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REVIEW

A review on polycyclic aromatic hydrocarbons: Source, environmental impact, effect on human health and remediation



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Abstract Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental pollutants generated primarily during the incomplete combustion of organic materials (e.g. coal, oil, petrol, and wood). Emissions from anthropogenic activities predominate; nevertheless, some PAHs in the environment originate from natural sources such as open burning, natural losses or seepage of petroleum or coal deposits, and volcanic activities. Major anthropogenic sources of PAHs include residential heating, coal gasification and liquefying plants, carbon black, coal-tar pitch and asphalt production, coke and aluminum production, catalytic cracking towers and related activities in petroleum refineries as well as and motor vehicle exhaust. PAHs are found in the ambient air in gas-phase and as sorbet to aerosols. Atmospheric partitioning of PAH compounds between the particulate and the gaseous phases strongly influences their fate and transport in the atmosphere and the way they enter into the human body. The removal of PAHs from the atmosphere by dry and wet deposition processes are strongly influenced by their gas/particle partitioning. Atmospheric deposition is a major source for PAHs in soil.

Many PAHs have toxic, mutagenic and/or carcinogenic properties. PAHs are highly lipid soluble and thus readily absorbed from the gastrointestinal tract of mammals. They are rapidly distributed in a wide variety of tissues with a marked tendency for localization in body fat. Metabolism of PAHs occurs via the cytochrome P450-mediated mixed function oxidase system with oxidation or hydroxylation as the first step.

Several different remediation technologies have been tested in efforts to remove these environmental contaminants. Among them, bioremediation is showing particular promise as a safe and cost-effective option. In spite of their xenobiotic properties, a variety of genera of gram-positive and -negative bacteria, fungi and algae have been isolated and characterized for their ability to utilize PAHs.

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The aim of this review is to discuss PAHs impact on the environmental and the magnitude of the human health risks posed by such substances. They also contain important information on concentrations, burdens and fate of polycyclic aromatic hydrocarbons (PAHs) in the atmosphere. The main anthropogenic sources of PAHs and their effect on the concentrations of these compounds in air are discussed. The fate of PAHs in the air, their persistence and the main mechanisms of their losses are presented. Health hazards associated with PAH air pollution are stressed.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are organic compounds that are mostly colorless, white, or pale yellow solids. They are a ubiquitous group of several hundred chemically related compounds, environmentally persistent with various structures and varied toxicity. They have toxic effects on organisms through various actions. Generally, PAHs enter the environment through various routes and are usually found as a mixture containing two or more of these compounds, e.g. soot. Some PAHs are manufactured in the industry. The mechanism of toxicity is considered to be interference with the function of cellular membranes as well as with enzyme systems which are associated with the membrane. It has been proved that PAHs can cause carcinogenic and mutagenic effects and are potent immunosuppressants. Effects have been documented on immune system development, humoral immunity and on host resistance [1,2]. PAHs can be formed both during biological processes and as products of incomplete combustion from either natural combustion sources (forest and brush fires) or man-made combustion sources (automobile emissions and cigarette smoke). Thus, PAHs are commonly detected in air, soil, and water. Therefore, PAHs are considered ubiquitous in the environment [3,4]. The ubiquitous nature of PAHs in the environment has been well summarized by Menzie et al. [5].

The term "PAH" refers to compounds consisting of only carbon and hydrogen atoms. Chemically the PAHs are comprised of two or more benzene rings bonded in linear, cluster, or angular arrangements [6,7]. Such molecular arrangements are illustrated in (Fig. 1). Although there are many PAHs, most regulations, analyses, and data reporting focus on only a limited number of PAHs, typically between 14 and 20 individual PAH compounds.

Polycyclic aromatic hydrocarbons have two or more single or fused aromatic rings with a pair of carbon atoms shared between rings in their molecules. PAHs containing up to six fused aromatic rings are often known as "small" PAHs, and those containing more than six aromatic rings are called "large" PAHs. The majority of research on PAHs has been conducted on small PAHs due to the availability of samples of various small PAHs. The simplest PAHs, as defined by the International Agency for Research on Cancer [8], are phenanthrene and anthracene, which both contain three fused aromatic rings. On the other hand, smaller molecules, such as benzene, are not PAHs. Naphthalene, which consists of two coplanar six-membered rings sharing an edge, is another aromatic hydrocarbon. Therefore, it is not a true PAH, though is referred to as a bicyclic aromatic hydrocarbon. The most

extensively studied PAHs are 7, 12-dimethylbenzo anthracene (DMBA) and benzo(a)pyrene (BaP) [2]. The most commonly analyzed PAHs are given in (Fig. 2).

The general characteristics of PAHs are high melting and boiling points (therefore they are solid), low vapor pressure, and very low aqueous solubility [10]. The latter two characteristics tend to decrease with increasing molecular weight, on the contrary, resistance to oxidation and reduction increases [10]. Aqueous solubility of PAHs decreases for each additional ring [11]. Meanwhile, PAHs are very soluble in organic solvents because they are highly lipophilic. PAHs also manifest various functions such as light sensitivity, heat resistance, conductivity; emit ability, corrosion resistance, and physiological action [12].

PAHs possess very characteristic UV absorbance spectra. Each ring structure has a unique UV spectrum, thus each isomer has a different UV absorbance spectrum. This is especially useful in the identification of PAHs. Most PAHs are also fluorescent, emitting characteristic wavelengths of light when they are excited (when the molecules absorb light).

The major source of PAHs is the incomplete combustion of organic material such as coal, oil and wood. PAHs are not synthesized chemically for industrial purposes. Nevertheless, there are a few commercial uses for many PAHs. They are mostly used as intermediaries in pharmaceuticals, agricultural products, photographic products, thermosetting plastics, lubricating materials, and other chemical industries [13]. However, the general uses of some PAHs are:

- *Acenaphthene*: manufacture of pigments, dyes, plastics, pesticides and pharmaceuticals.
- *Anthracene*: diluent for wood preservatives and manufacture of dyes and pigments.
- *Fluoranthene*: manufacture of agrochemicals, dyes and pharmaceuticals.
- *Fluorene*: manufacture of pharmaceuticals, pigments, dyes, pesticides and thermoset plastic.
- *Phenanthrene*: manufacture of resins and pesticides.
- *Pyrene*: manufacture of pigments.

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

2. Source of polycyclic aromatic hydrocarbons (PAHs)

The following three types: *pyrogenic*, *petrogenic*, and *biological* are the major PAH sources to the environment. In a

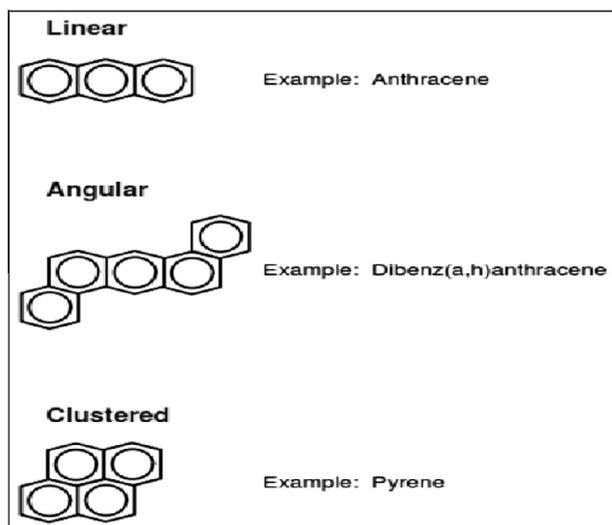


Figure 1 Molecular arrangement of the polycyclic aromatic hydrocarbons (PAHs) [6,7].

process called pyrolysis, *Pyrogenic* PAHs are formed whenever organic substances are exposed to high temperatures under low oxygen or no oxygen conditions. The destructive distillation of coal into coke and coal tar, or the thermal cracking of petroleum residuals into lighter hydrocarbons are Pyrolytic processes that occur intentionally. Meanwhile, other unintentionally processes occur during the incomplete combustion of motor fuels in cars and trucks, the incomplete combustion of wood in forest fires and fireplaces, and the incomplete combustion of fuel oils in heating systems. The temperatures at which the pyrogenic processes occur are ranging from about (350 °C to more than 1200 °C). Pyrogenic PAHs are generally found in greater concentrations in urban areas and in locations close to major sources of PAHs. In addition, PAHs can also be formed at lower temperatures. It is worth mentioning that crude oils contain PAHs that formed over millions of years at temperatures as low as (100–150 °C).

