10} the indicative PAHs were IND (574 $\mu\text{g g}^{-1}$), PER (472 $\mu\text{g g}^{-1}$), BbF (174 $\mu\text{g g}^{-1}$). As for the urban site, the indicative PAHs for various particle sizes were PER (192 $\mu\text{g g}^{-1}$), IND (174 $\mu\text{g g}^{-1}$), BkF (153 $\mu\text{g g}^{-1}$) for $\text{PM}_{1.0}$, PER (168 $\mu\text{g g}^{-1}$), IND (143 $\mu\text{g g}^{-1}$), BbF (98.6 $\mu\text{g g}^{-1}$) for $\text{PM}_{2.5}$ and PER (142 $\mu\text{g g}^{-1}$), IND (114 $\mu\text{g g}^{-1}$), BkF (92.8 $\mu\text{g g}^{-1}$) for PM_{10} . At the petrochemical industrial site, the corresponding indicative PAHs in terms of particle bound content were IND (174 $\mu\text{g g}^{-1}$), PER (113 $\mu\text{g g}^{-1}$), BbF (77.3 $\mu\text{g g}^{-1}$) for $\text{PM}_{1.0}$, IND (125 $\mu\text{g g}^{-1}$), PER (87.6 $\mu\text{g g}^{-1}$), BbF (45.0 $\mu\text{g g}^{-1}$) for $\text{PM}_{2.5}$ and IND (99.6 $\mu\text{g g}^{-1}$), PER (86.2 $\mu\text{g g}^{-1}$), BbF (35.9 $\mu\text{g g}^{-1}$) for PM_{10} . These results show that PAH are mostly contained in the fine particles as a result of a higher specific surface area and greater amounts of organic carbon which allow more PAH adsorption (Sheu *et al.*, 1997).

Indoor and Outdoor PAH Sources

Human beings spend a significant part of our lives indoors which makes the study of the PAH emission sources in the indoors quite vital. Apart from outdoor sources of PAH emissions in the indoor due to the air exchange, some indoor activities have been shown to be significant sources of PAH e.g., heating, cooking, and smoking. The degree to which indoor air compositions are influenced by outdoor environments compared to the effects of typical indoor activities is of great concern. Samples of indoor air within homes have been characterized and compared with the outdoor air in several studies and it has been clearly demonstrated that indoor and outdoor PAH concentrations match either well or poorly depending on the urban context, the nature of the pollution source, and the meteorological contour, as well as the infiltration rate of particles to the indoors (Romagnoli *et al.*, 2014).

Indoor Sources

Krugly *et al.* (2014) employs diagnostic ratios (DR) and principal component analysis (PCA) to identify the possible sources and evaluate exposure of children to PAHs in primary schools. The sampling for the PAHs was done during winter time. The targeted sites were five primary schools whereby, their locations in the city, ventilation type, heating system, vehicle traffic intensity, cooking among others were considered. Naphthalene had the highest concentration in all the sampling sites, ranging from 0.1–1153 ng m^{-3} . The indoor/outdoor ratio of the low molecular PAHs (Naphthalene, Fluorene and phenanthrene) were close and sometimes exceeded unity. This indicated an indoor source for these PAHs. For the DR, when $\sum\text{LMW}/\sum\text{HMW} > 1$, petrogenic sources is a possible source for PAH while pyrogenic source is indicated with the ratio being less than unity. The results from this ratio gave unexpected results. All the samples were above unity suggesting a pyrogenic source. This ratio has been deemed as very crude by some studies (Galarnau, 2008).

Tobacco smoke is identified as a major source of indoor PAHs in several studies with one study reporting that the concentration of BaP in a heavy smoker's home was approximately 10 times greater than that in a no-smoker's

home. However, cooking and heating are the main indoor sources for indoor PAHs emissions.

Outdoor Sources

Outdoor PAHs have been shown to exhibit wider variability, which could depend on the features of the environmental contours and vehicles at a site.

A study by Naumova *et al.* (2002) targeted the worst-case locations in terms of outdoor sources of air pollution. The homes were chosen based on their proximity to the identified sources. They recorded very high concentrations. The MMW-PAH signatures of the outdoor sample were not significantly different in the three cities in USA. However, the HMW-PAH signature differed significantly which suggested the cities had different major outdoor sources. The HMW-PAH signature of the indoor air in each city were similar to that of the outdoor concentrations suggesting that the outdoor was the dominant source of these high molecular weight PAHs.

Effect of seasons on the PAH concentration has also been studied. Winter has been characterized by higher PAH concentrations, while summer the lowest. This observation has been attributed to poor dispersion and chemical decomposition during winter time. The reverse is likely to occur in the summer when the presence of ozone promotes a further decrease in PAHs.

Indoor/outdoor ratios have been used in various studies to provide a rough identification of the pollution origin (Krugly *et al.*, 2014).

In highly urbanized areas, domestic heating and mobile sources are the principal sources of PAHs (Cheng *et al.*, 2007).

PAH Concentration in the Ambient Air of Urban and Rural Areas

The industrialization and increase in automobiles has significantly contributed to the rising levels of air pollution, especially in large urban areas. Numerous studies of atmospheric PAHs conducted in Europe, North America, and Northeast Asia have found that vehicular traffic emissions were the major contributors of PAHs in the urban atmosphere and many recent studies have focused upon traffic as a source of PAH in the urban areas (Lee *et al.*, 1995; Nielsen, 1996; Lin *et al.*, 2008a; Wingfors *et al.*, 2001).

In a study by Slezakova *et al.* (2013), where they employed correlation matrices to determine the correlation coefficients of PAH and other air pollutants (SO_2 , NO_2 , $\text{PM}_{2.5}$), relative humidity, wind speed and ozone. The results indicated that SO_2 , NO_2 , PM_{10} , CO, and solar radiation had positive correlation with PAH concentrations while O_3 and relative humidity and wind speed were negatively correlated. The total-PAH concentration from the study ranged between 16.8–149 ng m^{-3} and with a mean of 70 ng m^{-3} . Three ringed PAHs were the most abundant in air accounting for 53% of the total PAHs. This is expected because the low molecular weight of these PAH compounds. Phenanthrene had the highest concentration followed by acenaphthylene, fluorene, pyrene and fluoranthene with contributions of 27, 11, 9.4, 9.5, and 8.6%, respectively, to the total PAH concentration.

PAH Concentration in the Ambient Air of Heavy Industrial Cities

Heavy industrial cities are characterized by high number of manufacturing and chemical industries e.g., petrochemical, iron and steel etc. The activities of these industries have resulted to a significant contribution to the air pollutant emissions among other environmental problems. PAH emission sources from these cities have been found to be higher than those from both rural and urban areas (Kwon and Choi, 2014). This is due to the PAH contribution from the industrial complexes. Other sources of PAHs in these cities are vehicular sources which have been reported to be major PAH sources (Song *et al.*, 2015). Receptor models e.g., diagnostic ratios have also been used to identify other various sources that contribute to the PAH emissions. The results from these models have shown that some industries have unique PAH profiles e.g., heavy industry sites, including a thermal power plant, carbon plant, calcium carbide factory, paper mill, pharmaceutical factory and industrial park shared a common diagnostic PAHs signature (phenanthrene, fluoranthene, pyrene, chrysene) while the distinctive PAH emissions from ferroalloy plant were BaA and BaP (Kwon and Choi, 2014; Song *et al.*, 2015). Song *et al.* (2015) studied the PAH emissions from old heavy industrial cities in northern China. Their results showed that a petroleum resource city dominated with petrochemical industries had higher proportions of LMW- and MMW-PAHs while a chemical processing city had higher proportion of MMW- and HMW-PAH at the industrial sites.

Street dust has been used in most studies to analyze PAH in heavy industrial cities. This is because it is regarded as a sink of urban pollutant emissions and works as the major source of pollution in runoff (Boonyatumanond *et al.*, 2007). Kwon and Choi (2014) found the mean total-PAH content in soils of a multi-industrial city in South Korea was 960 ng g⁻¹. They used diagnostic ratios and the positive matrix factorization model to identify the sources of the PAHs in the soil. They found that vehicles and industrial complexes to be the major sources of PAHs in the city with diesel vehicles emissions contributing to over 50% of the total-PAHs.

Various studies have determined the ambient concentrations of PAHs in industrial areas of various cities and even compared with residential or rural areas. For example, Rehwagen *et al.* (2005) compared the concentrations of PAHs in the ambient air of La Plata (industrial, traffic influenced and control area), Argentina, and Leipzig (traffic influenced and control area), Germany. The results were such that the average total PAHs concentrations for the industrial area in La Plata was 7.26 n m⁻³ which was about 1.53 and 5.48 times greater than traffic-influenced and control areas of La Plata and 3.49 and 4.75 times higher than traffic-influenced and control areas of Leipzig, German. Another study by Fang *et al.* (2004) carried out in central Taiwan showed that the mean concentration of PAHs in Taichung industrial park were about 1230 ng m⁻³ which was 2.02 times higher than the values at Tunghai University Campus located in a suburban area. A study done at various sites in New Jersey, USA, shows that, the total PAH concentration in

the ambient air of an industrial site was 76.2 ng m⁻³ which was 3.22 times greater than at a background site but 1.29 and 1.26 lower than at a commercial and mobile sources sites (Lin *et al.*, 2011c). These observations were attributed to combustion processes involving coal, wood, and petroleum-derived fuels at the industrial areas (Fang *et al.*, 2004).

FATE OF PAHS IN THE ATMOSPHERE

Gas-Particle Partitioning of PAHs

Previously it has been shown that gas-particle partitioning of PAHs is an equilibrium process resulting from adsorption, absorption and dynamic mass transfer mechanisms (Yamasaki *et al.*, 1982; Pankow, 1987; Pankow and Bidleman, 1991, 1992). The gas-particle partitioning of PAHs in the atmosphere generally depends on total suspended particle concentrations, ambient temperature, humidity and atmospheric mixing height as well as the vapor pressures of the PAHs and size and physiochemical properties of particles e.g., organic carbon content (Offenberg and Baker, 2002; Akyüz and Çabuk, 2010; Wu *et al.*, 2014).

Experimental data from various studies have used the models developed previously (Yamasaki *et al.*, 1982; Pankow, 1987; Pankow and Bidleman, 1991, 1992) to successfully simulate gas-particle partitioning as follows:

$$K_p = \frac{F/TSP}{A} \quad (2)$$

K_p : gas-particle partitioning constant (m³ µg⁻¹),

TSP : concentration of total suspended particulate material (µg m⁻³),

F : particle phase concentration of PAHs (pg m⁻³),

A : gaseous phase concentration of PAHs (pg m⁻³).