In this respect, PAHs formed during crude oil maturation and similar processes are called *petrogenic*. Such *petrogenic* PAHs are common due to the widespread transportation, storage, and use of crude oil and crude oil products. Some of the major sources of *petrogenic* PAHs include oceanic and freshwater oil spills, underground and above ground storage tank leaks, and the accumulation of vast numbers of small releases of gasoline, motor oil, and related substances associated with transportation. It is well-known that PAHs can be formed during the incomplete combustion of organic substances. PAHs are also found in petroleum products.

On the other hand, it is not well-known that PAHs can be produced *biologically*. For example, they can be synthesized by certain plants and bacteria or formed during the degradation of vegetative matter. The mode of PAHs formation can be either natural or anthropogenic. (Fig. 3) illustrate such mode of PAHs formation [14–17].

Examples of natural sources of PAHs formation include: forest and brush fires, volcanoes, bacterial and algal synthesis, petroleum seeps, erosion of sedimentary rocks containing

petroleum hydrocarbons, and decomposition of vegetative litter fall. Examples of anthropogenic sources of PAHs range from:

- Large point sources include incomplete combustion (such as incinerators and some industrial processes).
- Smaller point sources include , dispersed sources (such as automotive emissions, smoke from wood-burning stoves, jet aircraft exhausts, cigarette and cigar smoke, and backyard barbecues).
- Other anthropogenic sources of PAHs include petroleum product spills, sewage sludge, and tarry or creosote waste materials.

It is important to mention that the incomplete combustion, either naturally or anthropogenically derived, has been identified as the single largest contributor of PAHs to the environment [18].

Sources of PAHs to the environment are numerous and generally well-known. The identification of the PAH content is based mainly on real environmental samples. Chemical fingerprinting includes several techniques which can help distinguish between groups of PAH sources. Such groups include coal-based, wood-based, or oil-based sources. This can be done by examining specific chemical indicators that contained in many samples. As such, source identification techniques often compliment studies involved in the establishment of general “background” ranges of PAHs in the environment. Chemical fingerprinting can also help identify and allocate non-point sources of PAHs to the environment in both industrial and residential areas [19].

As previously mentioned, the temperature of formation can provide one key to identifying PAH sources because higher temperatures of formation tend to produce PAHs with fewer alkylated chains than PAHs formed under lower temperature processes. For instant, PAHs in a power plant stack effluent, which are formed rapidly at very high temperatures will have a different pattern of PAHs than the PAH distribution found at a crude oil spill site. The later PAHs were, generally, formed at lower temperatures over millions of years [20].

Another method used to distinguish *pyrogenic* PAHs from *petrogenic* PAHs is to examine the number of five-member hydrocarbon rings in the PAHs. Five-member rings are more abundant in petroleum hydrocarbons than in *pyrogenic* substances, because the extensive time of petroleum hydrocarbon formation favors the marshaling of the rings. For materials formed pyrolytically the source material is rapidly converted into more stable six-member rings [21]. Thus, although the sources of PAHs to the environment are many, advances have been and continue to be made in the identification of these sources, and the distinction between *pyrogenic* PAHs and those not derived from pyrolytic sources [22].

3. Transport and Fate of PAHs in the environment

Fig. 4 illustrates PAHs dispersion through air and move through terrestrial and aquatic environments as a result of various processes. Fig. 4 shows some of these processes in broad form and shows how PAHs are added, dispersed, and degraded in the environment. It also illustrates how people can be exposed to PAHs through inhalation, ingestion, or direct dermal contact.

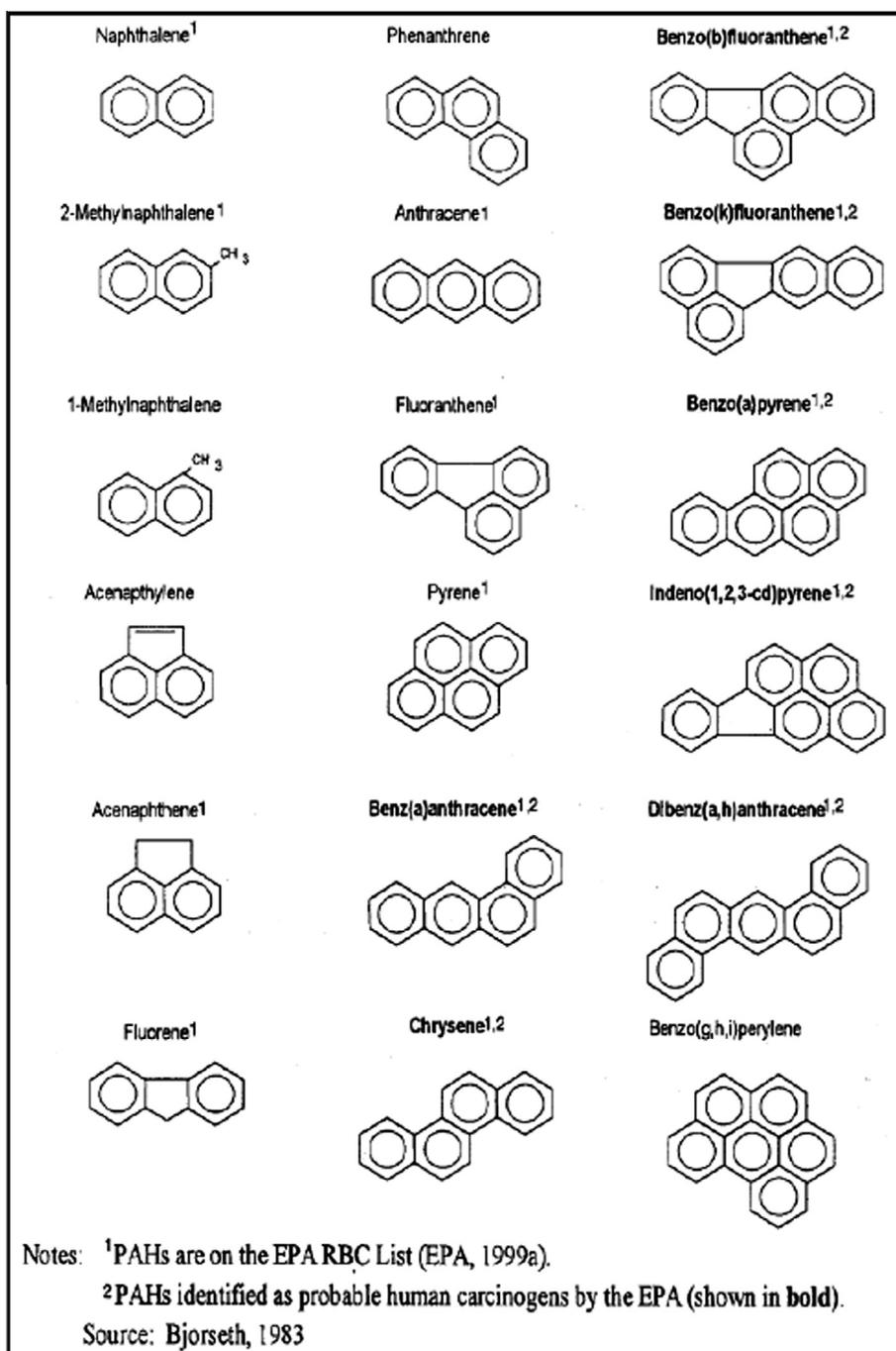


Figure 2 The most commonly analyzed polycyclic aromatic hydrocarbons (PAHs) [9].

3.1. Atmospheric emission and deposition of PAHs

The atmosphere is the most important means of PAH dispersal, it receives the bulk of the PAH environmental load resulting in PAHs being ubiquitous in the environment. PAHs are emitted to the atmosphere primarily from the incomplete combustion of organic matter. The combustion sources can be either natural or anthropogenic. The natural sources include volcanoes and forest fires. While the anthropogenic sources are vehicle exhaust, agricultural fires, power

plants, coke plants, steel plants, foundries and other industrial sources. PAHs tend to be found in greater concentrations in urban environments than in rural environments because most PAH sources are located in or near urban centers. Once released to the atmosphere, PAHs are found in two separate phases, a vapor phase and a solid phase in which the PAHs are sorbet onto particulate matter [24,25,18]. Hydrophobic organic chemicals with low vapor pressures, such as PAHs, are sorbet to atmospheric particulates more readily than chemicals with higher vapor

pressures, such as benzene. The variability in vapor pressures of different PAH compounds cause the individual PAHs to distribute in different concentrations in the vapor [26] and other sorbet phases [27].