Plotting log K_p against the logarithm of the subcooled liquid vapor pressure (P_L^0), gives:

$$\log K_p = m_r \times \log P_L^0 + b_r \quad (3)$$

P_L^0 : subcooled liquid vapor pressure (Torr),

m_r : slope of a plot of log K_p vs log P_L^0

b_r : y-intercept in a plot of log K_p vs log P_L^0 (Lohmann and Jones, 1998).

According to (Venkataraman *et al.*, 1999) the presence of PAHs in the nucleation and accumulation mode can be attributed to the adsorption and absorption mechanisms. Specifically for fine particles, presence of PAHs in the nucleation mode is due to surface area dependent adsorption while the predominance in the accumulation mode is related to both surface area dependent adsorption as well as organic matter dependent absorption mechanisms (Venkataraman *et al.*, 1999). On the other hand, the adsorption-absorption mechanisms are not sufficient to explain the presence of PAHs in coarse particles but can be explained via dry deposition scavenging of both gaseous and nucleation mode PAHs (Venkataraman *et al.*, 1999).

Most studies show that LMW-PAHs consisting of 2–3 rings are mostly associated with gas phase, while the MMW-PAHs with 4 rings are equally distributed between

gas and particle phases, while those with 5–7 rings, the HMW-PAHs are primarily distributed in the particle phases (Akyüz and Çabuk, 2010). Additionally, Akyüz and Çabuk, (2010) showed that the temperature dependence of PAHs in the gas phase can be described by the Clausius-Clapeyron equation whereby the shallow slope showing low temperature dependence indicates long range transport, while steep slopes showing high temperature dependence indicates sources on the vicinity.

Studies by Akyüz and Çabuk (2010) and Fernández *et al.* (2002) indicate that seasonal variations in gas particle partitioning, especially for particle associated PAHs, were significant in the cold seasons owing to use of local heating.

For gas-particle partitioning in a traffic site, 90% were in the gas phase (Tasdemir and Esen, 2007). As for the individual congeners Nap, AcPy, Acy, Flu, PA, Ant, FL and Pyr the fractions of in the gas phase were above 90%, while for BaA, CHR, BbF, BkF, BaP, IcdP, DahA, and BghiP the fractions in the particle phase were above 80% (Tasdemir and Esen, 2007).

Particle Size Distribution of PAHs

As mentioned earlier the PAHs are partitioned between particle and gaseous phase. In this section, the particle size distribution (PSD) of the PAHs in the particles will be evaluated. Measurements of size distribution is usually done using low volume cascade impactors (Kawanaka *et al.*, 2004; Duan *et al.*, 2005; Wu *et al.*, 2006), Anderson Impactor (Venkataraman *et al.*, 1999) micro-orifice uniform deposit impactor (MOUDI) (Venkataraman *et al.*, 2002; Duan *et al.*, 2005), dry deposition plates and Noll Rotary Impactor (NRI) (Chen *et al.*, 1997; Sheu and Lee, 1998) including PM₁₀ high volume sampler (Venkataraman *et al.*, 1999; Oliveira *et al.*, 2011). Venkataraman *et al.* (2002), notes that knowing the relative abundance of various PAH species in particulate matter, allows us to evaluate the mutagenic/carcinogenic risks (Shen *et al.*, 2013) as well as the source identification. Additionally, the size distribution of PAHs affect the transport, atmospheric wet and dry deposition as well as deposition in the human respiratory system of PAHs (Kawanaka *et al.*, 2004; Kameda *et al.*, 2005; Wu *et al.*, 2006; Kwon *et al.*, 2013).

Generally, the PSD is unimodal and the mass median aerodynamic diameters (MMAD) are generally in the sub-micron size range (Venkataraman *et al.*, 2002; Yang *et al.*, 2005a). The size distribution of PAHs is dependent on the vapors pressure of PAHs and the adsorption and absorption affinity based on physical and chemical characteristics of the particles (Venkataraman *et al.*, 1999). Other factors that affect size distribution include type of source especially fuel used, distance from the source and season variations (Duan *et al.*, 2005). The mechanisms responsible for size distribution of PAHs include adsorption to nucleation mode particles, adsorption and absorption to accumulation mode particles and multilayer adsorption to the coarse particles (Duan *et al.*, 2005).

Venkataraman *et al.* (2002) while evaluating the size distribution of PAHs emitted from combustion of wood, dung cake and biofuel briquette, found out that the MMADs were

in the range of 0.40–1.10 μm . These observations were similar to the study by Kawanaka *et al.* (2004), whereby the distribution of total PAHs and individual PAHs was unimodal with a MMADs range of 0.48–0.68 μm and the PAH size distribution in Helsinki was unimodal with the peak appearing at 1.0 μm . In a previous study Venkataraman *et al.* (1999) characterized the size distribution of PAHs $dC/(d\log Dp)^{-1}$ in urban aerosols from Mumbai, India. In this study the PAH size distribution were bimodal whereby the fine mode mass median diameter were ranging from 0.38 to 0.45 μm , while the coarse mode mass median diameters were ranging between 2.7 and 4.7 μm with about 55% of the particle size being in the submicron range (Venkataraman *et al.*, 1999). Mostly, the semi-volatile PAHs are dominant in the coarse modes, while the non-volatile PAHs are found in the fine modes (Venkataraman *et al.*, 1999).

Similar comparisons were made for size distributions of PAHs from combustion of fuel wood, brushwood and bamboo in China (Shen *et al.*, 2013). In this study, the highest fraction 39.4% of PAHs were associated with PM with diameter 0.4–1.1 μm for fuel wood and bamboo, while for brushwood the largest fraction was associated with PM with size range 2.1–10 μm . The corresponding MMAD for fuel wood, brushwood and bamboo were 0.75, 1.4 and 0.92 μm , respectively, which were significantly different for the three kinds of fuels.

The particle size distribution of PAHs for a petrochemical industry site and urban site in Southern Taiwan were previously studied by Sheu and Lee (1998) such that the mean mass diameters of PAHs from the petrochemical site were higher than those at the urban site. The overall MMD were 1.61 and 1.28 μm , for petrochemical site and urban site, respectively. The differences in MMD from the two sites were due to the fact that the emission of PAHs in urban sites from vehicle exhaust were mainly in the submicron fractions (Sheu and Lee, 1998).

A study by Wu *et al.* (2006) compared size distributions of PAHs between urban and rural sites in China. In this particular study, there were no significant differences between the size distribution in urban and rural areas from the $dC/(Cd\log Dp)$ vs. $\log Dp$. The results showed that the LMW-PAHs are majorly distributed in the accumulation and coarse modes while the MMW- and HMW-PAHs are distributed in the accumulation mode size range (Wu *et al.*, 2006). The reasons for these observations were cited to include the fact that distribution of LMW-PAHs in coarse particles are due to differences in size distributions and different gas-partitioning behavior considering that the LMW-PAHs are emitted in gaseous phase and then get associated with coarse particles via volatilization and condensation. On the other hand, the HMW-PAHs take longer time to partition between gas and particle phases owing to their lower subcooled vapor pressure and Henry constants thus they are found mostly in finer particles (Duan *et al.*, 2005; Wu *et al.*, 2006).

The ambient air in a bus station in southern Taiwan had a dominant unimodal PAH particle distribution mainly in the submicron range (0.056–1.0 μm) which has more surface area that allows PAHs to adsorb onto organic

fraction of particles. The findings can be explained by the fact that the accumulation and condensation of young aerosols from vehicular emission were majorly responsible for PAHs in particles while the lower PAH presence in coarse particles can be from resuspension of aged particles. (Oliveira *et al.*, 2011) conducted studies in one of the longest urban road tunnel in Portugal, and the size distribution of PAHs in the PM₁₀ was bimodal with highest concentrations in the fine particles (84%) and about 1.8% in the coarse particles. In the same study, the more volatile PAHs were not detected in abundance, since they are emitted in gaseous phase. In a similar study in Guangzhou, China the size distribution of LMW-PAHs was trimodal with peak appearing in nucleus mode (0.1 μm), accumulation mode (0.7 μm) and coarse mode (3 μm) (Duan *et al.*, 2005). The distribution in fine particles was attributed to fresh emissions from high temperature sources, while the accumulation mode represents condensation of PAHs on preexisting aerosols. The distribution on coarse particles is generally due to volatilization of PAHs from fine particles and condensation onto coarse particles (Duan *et al.*, 2005). As for the MMW-PAHs the distribution was generally bimodal (accumulation and smaller coarse modes), while that of HMW-PAHs was unimodal (accumulation mode). Most of the PAHs are distributed in the accumulation mode with 60% of LMW-, 75% of MMW-, and 90% of HMW-PAHs being abundant in sizes between 0.1 and 1.8 μm (Duan *et al.*, 2005).

On evaluating the PAH distribution from the exhaust of four stroke gasoline fueled motorcycle (Yang *et al.*, 2005a) found out that the size distribution of total PAHs was bimodal with the peaks appearing at 0.056–0.1 μm and 0.18–0.32 μm . The bimodal distribution was as a result of formation of PAHs in accumulation mode due to incomplete combustion and nucleus mode. The corresponding cumulative frequency shows the cumulative fractions associated with diameters less than 1.0 μm and 2.5 μm were 77.0% and 84.3%, respectively while the MMD for PAHs was 0.45 μm .

Sugiyama *et al.* (2000) assessed the differences between the particle size distribution of the indoor and outdoor aerosols and found out that the PAH contributions were highest in particles with aerodynamic diameter less than 2.5 μm for both indoors and outdoors. On the other hand, the proportions of PAHs on the indoor fine particles were higher than the proportion in outdoor particles.

Seasonal variations can be exemplified by the study of Lee *et al.* (2008) in which the PAH particle size distributions for summer were bimodal (ranging between 0.43–0.65 and 4.7–5.8 μm) while those for winter were unimodal (range of 0.65–1.1 μm). Lack of a coarse fraction peak in winter is due to lower temperatures resulting to reduced gas-particle partitioning via volatilization.

The size distribution of particle bound total-PAH content was evaluated by Sheu *et al.* (1997) whereby the smaller particle with sizes 0.056–3.2 μm had greater PAH content compared to the coarse particles with sizes larger than 3.2 μm . This because the coarse particles mostly are aged particle with mostly inorganic content, while the smaller sized particles have higher surface areas and are usually made up of soot with high affinity to PAH attachment

(Sheu *et al.*, 1997). The cumulative fraction of particle size distributions for total PAHs for particle sizes below 1, 2.5, 10 and 25 μm were 51%, 74%, 91% and 96% at a traffic intersection and 38%, 56%, 86% and 94% at rural site, respectively (Sheu *et al.*, 1996c).