Relationship between vapor pressure and molecular weight for typical PAHs is given in (Fig. 5) [29]. As shown in this figure, benzo(a)pyrene has the lowest vapor pressure and naphthalene has the highest vapor pressure. In addition, the correlation between vapor pressure and molecular weight is quite good with a correlation coefficient of 0.9017 [28]. PAHs with lower vapor pressures (e.g., benzo(a)pyrene) will tend to be sorbet to particles, while PAHs with higher vapor

pressures (e.g., naphthalene) will tend to be associated with the vapor phase. As a result, the relative distribution of PAHs in the two phases will be different, for an air sample.

It was stated by “Electric Power Research Institute (EPRI)” [29] for air samples collected from Portland, Oregon, that there are two differences between the PAH concentrations in the vapor and particulate phases. First, the total PAH concentration for the vapor phase (741 ng/m³) is much higher than that of the particulate phase (12 ng/m³). Second, the lower molecular weight, higher vapor pressure PAHs are detected in the vapor phase whereas the higher molecular weight, lower vapor pressure PAHs is not. In contrast, the vapor phase has

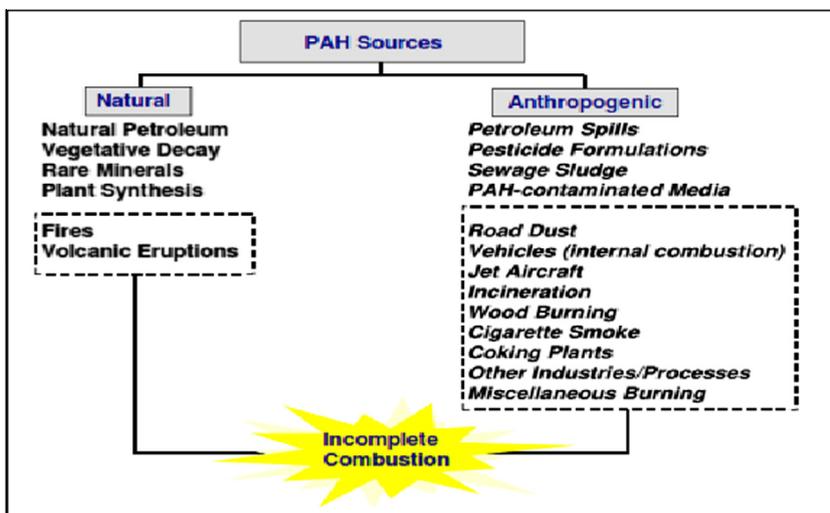
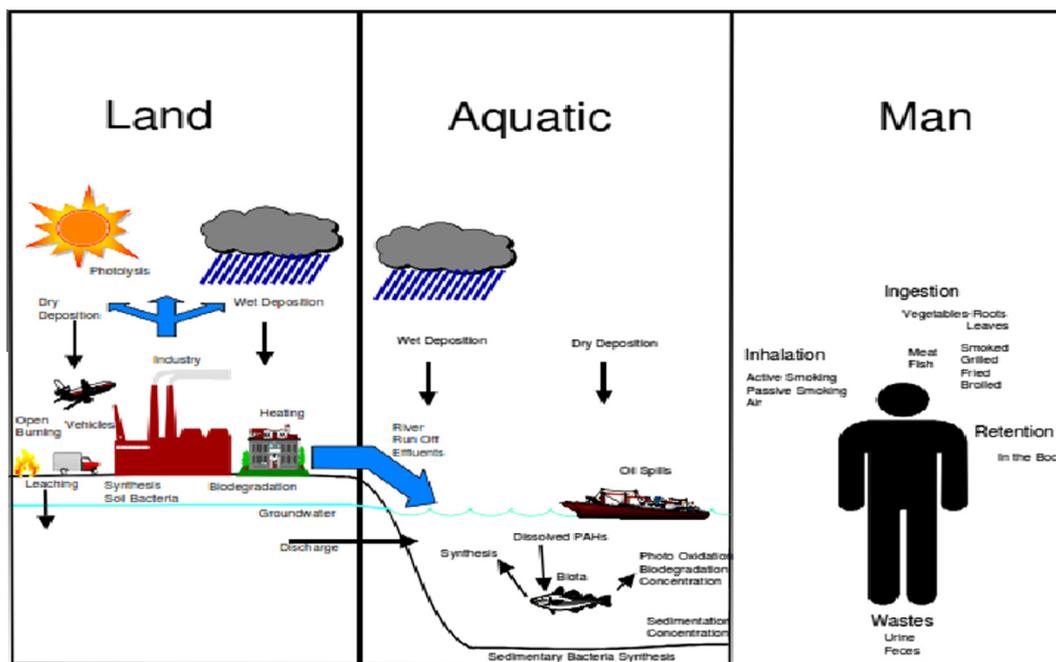


Figure 3 Natural and anthropogenic sources of polycyclic aromatic hydrocarbons (PAHs).



Source: Suess, 1976

Figure 4 Dispersion of PAHs through the air, the terrestrial and aquatic environments [23].

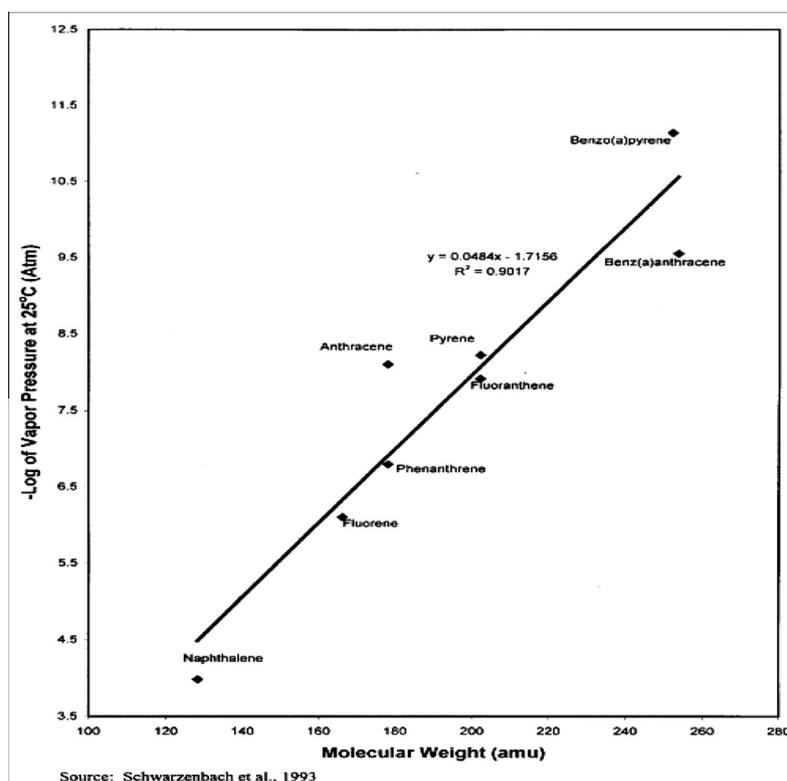


Figure 5 Relationship between vapor pressure and molecular weight for typical PAHs [28].

much lower concentrations of the higher molecular weight PAHs than the particulate phase [29]. A significant correlation was also found between the amounts of dust in the air and PAH concentrations in the particulate phase [27]. Hence, the concentrations of PAHs in the gas phase increase in summer or in general in tropical regions, whereas particulate phase PAHs are dominant during winter or in general in Arctic regions [30,31]. Meanwhile, humidity has an effect on the adsorption of PAHs onto particulate phases [32]. Moreover, PAH adsorption also depends on the types of suspended particulates (e.g., soot, dust, fly-ash, pyrogenic metal oxides, pollens, etc.) [18].

PAHs are to be collected on filter or sorbent followed by extraction that is normally carried out by a number of organic solvents using Soxhlet or ultrasonication treatments. Such solvent-based methods are successfully used for a wide range of PAHs. Detection of PAHs and their derivatives can be achieved using GC-MS method. It is reliable and accurate to determine the concentrations of PAHs and their derivatives [33].