Dry and Wet Deposition of PAHs

After being partitioned between particle and gas phase in the atmosphere, the next fate of PAHs in the atmosphere include deposition and transport. Deposition is the scavenging action or removal of pollutants from the atmosphere onto receptor sites such as soil, vegetation, water bodies, which are the final sinks and is of importance as it shows the exposure level of the population to the air toxics (Chandra Suryani *et al.*, 2015). Dry and wet depositions are the two major types of atmospheric deposition of SVOCs.

Dry deposition involves adsorption of SVOCs onto particles from the atmosphere at the air-surface interface (Davidson and Wu, 1990a; Wu *et al.*, 1992). The main mechanisms through which dry deposition occurs are: aerodynamic transport, boundary layer transport, and interactions with the receptor surface (Giorgi, 1988; Davidson and Wu, 1990b). Dry deposition is the dominant removal mechanism for coarse particles, which are easily affected by gravity, during non-precipitation days (Giorgi, 1988) and is affected by wind, temperature, humidity, size and shape of particles as well as the surface characteristics of particles (Giorgi, 1988; Oh *et al.*, 2002; Moon *et al.*, 2005; Wang *et al.*, 2010; Fang *et al.*, 2011; Amodio *et al.*, 2014).

On the other hand, wet deposition is the major removal mechanism during precipitation periods and involves scavenging of SVOCs bound to particles and gaseous phase SVOCs by action of rainfall, snow, mist or cloud droplets (Moon *et al.*, 2005; Melymuk *et al.*, 2011). The overall wet deposition is a summation of SVOCs dissolved into the precipitation and the SVOCs bound to particles scavenged by precipitation (Chandra Suryani *et al.*, 2015).

Dry deposition is determined using adsorption surrogate surfaces like a smooth plate made of polyvinyl chloride similar to the ones employed in wind tunnels with a sharp leading edge mounted on a wind vane and covered with aluminum strips coated with silicon grease to collect impacted particles and gaseous phase PAHs (Sheu and Lee, 1998). These kinds of surrogate surfaces present a problem in the fact that they are not representative of the interaction between the SVOCs and the natural surfaces (Lee and Lee, 2004). Glass buckets can be used to estimate bulk deposition (dry +wet) (Zhang *et al.*, 2008). An improved atmospheric PAH deposition collector has been developed by Lee and Lee (2004) which avoided problems of channeling and drying up of adsorption surface during dry periods, while using surrogate solution made of deionized water and methanol increased the Henry's law constant of PAHs allowing them to be dissolved better than just plain water. Another study by Birgöl *et al.* (2011), also utilized an automatic wet-dry deposition sampler (WDDS), which has a rain sensor to allow closing of the dry deposition part and opening the wet deposition part depending on weather conditions. Another method of deposition determination involves monitoring

PAH concentrations in gaseous and particulate poses and deposition obtained by multiplying the deposition velocity with ambient concentrations of PAHs (Zhang *et al.*, 2008).

Dry deposition is dependent on site, sources, atmospheric concentrations and meteorological conditions as reported by Sheu and Lee (1998), whereby the total PAHs deposition fluxes at a Petrochemical site were approximately 1.4 times greater than those recorded at an urban site. Clear differences depending on the season were observed by Lee and Lee (2004) such that the atmospheric deposition of PAHs were much higher in winter than in summer, which was attributed to higher temperatures in summer which reduced atmospheric deposition of gaseous phase PAHs. Additionally, in winter, increased use of fossil fuels for heating purposes and lower mixing heights were the main factors responsible for higher PAHs depositions. In the study, the dry deposition and wet deposition fluxes recorded in winter were approximately 5 and 38 times higher than those in summer, respectively. A study by Sheu and Lee (1998), reported the mean dry deposition fluxes from a petrochemical industrial site in Taiwan to be 253, 132, and 204 $\mu\text{g m}^{-2} \text{day}^{-1}$ for months of April/May, June and November, respectively. In the same study, the dry deposition fluxes in an urban area averaged at 153, 141 and 143 $\mu\text{g m}^{-2} \text{day}^{-1}$ for months of March, April and May respectively (Sheu and Lee, 1998).

In a previous study, Sheu *et al.* (1996b) had evaluated the dry deposition velocities at traffic intersections in Taiwan and found that they ranged between 0.20 and 0.43 cm sec^{-1} for day times and 0.16 and 0.25 cm sec^{-1} for night times. The deposition velocities for total PAHs assessed for an urban site and a petrochemical industrial site were in the range of 0.15–0.28 cm sec^{-1} and 0.19–0.36 cm sec^{-1} , respectively (Sheu *et al.*, 1996a). The same study found out that the deposition velocities of HMW-PAHs were 2 magnitude higher than those of LMW-PAHs because the LMW-PAHs were mainly in gaseous phase whose deposition occurred by diffusion. About 5% of the total PAH dry deposition fluxes reported by Sheu *et al.* (1996a) were contributed by the gas phase, while 95% by particulate phase.

Additionally, in a subsequent study Sheu *et al.* (1997) reports that for LMW-PAHs a larger fraction of their deposition fluxes was contributed by the gas phase, while for the HMW-PAHs the fraction contributed by the gas phase was less than 3%. Cumulative fractions shows that based on the total mass of PAHs the particles with diameters larger than 10 μm contributed about 88–92% indicating that even though PAHs are more bound to fine particles, the coarse particles are responsible for the dry depositions via gravitational settling mechanisms (Sheu *et al.*, 1997).

In Ulsan Bay Korea, the mean dry deposition fluxes were 18.9 and 3.63 $\text{ng m}^{-2} \text{h}^{-1}$ in winter and summer respectively, while the wet deposition fluxes were 3280 and 85.5 $\text{ng m}^{-2} \text{cm}^{-1}$ for winter and summer seasons, respectively (Lee and Lee, 2004). Similar results were observed by Zhang *et al.* (2008) such that the trend of PAH deposition fluxes was winter > spring > autumn > summer. The bulk deposition fluxes in this study ranged from 3.10 to 5.31 $\mu\text{g m}^{-2} \text{day}^{-1}$ for 4 sites in Tongzhou District in China, and averaged at 5.14 $\mu\text{g m}^{-2} \text{day}^{-1}$ (Zhang *et al.*, 2008)

On the contrary, Bozlaker *et al.* (2008) reported that the atmospheric deposition of PAHs from an industrial region were higher in summer (5792 $\text{ng m}^{-2} \text{day}^{-1}$) than in winter (2650 $\text{ng m}^{-2} \text{day}^{-1}$) and attributed it to presence of resuspended soil and road dust particles. The bulk deposition of a total 12 PAHs in a park in Guangzhou city averaged at 1270 $\text{ng m}^{-2} \text{day}^{-1}$ (Li *et al.*, 2009). Birgül *et al.* (2011) presented the wet deposition, separately as average dissolved phase ($7.4 \pm 7.3 \mu\text{g m}^{-2} \text{day}^{-1}$) and particle phase $21 \pm 30 \mu\text{g m}^{-2} \text{day}^{-1}$, while the average dry deposition was $4.0 \pm 5.0 \mu\text{g m}^{-2} \text{day}^{-1}$, for Bursa city in Turkey.

Size Distribution of PAHs in Road Dusts

PAHs in road dusts are majorly derived vehicle exhausts fumes, lubricating oils, weathered materials of road surfaces, tire weathered particles, asphalt-paved roads, construction materials, and atmospherically deposition of PAHs (Boonyatumanond *et al.*, 2007; Dong and Lee, 2009; Lee and Dong, 2010). The amount and distribution of PAHs in the road dusts are affected by the type of road surface, type of vehicles, volume and speed of traffic on the roads as well as the activities in the vicinity of the roads, prevailing weather conditions and rate of atmospheric deposition (Liu *et al.*, 2007b; Hassanien and Abdel-Latif, 2008; Dong and Lee, 2009; Lee and Dong, 2010). In the road dust, the highest loading of PAHs are found in the light fractions as shown by the study by Murakami *et al.* (2005) whereby the light fraction particles constituted only 0.69–4% of total particle weight but contained 28–44% of the total PAHs. The size distribution of PAHs in road dust in terms of (df/dlogDp vs. Dp), where f is mass fraction of the certain particle-size interval and Dp the particulate matter aerodynamic diameter was unimodal for two traffic intersections in Kaohsiung City, Taiwan (Yang *et al.*, 1999). For two sites, the peak at 65.3 μm suggesting that the PAHs in road dusts are majorly due to PAH adsorption by the road dust (Yang *et al.*, 1999). This particle size distribution of PAHs in road dust is significantly different to the bimodal peaks of the ambient air, which are mainly in the fine particle regime.

TOXICITY AND CARCINOGENIC POTENTIAL OF PAHS

Toxicity and Biomarkers

Human being are exposed to PAHs through their work environments for example workers working in carbon black manufacturing industry (Tsai *et al.*, 2001; Tsai *et al.*, 2002a), highway booth tolls (Tsai *et al.*, 2002b, 2004a), sinter plants (Lin *et al.*, 2008c) including indoors (Chou *et al.*, 2015). Biomarkers are indicators of exposure or to quantify the effect, when an organism interacts with xenobiotic agents (ATSDR, 1995). Some of the PAH exposure biomarkers used in human studies include urinary 1-hydroxypyrene (Tsai *et al.*, 2002a, 2004b), urinary 8-hydroxy-29-deoxyguanosine (8-OHdG) and malondialdehyde (MDA) (Pan *et al.*, 2011), urinary 1-hydroxypyrene-glucuronide (1-OHPG) (Lai *et al.*, 2012), 1-nitropyrene, benzo[a] pyrene, and benzo[g,h,i] perylene, as well as some measurable DNA adducts and evaluation of mutations occurring due to PAH exposure

(ATSDR., 1995). On the other hand, the biomarkers used to characterize the effect of PAH exposure include measurements of DNA adduct formations, and/or quantifying the induction of sister chromatid exchange in human lymphocytes (ARSDR, 1995).

From various animal studies (Chen *et al.*, 2003b), PAHs and their derivatives are classified as mutagenic, tumorigenic and carcinogenic (Henner *et al.*, 1997; Yu, 2002) and even have teratogenic capacities (Włóka *et al.*, 2014). They have deoxyribonucleic acid (DNA) adducting and immunorepressive properties after being inhaled, ingested or assimilated into the body through dermal contact (Henner *et al.*, 1997; Dimitriou-Christidis, 2006; Lee and Dong, 2010). The HMW-PAHs, which are associated with particulate phase, are more toxic than that of LMW-PAHs or even the MMW-PAHs (Amodu *et al.*, 2013). The US EPA recognizes 16 PAHs that are highly toxic with benzo[a]pyrene being the surrogate and marker for the PAHs owing to its high human risk and availability in the environment (Pashin and Bakhitova, 1979; Skupinska *et al.*, 2004).