3.2. PAHs in surface soils

Atmospheric PAHs are continuously deposited to the earth by dry or wet deposition processes. Some of these PAHs are from nearby sources, such as automotive exhaust from adjacent roadways. Other PAHs are from more distant sources and have been carried various distances through the air. In the mean time, PAHs can be added to soils if fill materials contain PAHs. When PAHs are deposited onto the earth's surface,

they can become mobile. Since the majority of PAHs in the soil will be bound to soil particles [16,34], the most important factors influencing PAH mobility of particulates in the subsurface will be sorbent particle size and the pore throat size of the soils. Such pore throat can be defined as the smallest opening found between individual grains of soil [35]. If particles to which PAHs are sorbed cannot move through the soil then the movement of PAHs will be limited because they tend to remain sorbed to particles.

The tendency of PAHs to be sorbed to soil depend on both the properties of the PAH and the soil. Therefore, PAH sorption is one of the processes that govern the soil mobility of individual PAHs. Numerous studies of the correlation of the partition coefficient with soil properties have found that the organic carbon content (f) usually yields the most significant correlation [29].

The octanol-water partitioning coefficient of PAHs is also important in determining the sorption of PAHs to soils. The octanol-water partitioning coefficient (K_{ow}) is related to the solubility of an organic compound in water [28]. As the K_{ow} increases, the aqueous solubility decreases and the tendency for sorption to a particular soil increases. Nevertheless, the K_{ow} and solubility can affect PAH mobility in soil. Other factors such as soil conductivity also have a significant influence on PAH movement.

A simplified solvent extraction and GC/MS/MS is employed for a rapid determination of 18 polycyclic aromatic hydrocarbons (PAHs) in soil. The GC/MS/MS is to be operated in pseudo multiple reactions monitoring mode (PMRM) [36].

3.3. PAHs in sediments

PAHs are deposited to the sedimentary environment by similar processes that govern the deposition to surface soils. In rural areas, the PAHs sorbet to atmospheric particles can settle on the surface of lakes, streams, and oceans by dry or wet deposition. There they are dispersed by currents and eventually become integrated with the sediment. On the other hand, sediments near urban centers are influenced by atmospheric deposition of PAHs. They also receive inputs of PAHs from storm and sanitary sewer effluents as well as roadway runoff. Eventually, some of the PAHs will be sorbet to particles, settle, and become part of the sedimentary record. This record has been used by several authors by examining the depositional history in sediment cores to identify trends of PAH input into the environment. These cores are usually taken in anoxic sediment, where there is no oxygen in the water [29,37].

Once PAHs are incorporated into sediments they are somewhat immobile because their non-polar structures inhibit them from dissolving in water. Nevertheless, PAHs are not completely insoluble, particularly the lower molecular weight PAHs. Thus, small amounts of PAHs do dissolve and become included in the pore water where they are bioavailable. The presence of pore water organic colloids can increase the concentrations of PAHs beyond their aqueous solubility because PAHs will be sorbet onto these organic colloids. These in turn are easily transported through the pore spaces of the sediment. Thus, the sorption to colloids can increase the mobility and bioavailability of PAHs in sediments [38].

3.4. Ecotoxic effects of PAHs

The toxicity of PAHs to aquatic organisms is affected by metabolism and photo-oxidation. They are generally more toxic in the presence of ultraviolet light. PAHs have moderate to high acute toxicity to aquatic life and birds. PAHs in soil are unlikely to exert toxic effects on terrestrial invertebrates, except when the soil is highly contaminated. Adverse effects on these organisms include tumors, reproduction, development, and immunity.

Mammals can absorb PAHs by various routes e.g. inhalation, dermal contact, and ingestion [38–40]. On the other hand, plants can absorb PAHs from soils through their roots and translocate them to other plant parts. Uptake rates are generally governed by concentration, water solubility, and their physicochemical state as well as soil type. PAH-induced phytotoxic effects are rare. Full information and the database on this are still limited. Certain plants contain substances that can protect against PAH effects. Other plants can synthesize PAHs that act as growth hormones [40].

PAHs are moderately persistent in the environment, and can be bio-accumulated. The concentrations of PAHs found in fish and shellfish are expected to be much higher than in the environment from which they were taken. Bioaccumulation has been also shown in terrestrial invertebrates. Nevertheless, metabolism of PAHs is sufficient to prevent biomagnifications [41,42].

4. Occurrence of PAH in foods

Raw foods should usually not contain high levels of PAH. In areas remote from urban or industrial activities, levels of

PAH found in unprocessed foods reflect the background contamination. Such PAH usually originates from long distance airborne transportation of contaminated particles as well as natural emissions from volcanoes and forest fires. In the neighborhood of industrial areas or along highways, the contamination of vegetation can be ten-fold higher than in rural areas. Processing of food (such as drying and smoking) and cooking of foods at high temperatures (grilling, roasting, frying) are major sources generating PAH [43,44]. Levels as high as 200 µg/kg of PAH have been found in smoked fish and meat. In barbecued meat, 130 µg/kg of PAH has been reported (Standing Committee on Foodstuffs, 2001). Generally, the average background values are in the range of 0.01–1 µg/kg in uncooked foods. Contamination of vegetable oils (including olive residue oils) with PAH usually occurs during technological processes like direct fire drying. In this respect, the combustion products may come into contact with the oil seeds or oil [45,46].

The occurrence of PAH in foods is governed mainly by the same physicochemical factors that determine their absorption and distribution in man. These factors are the relative solubility of PAH in water and organic solvents. Such solubility determines their capacity for transport and distribution between different environmental compartments and their uptake and accumulation by living organisms. The transportation of PAH in the atmosphere is influenced by their volatility. The chemical reactivity of PAH influences adsorption to organic material or degradation in the environment. All these factors determine the persistence and capacity of PAH to be bio-accumulated in the food chain [47,48]. PAH are lipophilic and generally have a very poor aqueous solubility. On the contrary, PAH accumulate in lipid tissue of plants and animals. On the other hand, PAH will not tend to accumulate in plant tissues with a high water content and limited transfer from the soil to root vegetables will occur. The rate of transfer varies widely and is also influenced by soil characteristics, the plant and the presence of co-pollutants. PAH is strongly adsorbed to the organic fraction of soils and do not penetrate deeply into most soils, therefore limiting both leaching to groundwater and availability for uptake by plants. Some PAH are semi volatile but most of them tend to adsorb on organic particulate matter.

Heavier PAH preferentially associate with particulate matter so atmospheric fall out is a principal route of contamination [49]. PAH with 5 or more aromatic rings are found predominantly on particulates, (usually on small (<2.5 µm) particles such as fly ash and soot). PAH with 2 or 3 rings are almost entirely in the vapor phase. PAH with 4 rings is in an intermediate position. Consequently, vegetables with large leaves, grazing cattle and poultry which may ingest particulate matter from soil are susceptible to contamination by PAH adsorbed to particles. The waxy surface of vegetables and fruits can concentrate low molecular mass of PAH mainly through surface adsorption. PAH concentrations are generally greater on plant surface (peel, outer leaves) than on internal tissue. Careful washing may remove up to 50% of the total PAH. Particle bound PAH are easily washed off the surface whereas those in the waxy layer are less efficiently removed. Washing may alter the apparent high to low molecular mass PAH profile. When particulates fall out into surface water, they are transported in suspension and surface. The adsorbed PAH finally end up in fresh water or

marine sediments. PAH are strongly bound to these sediments which constitute a potential pollution reservoir for PAH release under specific conditions. Thus, sediment-dwelling and filtering organisms are most susceptible to contamination. Most organisms have a high bio-transformation potential for PAH resulting in no significant bio-magnification in the aquatic food chain. Nevertheless, filter-feeding bivalves (e.g. mussels and oysters) filter large volumes of water and have a low metabolic capacity for PAH. They may accumulate PAH. The water-soluble low molecular mass PAHs are rapidly degraded in water. However, the continuous release of PAH by wastewater, which is discharged to the marine environment, can result in elevated concentrations in bivalves grown close to industrialized areas. The accumulation of sediment-adsorbed PAH depends on the characteristics of the contaminant [50]. The main route of human exposure to sedimentary PAHs is through marine lives which make up part of the human diet. PAHs contained in sediments and pore water are taken in by benthic organisms such as lobsters, muscles, and clams which are either consumed directly by humans or are consumed by higher predators which also are a part of the human diet, such as squid and fish [51].

Processing procedures, such as smoking and drying, and cooking of food is commonly thought to be the major source of contamination by PAH. Depending on a number of parameters including time, type of fuel, distance from the heat source and drainage of fat, type (grilling, frying, roasting), cooking number of compounds including PAH are formed in the food.

A comparison of PAH levels in duck breast steaks, undergoing various processing and cooking treatments for 0.5–1.5 h, showed that charcoal grilled samples without skin contained the highest amount of total PAH (320 µg/kg), followed by charcoal grilling with skin (300 µg/kg), smoking (210 µg/kg), roasting (130 µg/kg), steaming (8.6 µg/kg) and liquid smoke flavoring (0.3 µg/kg). For PAH that are classified as carcinogenic (IARC class 1 or 2 A and B), the trend was the same with the exception that smoked samples contained the highest amount (35 µg/kg). In addition, the highest amounts of total and carcinogenic PAH were observed after smoking of duck breast samples for 3 h (53 µg/kg) [52].

Contamination of water may lead to intake of PAH through drinking water and cooked foods. The levels are usually below 1 ng/L in drinking water. However, the level can be higher when asphalt or coal tar coating of storage tanks and water distribution pipes are used.

5. Effect on human health

17 PAHs have been identified as being of greatest concern with regard to potential exposure and adverse health effects on humans and are thus considered as a group. Biological monitoring of exposure to PAHs is of primary interest, due to the widespread diffusion of these compounds and to their toxicological relevance. However, the health effects of individual PAHs are not exactly alike. In fact, the International Agency for Research on Cancer [8] classifies some PAHs as known, possibly, or probably carcinogenic to humans (Group 1, 2A or 2B). Among these are benzo[*a*]pyrene (Group 1), naphthalene, chrysene, benz[*a*]anthracene, benzo[*k*]fluoranthene and benzo[*b*]fluoranthene

(Group 2B) [8]. Some PAHs are well known as carcinogens, mutagens, and teratogens and therefore pose a serious threat to the health and the well-being of humans. The most significant health effect to be expected from inhalation exposure to PAHs is an excess risk of lung cancer [53].

5.1. Routes of exposure

The major route of exposure to PAHs in the general population is from breathing ambient and indoor air, eating food containing PAHs, smoking cigarettes, or breathing smoke from open fireplaces [54]. Tobacco smoke contains a variety of PAHs, such as benzo[*a*]pyrene, and more than 40 known or suspected human carcinogens [55]. Some crops, such as wheat, rye, and lentils, may synthesize PAHs or absorb them via water, air, or soil. Water can also contain certain amounts of PAHs since those chemicals can leach from the soil into water or they can enter water from industrial effluents and marine accidental spills during oil shipment. Soil also contains PAHs, primarily from airborne fallout [56]. Therefore, PAH exposure occurs on a regular basis for most people.

Routes of exposure include ingestion, inhalation, and dermal contact in both occupational and non-occupational settings. Occupational exposure may also occur in workers breathing exhaust fumes, such as mechanics, street vendors, motor vehicle drivers, including workers in mining, metal working, or oil refining. Some exposures may involve more than one route simultaneously, affecting the total absorbed dose (such as dermal and inhalation exposures from contaminated air) [57,1,58]. People can be exposed to PAHs in the air and surface soil by direct inhalation, ingestion or dermal contact.

5.2. Metabolism

Exposure to PAHs is never to single PAHs. Understanding what differences may occur in mixtures of PAHs gives an accurate assessment of the dangers of PAHs. Therefore, understanding the dynamics of single metabolism of PAHs and possible toxic effects is a necessary. This will guide to understand the accurately impact of PAHs and will guide to a well remediation strategies.

Studies were carried out comparing the metabolism of the PAHs Phenanthrene (PHE), Flouranthene (FLA) and Benzo (a)pyrene (BAP) in single, binary, and ternary mixtures by monitoring the disappearance of the parent compound. It was observed that PAH metabolism in the single PAH experiment differed from metabolism in both binary and ternary mixtures. Enzyme competition was evident in the metabolism of mixtures, changing significantly the metabolism patterns of individual PAHs. PAH structure was also seen to affect metabolism in mixtures and the possible creation of toxicity effects during mixture metabolism. PAH concentration changed over time with faster change during single PAH metabolism followed by ternary mixture metabolism and finally binary metabolism [59,60].

Due to the high lipophilicity of this class of compounds, their bioavailability after ingestion and inhalation is significant. Scientific investigations have shown that detectable levels

of PAH occur in almost all internal organs, particularly in organs that are rich in adipose tissue. These organs can serve as storage depots from which the hydrocarbons can be gradually released. Once the PAHs enter the organism they require a multistep metabolic activation by specific enzymes. The enzyme system that is primarily responsible for PAH metabolism is the mixed-function oxidase system. The first reaction is an epoxidation. PAH epoxides can then be conjugated with glutathione and this is regarded as a true detoxification reaction. The epoxides that are not conjugated with glutathione are converted into phenols and diols. Such PAH metabolites, nevertheless, are sometimes not sufficiently polar to be excreted. Therefore, they have to be conjugated with glucuronic or sulfuric acids to enable excretion. Most metabolites of PAH are excreted in feces and urine [61].

5.3. Short-term health effects (acute)

The impact of PAHs on human health depend mainly on the length and route of exposure, the amount or concentration of PAHs one is exposed to, as well as the relative toxicity of the PAHs [54]. A variety of other factors can also affect health impacts including subjective factors such as pre-existing health status and age. The ability of PAHs to induce short-term health effects in humans is not clear. Occupational exposures to high levels of pollutant mixtures containing PAHs have resulted in symptoms such as eye irritation, nausea, vomiting, diarrhoea and confusion [62]. Nevertheless, it is not known which components of the mixture were responsible for these effects and other compounds commonly found with PAHs may be the cause of these symptoms. Mixtures of PAHs are also known to cause skin irritation and inflammation. Anthracene, benzo(a)pyrene and naphthalene are direct skin irritants. But, anthracene and benzo(a)pyrene are reported to be skin sensitizers, i.e. cause an allergic reaction in skin in animals and humans [63].

5.4. Long-term health effects (chronic)

Health effects from long-term or chronic exposure to PAHs may include decreased immune function, cataracts, kidney and liver damage (e.g. jaundice), breathing problems, asthma-like symptoms, and lung function abnormalities. Meanwhile, repeated contact with skin may induce redness and skin inflammation. Naphthalene, a specific PAH, can cause the breakdown of red blood cells if inhaled or ingested in large amounts. If Man is exposed to PAHs, the harmful effects that may occur largely depend on the way of exposure [64–66].

5.5. Carcinogenicity

Although unmetabolized PAHs can have toxic effects, a major concern is the ability of the reactive metabolites, such as epoxides and dihydrodiols, of some PAHs to bind to cellular proteins and DNA [1]. Biochemical disruptions and cell damage occurrence lead to mutations, developmental malformations, tumors, and cancer. Evidence indicates that mixtures of PAHs are carcinogenic to humans. The evidence comes primarily from occupational studies of workers

exposed to mixtures containing PAHs. Such long-term studies have shown an increased risk of predominantly skin and lung as well as bladder and gastrointestinal cancers. Nevertheless, it is not clear from these studies whether exposure to PAHs was the main cause as workers were simultaneously exposed to other cancer-causing agents (e.g. aromatic amines) [64].

In laboratory studies, animals exposed to levels of some PAHs over long periods have developed lung cancer from inhalation, stomach cancer from ingesting PAHs in food, and skin cancer from skin contact [67]. Benzo(a)pyrene is notable for being the first chemical carcinogen to be discovered. In addition, it is the most common PAH to cause cancer in animals. Based on the available evidence, a number of PAHs are classified as carcinogenic to animals [67]. Meanwhile, some PAH-rich mixtures are also classified as carcinogenic to humans [68]. The EPA has classified the following seven PAH compounds: benz(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, chrysene, dibenz(ah)anthracene, and indeno(1,2,3-cd) pyrene as probable human carcinogens [67].