Some of PAHs in themselves are neither carcinogenic nor mutagenic but they form epoxides and diolepoxides after being metabolized in organisms' bodies which easily adduct to the DNA via covalent bonds (Yu, 2002). The epoxides have a higher capability of being adducted to nucleic acids in the body leading to malignant transformations (Pashin and Bakhitova, 1979). Therefore the more reactive sites the PAHs have the more toxic they are. For example, benzo[a]pyrene have reactive positions on which protons can be replaced forming bonds with nucleic acids resulting into malignant transformations and tumor formations (Pashin and Bakhitova, 1979). Another factor affecting the carcinogenicity and mutagenicity of PAHs is the degree of nonplanarity. Toxicity can also be induced via light activation when 3 to 4 ringed PAHs absorb UV light and get to excited states where they can easily generate reactive species that can damage cell membranes, nucleic acids and proteins (Yu, 2002). Possible human health effects from PAH exposure are skin inflammations, cataracts, kidney problems, liver defects and jaundice. Exposure to PAHs can lead to cancers of the lung, breast, skin and esophageal (Guo *et al.*, 2011).

Cancer Risk of Ambient Air PAHs

As mentioned earlier, various animal studies have shown PAHs to be cancer inducing in human beings from about 220 years ago, when soot in the London chimneys was associated with deteriorating health of chimney sweepers (Khalili *et al.*, 1995). The exposure routes of human being to PAHs in the ambient air include smoking of cigarettes, atmospheric deposition onto vegetables and food crops, which are ingested, breathing air loaded with gaseous and particle-adsorbed PAHs as well as via the skin. The larger PAHs which are generally associated with the particle phase are most toxic and have the highest carcinogenic potentials.

According to Nielsen *et al.* (1996), measurements of PAH content and mutagenic activity of the ambient air are indicative of the carcinogenic potential of the atmosphere, since there are numerous and complex mixtures of

carcinogenic compounds present in the atmosphere. One approach of evaluating the potency and toxicity of individual PAHs is using equivalent toxicity compared to BaP, which is assigned a relative potency of unity and these are summed up to obtain the total BaP_{eq} (Menichini *et al.*, 1999). Using this approach, Nielsen *et al.* (1996) investigated the cancer risk exposed to the population in Copenhagen during winter to be 22.8 lung cancer cases in one million individuals based on total-BaP_{eq} ng m⁻³ of 6.9 for a busy street. The corresponding figure for a park, was 6.6 cases in a million based on a toxicity value of 2.0 total-BaP_{eq} ng m⁻³. Other approaches include comparative potency approach, where either one can correlate the human risk to defined mutagenicity tests or correlate the mutagenicity of the ambient air to the specific BaP mutagenic activity (Nielsen *et al.*, 1996) all of which result in different exposure values. Menichini *et al.* (1999) did a carcinogenic risk assessment of six possible carcinogenic PAHs in Rome, Italy for a period of 5 years. The average profile of these PAHs was constant for the sampling period but seasonal variations were observed for each PAH/BaP ratio, whereby the highest were observed in summer as a result of the high number of daylight days and greater light intensity translated to increased degradation of BaP. According to Menichini *et al.* (1999), the seasonal variability does not alter the carcinogenic risk, since using the BaP relative ratios based on a few samples and short sampling period may result in overestimating or underestimating the carcinogenic burden of individual PAHs.

The exposure risk of workers and customers at night market in metropolis area in China was investigated by Zhang *et al.* (2015) using various equations to predict daily inhalation exposure levels (IEL), incremental lifetime cancer risk (ILCR), and estimation of maximum exposure time (t_{max}) all based on BaP concentration. Zhang *et al.* (2015) ascertained that the IEL ranged between 0.451–3.43 $\mu\text{g day}^{-1}$ and averaged at 1.75 $\mu\text{g day}^{-1}$, which presented considerable risk to night market workers. Considering the ILRC, the workers with less than 1 year experience had risk of the order 10^{-7} , which was lower than the acceptable risk of 10^{-6} as proposed by US EPA (Wu *et al.*, 2014), but those with an experience of 20 years they had risk above 10^{-6} , but still was lower than priority risk level of 10^{-4} . In the same study, the determined t_{max} were < 7 minutes for one year olds, < 11 minutes for three year olds, < 29 for ages between 5 to 10, < 57 minutes for 15 year olds, < 1.34 hours for 20 year olds and < 5.60 hours for 50 year olds (Zhang *et al.*, 2015). Other studies have also reported exposure risks for toll booth workers in Taiwan Highways (Tsai *et al.*, 2004a, b; Lai *et al.*, 2012), exposure of Taiwanese temple goers and workers from incense burning (Chiang *et al.*, 2009) and vendors of broiled food in Taiwanese night markets (Kuo *et al.*, 2006) as well as black carbon workers (Tsai *et al.*, 2001) and from wildland fire episodes (Pongpiachan, 2015).