5.6. Effects of PAH on the immune system

It has been reported that the PAHs induce suppress immune reaction in rodents [63]. The precise mechanisms of PAH-induced immune-toxicity are still not clear. It was concluded that the immune-suppression may be involved in the mechanisms by which PAH induce cancer. The immune-toxic effects of PAH have been investigated for many years. Whatever the route of exposure, the resulting effects have been considered mostly at the systemic level. However, very few studies have looked for alterations of the local gut immune system. Immuno-suppression is associated with an increased susceptibility of the exposed individuals to the development of cancers or of infectious diseases. It was stated that the immune-potential results in an increased secretion of cytokines by immune cells, that leads to inflammation. Under specific circumstances, this may facilitate tumor development, expression of hypersensitivity (allergy, contact hypersensitivity) or auto immunity. Depending on various parameters in the design of the protocol such as route of exposure, end point, high or low level of dosage, model used, immune-suppression or immune-potential can be observed [68]. Nevertheless, the published reports indicate that the immune-suppression is the most frequent effect reported after exposure to PAH [68]. In addition, the literature stated that the immune-potential is reported to occur after either atmospheric or topic exposure, or by using in vitro systems [68]. In term of the route of exposure, most of literature have used either subcutaneous and intra-peritoneal injection or inhalation [68–70]. Experimental studies were conducted on the immuno-toxicity that resulted from ingestion of PAH in contaminated food after oral intake of a diet contaminated with PAH.

Furthermore, it has been reported that some PAH when taken into the diet may induce DNA adducts in the lungs. In addition, translocations from one organ to another may result in “at distance” effects. It is worth mentioning that most of the immune-toxic effects that are reported for PAH are not

thought to be due to parent compounds but it refers to their reactive epoxide metabolites [68,69].

5.7. Genotoxicity of PAH

Geno-toxic effects for some PAH have been demonstrated both in rodents and in vitro tests using mammalian (including human) cell lines. Most of the PAHs are not geno-toxic by themselves and they need to be metabolised to the diol epoxides which react with DNA, thus inducing geno-toxic damage. Geno-toxicity plays important role in the carcinogenicity process and could be also in some forms of developmental toxicity [71,72].

PAHs undergo multiple metabolic transformations which may lead to the formation of electrophilic derivatives (e.g. dilepoxides, quinones, conjugated hydroxyalkyl derivatives) capable of covalent interaction with nucleophilic centers of macromolecules. The mechanism of mutagenicity of PAH has been mainly investigated using benzo[a]pyrene and benzo[a]pyrene-7,8-diol-9,10-epoxide (BaPDE) as model compounds [73,74]. Binding of benzo[a]pyrene and BaPDE to nucleic acids mainly occurs at exocyclic amino groups of purines. The mutational spectrum induced by BaPDE in bacteria shows a prevalence of G > T transversions [73,74]. A similar spectrum of base-pair substitutions is induced by BaPDE in mammalian cells in vitro [75], and by benzo[a]pyrene in vivo in transgenic mice [76] and in the Ha-ras oncogene in mouse skin tumours [77,78]. Molecular analysis of p53 mutations in lung cancers of smokers shows a similar prevalence of G > T transversions [79], possibly reflecting the contribution of PAH to tobacco smoke carcinogenesis. In addition to base pair substitutions, bulky adducts of PAH to DNA bases can induce frameshift mutations, deletions, S-phase arrest, strand breakage and a variety of chromosomal alterations [80,81].

5.8. Teratogenicity

Embryotoxic effects of PAHs have been described in experimental animals exposed to PAH such as benzo(a)anthracene, benzo(a)pyrene, and naphthalene [82]. Laboratory studies conducted on mice have demonstrated that ingestion of high levels of benzo(a)pyrene during pregnancy resulted in birth defects and decreased body weight in the offspring [83]. It is not known whether these effects can occur in humans. Nevertheless, it was reported and demonstrated that exposure to PAH pollution during pregnancy is related to adverse birth outcomes including low birth weight, premature delivery, and heart malformations [84]. High prenatal exposure to PAH is also associated with lower IQ at age three, increased behavior problems at ages six and eight, and childhood asthma. Cord blood of exposed babies shows DNA damage that has been linked to cancer [85,86].

6. Removal of polycyclic aromatic hydrocarbon

PAHs are removed from the environment by several methods, including: biodegradation [87,88] and photochemical degradation. On the other hand, removal of PAHs from Atmosphere was also reported [89–91].

6.1. PAH degradation

Degradation of PAHs in the environment includes: biodegradation, photooxidation, and chemical oxidation adsorption to soil particles, leaching, bioaccumulation [92]. Each of these processes affects individual PAHs in a different manner. This is mainly due to the fact that each PAH has a unique structure and a set of physical, chemical, and biological properties. The majority of the articles examined for this literature study discussed biodegradation by either anaerobic or aerobic microorganisms. Few articles studied other modes of PAH degradation, such as photolysis or oxidation.

6.1.1. PAH biodegradation

Biodegradation of PAHs was the most frequently studied degradation process described in the literature. The first PAH biodegradation studies focused on aerobic degradation. Nevertheless, anaerobic degradation has been demonstrated, more recently, under denitrifying conditions [93,94]. In order for bacteria to degrade any given PAH, it must be made available for uptake by the bacteria [95–97]. PAHs become bioavailable when they are in either the dissolved or the vapor phase. PAHs sorbet onto soil particles cannot be readily degraded by bacteria because the PAHs are separated from the enzymes that are used by bacteria to break them down [98–101]. However, the bioavailability of a given PAH is complicated. For example, the age of PAHs in the soil has been shown to affect how rapidly they will be desorbed from the soil [102]. PAHs will also desorb at different rates over time.

Hatzinger and Martin [98] demonstrated that fresh C-14 labeled phenanthrene and chrysene desorbed rapidly. On the other hand, phenanthrene and chrysene that had been exposed to soil for a long period of time desorbed more slowly. Initially, PAHs are desorbed rapidly followed by a period of slower desorption [103]. Such a change in desorption rate is caused mainly by decreases in the concentration gradient as the PAHs desorbed. As the concentrations of the individual PAHs reach the aqueous solubility levels, the rate of desorption will decrease because the concentration gradients between the sorbet and aqueous phases have decreased. The important factor in the PAHs bioavailability is their solubility character. The aqueous solubility of PAHs is strongly dependent on their molecular weights [104,105]. For example, angular carbon ring arrangements are thermodynamically the most stable configuration, but the open areas (referred to as bay regions) formed between the angled benzene rings are subject to attack by enzymes. This makes these angular structures more biodegradable than the linear or clustered structures. PAH degradation also can be impacted by competitive inhibition.

On the other hand, the rate of PAH degradation can be reduced if the bacteria involved in degrading PAHs find a chemical that is utilized more easily as a food source. Competitive inhibition occurs when the active sites of enzymes used by bacteria to break down PAHs as a carbon source are non-specific. These non-specific enzymes can attach themselves to a number of different chemicals. If other chemicals are present that are more easily broken down, the enzyme will degrade those chemicals as its carbon source and the PAHs will persist [106]. It is also evident that anthracene could be completely mineralized by *Sphingomonas*, *Nocardia*, *Beijerinckia*,

Paracoccus, and Rhodococcus with dihydriol as the initial oxygenated intermediate [107].

6.1.2. Photolysis degradation

Photolysis is defined as the destruction of a compound from reactions initiated by the absorption of light [108]. These reactions occur when light absorbed by PAHs excites the electrons within the molecules. This excitation creates an unstable structural arrangement. Consequently, such unstable structural arrangement allows several physical and chemical processes to act on the compound [28]. Photolysis reactions involving PAHs are similar to biodegradation reactions (i.e. the PAHs degrade more effectively when they are in the vapor or aqueous phases) [109]. Little photo-degradation occurs when PAHs are sorbed to particles in the atmosphere or soil. These reactions occur more effectively with increasing particle surface area. Photolysis reactions are also greater on light colored particles, such as silica gel or alumina, than on darker particles, such as carbon black. For example, anthracene has a half-life of 0.5 h on alumina and 310 h on carbon black [110].

As in microbial degradation, photodegradation reactions depend heavily on the structure of the PAH being degraded. In general, linear, 2-ring, and some clustered PAHs degrade rapidly under direct light. Angular PAHs (e.g., phenanthrene and dibenz(a,h)anthracene) is the slowest in degradation. This is mainly because they are the most structurally stable molecules [111]. Furthermore, photolysis tends to be more effective for low molecular weight compounds, such as naphthalene, because these compounds are more bioavailable and will have longer exposure times to sunlight [111]. Finally, PAH molecules, when they are sorbed to fly ash particles, may be deposited inside the fly ash pore structure. When this occurs, the portion of the PAHs in the pore structure becomes shielded from sunlight which stops photolytic reactions from occurring [112]. Other methods of PAH degradation appear less frequently in the scientific literature than microbial degradation and photolysis. Often chemical oxidation is included as a subsection of articles on biodegradation and photolysis.

6.1.3. Chemical degradation

Chemical oxidation appears to be a minor PAH degradation mechanism under most environmental conditions. In the case of chemical oxidation, either naturally or as part of treatment technologies [113], the rates of PAH oxidation depend on several properties of the system. The molecular weight and structure of the compound, its physical state, temperature, and the strength of the oxidizing agent all impact the outcome. It was reported that chemical treatment and/or physical treatment could remove PAHs efficiently from surface water [114]. Alebic-Juretic et al. reported that fluoranthene was the most stable of the PAHs tested for oxidation by ozone [115]. This could be one reason why fluoranthene is often present in high concentrations in the soil data reviewed. Zhang et al. also reported that the synergistic effect of UV irradiation and TiO₂ or ZnO catalysis was efficient for degradation of PAHs in contaminated soil [116,117]. Iron oxides and oxalic acid can set up a photo-Fenton-like system without additional H₂O₂ in solid phase to enhance the

photodegradation of pyrene under UV irradiation [118]. On the other hand, sono-chemical degradation of PAHs using high frequency of ultrasound was also investigated [119,120].

6.2. Removal of PAHs from atmosphere

PAHs are removed from the atmosphere either by dry deposition or wet deposition, as well as degradation by various pathways [89–91].

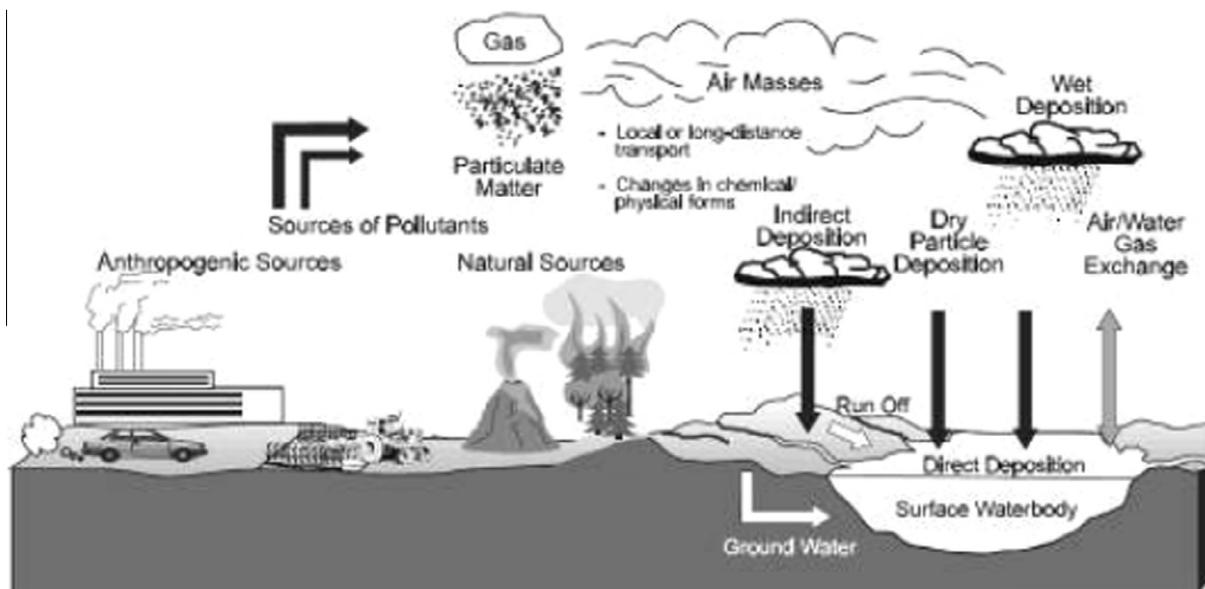
6.2.1. Dry deposition

Dry deposition occurs when PAHs sorbed to atmospheric particles settle to earth in the absence of precipitation as shown in Fig. 6 [108,121–123]. Dry deposition rates vary depending on the specific properties of the PAH, sorbent particle, and atmospheric conditions. For example, large particles will tend to settle faster than small particles because large particles tend to be heavier than smaller particles. Such heavier particles require stronger atmospheric currents to keep them suspended as compared to small particles. Therefore, atmospheric condition is the most important factor affecting the rate of dry deposition. Moreover, particles will settle faster in a more placid atmosphere than in an unstable one because the wind and atmospheric currents in an unstable atmosphere have enough energy to prevent particles from settling.

On the other hand, temperature will also affect the rate at which PAHs are deposited from the atmosphere. For example, higher temperatures will cause a greater fraction of the total PAHs to be in the vapor phase and lower temperatures will increase sorption of PAHs [124,125]. This phenomenon can be seen in the particle/vapor PAH distributions from winter to summer displayed in Fig. 7 [126]. In this figure, the PAH compounds are shown so that the vapor pressures decrease from left to right on the x-axis. In addition, the y-axis is in terms of percentage of each individual PAH, rather than concentration, with the sum of the vapor and particulate phases for each PAH compound adding up to 100%. Fig. 7 clearly demonstrates the effects of vapor pressure and temperature on the vapor/particle phase distribution of some PAHs. For example, about 93% of naphthalene was found in the vapor phase in air sampled in summer while only about 53% of naphthalene was in the vapor phase in air sampled during winter (Harrison et al., 1996). Nevertheless, for PAHs with very low vapor pressures, such as benzo(a)pyrene and dibenz(a,h)anthracene, there were no significant differences between the vapor and particulate phase distributions in either summer or winter. Therefore, temperature will have a significant impact on the concentrations and distribution of PAHs in the vapor and particulate phases [127,128].

6.2.2. Wet deposition

Wet deposition is illustrated in Fig. 6 according to US.EPA (2000). Wet deposition is defined as the scrubbing of contaminants sorbed onto particulates out of the atmosphere by precipitation, as well as the dissolution of vapor phase contaminants into precipitation [129,130]. The amounts of PAHs removed from the atmosphere by wet deposition vary



Source: U.S. EPA 2000

Figure 6 Removal of PAHs from atmosphere by either dry deposition or wet deposition [121].

depending on the phase. Generally, sorbed PAHs are more easily removed from the atmosphere than vapor phase PAHs. It was reported by Dickhut and Gustafson that very little of the total phenanthrene in the atmosphere was associated with particulates. Nevertheless, a considerable amount of the total phenanthrene removed from the atmosphere during a precipitation event as particle-based phenanthrene. This finding suggests that precipitation is more effective in removing the sorbed rather than the vapor phase PAHs [131]. In general, vapor phase PAHs are more efficiently removed from the atmosphere under cold conditions as compared to warm conditions [132,133]. Therefore, more vapor phase PAHs should be removed from cold climates and higher latitudes than from warmer areas. This, potentially, results in the enrichment of lower molecular weight PAHs (i.e., those with higher vapor pressures) in the soils of cold climate areas. According to Gustafson and Dickhut, PAHs are more efficiently removed from the air in the spring and summer than in the winter and fall. Therefore, PAH concentrations in the soil of cold climate areas may be greater than in warm climate areas. This finding appears to contradict the finding of Gustafson and Dickhut which indicated that particulates are more readily removed in the warmer seasons than in the colder seasons [134]. This difference may be attributed to PAHs being associated with larger particles in the warmer months, which are more easily removed from the atmosphere. Nevertheless, another study showed that snow is about two orders of magnitude more effective at removing atmospheric particles than rain [135]. Based on the results from different scientific studies, it can be seen that more work needs for better characterizing the patterns of PAH removal from the atmosphere so that these processes can be better understood.

7. Controlling the PAHs concentration in the environment

- U.S. government agencies have regulated standards that are relevant to PAHs exposures in the workplace and the environment. U.S. government agencies have also established a standard relating to PAH in the workplace as well as a standard for PAH in drinking water.
- The Occupational Safety and Health Administration (OSHA) [136] have established standards that are relevant to PAHs exposures under OSHA's Air Contaminants Standard for substances termed coal tar pitch volatiles (CTPVs) and coke oven emissions. Employees exposed to CTPVs in the coke oven industry should be covered by the coke oven emissions standard. This OSHA standard requires employers to control employee exposure to coke oven emissions. It requires that the employers should use engineering controls and work practices for employee protection. The employer through the engineering and work practice controls shall, nonetheless, supply the employee with respiratory protection to reduce exposures to or below the permissible exposure limit. The OSHA standard also includes elements of medical surveillance for workers exposed to coke oven emissions.
- The OSHA PEL (permissible exposure levels) for PAHs in the workplace is 0.2 mg/m^3 for 8-h TWA (time-weighted average).
- The National Institute for Occupational Safety and Health (NIOSH) [137] has recommended that the workplace exposure limit for PAHs be set at the lowest detectable concentration, which was 0.1 mg/m^3 (REL = recommended exposure limit) for coal tar pitch volatile agents for a 10-h workday, 40-h workweek.