CONCLUSIONS

Sources of PAHs are either anthropogenic or natural sources. Anthropogenic sources include chemical and combustion processes while the natural sources may include

vegetation, peat, natural oil seep, forest fires or volcanoes. In combustion sources they can either be pyrogenic, petrogenic, or biogenic depending on their specific fuel and combustion characteristics. Among the control strategies discussed herewith altering the feedstock and fuel characteristics achieved the highest PAH emission reduction by fuel reformulation or co-combustion of process feedstock to dilute the PAH content. Most of the output/input studies show that PAHs are clearly destroyed in most of the combustion processes rather than being formed.

The fates of PAHs in the atmosphere after emission include gas-particle phase deposition, long-range transport, wet and dry deposition and resuspension from receptor surfaces. Quantification of the concentrations and the deposition fluxes in the atmosphere uses various sampling methods such as passive samplers, deposition plates among others. There are various artifacts associated with these methods and these artifacts have since been studied and novel sampling methods proposed to minimize errors for scientific purposes. From the particle size distribution of PAHs, mostly the LMW-PAHs are adsorbed onto fine particles while the HMW-PAHs are adsorbed onto aged particles. Mobile sources are associated with PAHs adsorbed on fine particles.

Most deposition studies reported higher deposition in industrial or urban regions compared to other areas whereas in terms of seasonality the highest deposition fluxes were registered in winter. Cumulative fractions shows that based on the total mass of PAHs the particles with diameters larger than 10 μm contributed about 88–92% of the dry deposition of PAHs from the atmosphere, indicating that the coarse fractions are responsible for the deposition of PAHs even though PAHs are more bound to fine particles. On the other hand, the fine particles, whose mean aerodynamic diameter is below 2.5 μm , pose the highest risk to human being. This is because the particle bound content results and particle size distributions of PAHs indicate that the fine particles have the host PAH content owing to their large surface areas and high carbon content.

The concern about PAHs is usually revolving around their toxicity and carcinogenic potential. Among the various PAH homologues, benzo(a)pyrene is the most toxic PAH with the highest mutagenic and carcinogenic potential upon which the toxicity of other PAHs and the carcinogenic risk to human of PAH mixtures are based.

Among the most susceptible populations are those grilling and broiling food in night markets for many years, tollbooth workers exposed to vehicle exhausts for long hours, workers in black carbon factories and steel industries, as well as residents living in regions with high occurrences of wild forest fires. Exposure limits are also age-dependent as younger children and toddlers have lower maximum exposures times compared to grownups.

In conclusion, this study notes that many studies have been done to evaluate various aspects concerning the PAHs in the atmosphere. In spite of this fact and observation, this study recognizes that PAHs are still major and “hot” topic and proposes more and in depth studies especially concerning the assessment of effectiveness of emission control technologies

as well as of emission standards set by various bodies around the world.

NOMENCLATURE and ABBREVIATIONS

°C	degree Celsius
1-OHPG	urinary 1-hydroxypyrene-glucuronide
8-OHdG	urinary 8-hydroxy-29-deoxyguanosine
A/F	adsorbent-retained and filter-retained proportions
ACFs	activated carbon fibers
APCDs	air pollution control devices
BSEC	brake specific energy consumption
BSFC	brake specific fuel consumption
CO	carbon monoxide
DR	diagnostic ratios
DNA	Deoxyribonucleic acid
DOC	diesel oxidation catalyst
DPF	diesel particulate filter
EU	European Union
FBFO	fishing boat fuel oil
FID	flame ionization detector
FFV	flexible fuel vehicles
FTP	Federal Test Procedure
GC	gas chromatography
GPC	gel permeation chromatography
GC/MS	gas chromatography coupled with mass spectrometry
H ₂	hydrogen
HC	Unburnt Hydrocarbons
HWI	hospital waste incinerators
HMW	high molecular weight
HPLC	high performance liquid chromatography
IARC	International Agency for Research on Cancer
IEL	inhalation exposure levels
ILCR	incremental lifetime cancer risk
IUPAC	International Union of Pure and Applied Chemistry
LMW	low molecular weight
LC	liquid chromatography
LFG	lead-free gasoline
LOD	limit of detection
LOQ	limit of quantification
LTO	landing and takeoff
MDA	malondialdehyde
MMAD	mass median aerodynamic diameters
MMW	medium molecular weight
MOUDI	micro-orifice uniform deposit impactor
MSD	mass spectroscopy detectors
MTBE	methyl-tert-butyl-ether
NO ₂	Nitrogen dioxide
NO _x	Nitrogen Oxides
NRI	Noll Rotary Impactor
O/I	output and input ratios
PAHs	Polycyclic aromatic hydrocarbons
PCA	principal component analysis
PICs	products of incomplete combustion
PLG	premium gasoline
PM ₁₀	particulate matter with diameter less than 10 μm

PM _{2.5}	particulate matter with diameter less than 2.5 µm
PSD	particle size distribution
PUF	polyurethane foam
RFG	Reformulated gasoline
SVOCs	semi-volatile organic compounds
SO ₂	Sulphur dioxide
TPA	terephthalic acid
<i>tt</i> -DDE	trans, trans-2,4-decadienal
TLC	thin layer chromatography
<i>t</i> _{max}	maximum exposure time
TSP	total suspended particles
TWC	three way catalysts
US EPA	US Environmental Protection Agency
UV	ultra violet
V/P	vapor phase and particle phase ratio
WDDS	wet-dry deposition simplifier

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