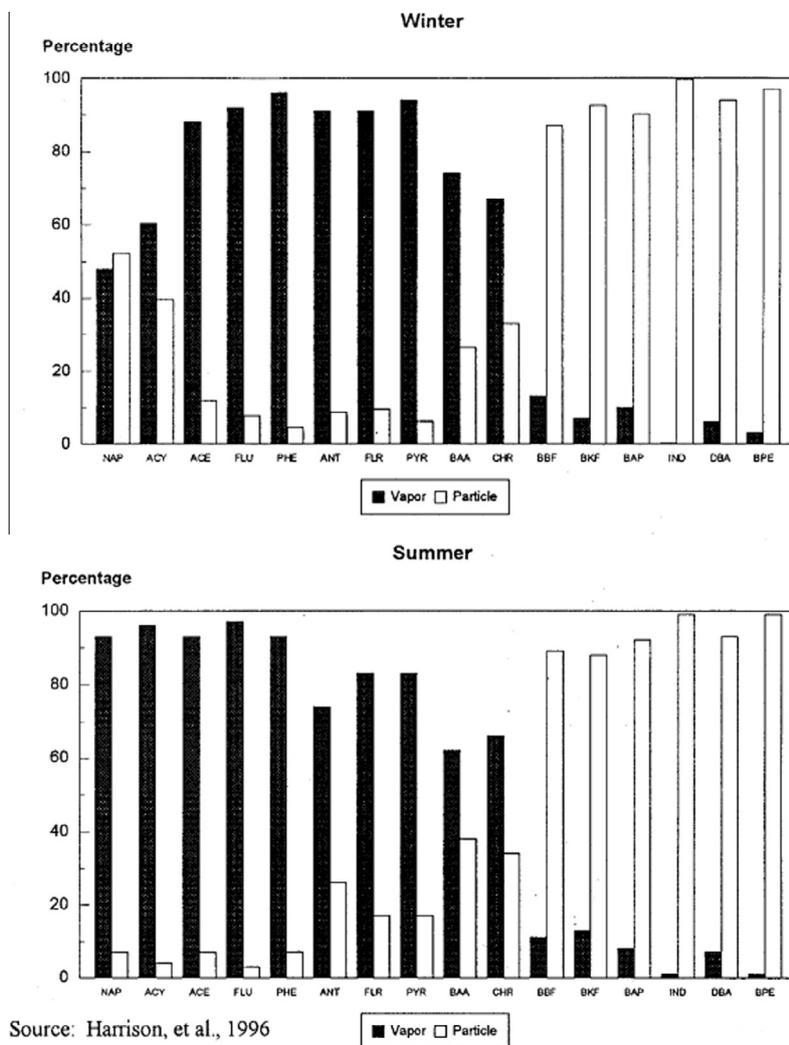


Figure 7 Illustration of the particle/vapor PAH distributions from winter to summer [126].

- In 2000, EPA [121] has established ambient water quality criteria to protect human health from the carcinogenic effects of PAH exposure. The goal of these criteria was to set a non-detectable level (zero concentration for carcinogenic PAHs in ambient water). The EPA developed a maximum contaminant level (MCL) for benzo(a)pyrene at 0.2 ppb. It is well known that benzo(a)pyrene (BaP) is the most carcinogenic PAH.
- WHO guidance (2003) [15] set the unit risk of lung cancer of BaP at $87 \times 10^{-6} \text{ ng m}^{-3}$ for lifetime exposure. According to many member states of WHO, the guideline values for BaP is between 0.1 and 1.3 ng m^{-3} .
- According to the European Commission [138], the target annual average concentration is not to be exceeded in the PM10 fraction in 1 ng m^{-3} . It is reported in recent data that this target has been exceeded in many locations around Europe, particularly in the east countries.
- According to the Egyptian Environmental Association Affairs (EEAA) [139] the Water Quality Standards and Guidelines limits the benzo(a)pyrene (BaP) at $0.7 \text{ } \mu\text{g/L}$.

8. Conclusion

- PAHs are subset of a set of compounds known as polycyclic organic matters (POM). They are, originally, organic compounds primarily that are formed from the incomplete combustion of organic materials or pyrolysis of organic material. These compounds are related to the use of oil, gas, coal and wood in energy production. Other contributors to ambient air levels include indoor smoking and heating.
- Polycyclic aromatic hydrocarbons (PAHs) are transported in the atmosphere in gas and/or particle phases and they are deposited by wet and dry deposition.
- Particulate matters play significant and continuous role in the chemistry of the atmosphere. They also play significant role in human health.
- Daily exposures to particulate matter associated with increased incidences of premature death, chronic asthma and increased hospital admissions as well as respiratory problems in children.

- The occurrence of PAHs in foods is due both: deposition from the air on the surface of plants, and the pollution resulting from manufacture processes such as drying, roasting, or smoking. Moreover, the presence of PAHs in baby foods results in health risk to the infant, since they are more sensitive than adults to such contaminants.
- Many PAHs compounds are classified as probable human carcinogens.
- PAHs constitute a major class of chemical carcinogens present in the environment.
- Several PAHs and their epoxides are highly toxic, mutagenic and/or carcinogenic to microorganisms as well as to higher systems including humans.
- The polycyclic aromatic hydrocarbons compounds (PAHs) require activation to electrophilic metabolites to exert their mutagenic or carcinogenic effects.
- Exposure to PAHs always involves complex mixtures that may induce synergistic or antagonistic effects on the genotoxic properties that make risk assessment more difficult.
- The PAH-degrading microorganism includes algae, bacteria, and fungi. It involves the breakdown of organic compounds through biotransformation into less complex metabolites, and through mineralization into inorganic minerals, H₂O, CO₂ (aerobic) or CH₄ (anaerobic).
- Polycyclic aromatic hydrocarbons compounds (PAHs) may undergo adsorption, volatilization, photolysis, and chemical degradation. However, microbial degradation is the major degradation process.
- Bioremediation is the tool to transform such compounds to less hazardous/nonhazardous forms with less input of chemicals, energy, and time. Polycyclic aromatic hydrocarbons degradation depends on several factors including: the environmental conditions, number and type of the microorganisms, nature and chemical structure of the chemical compound being degraded.

9. Recommendations for the protection of human health and the environment

- Assessment of exposure to PAHs is important due to the widespread presence of PAHs in the environment and their toxicological relevance. Particular assessment of exposure to PAHs should be given to workers (e.g. involved in production of metallurgic coke, aluminum, or carbon electrodes, asphalt workers) and for the general population.
- The biological impact in terms of the total PAHs intake into the body via respiratory, dermal, and gastrointestinal routes should be monitored precisely.
- Owing to their proven immune-toxic effects, coal-tar shampoos should be used for anti-dandruff therapy only if no other treatment is available.
- Due to the immune-toxic and carcinogenic effects of PAH in coke-oven workers, exposure to PAH in occupational settings should be eliminated or minimized. This could be done by reducing emissions to the maximum extent. If this not possible, then at least an effective personal protection should be provided.
- Public awareness and education about the sources and health effects of exposure to PAH should be improved.

- In many countries, the use of unvented indoor fires should be avoided. They should be replaced by more efficient, well-vented combustion devices.
- Protection of non-smoker as well as the risk of exposure to PAH from passive smoking should be stressed. Besides, measures should be taken to avoid it.
- Urban air pollution should be monitored all year round and not only seasonally.
- Filtration of industrial emissions should be taken.
- Treatment of industrial effluents must be carried out strictly, particularly in the developing countries.
- The use of catalytic converters and particle traps on motor vehicles should strictly be taken.

References

- [1] B.G. Armstrong, E. Hutchinson, J. Unwin, T. Fletcher, *Environ Health Perspect* 112 (9) (2004) 970–978.
- [2] CCME (Canadian Council of Ministers of the Environment). Canadian soil quality guidelines for potentially carcinogenic and other PAHs: scientific criteria document. CCME: Winnipeg: 2010.
- [3] A. Baklanov, O. Hänninen, L.H. Slørdal, J. Kukkonen, N. Bjergene, B. Fay, *Atmos Chem Phys* 7 (2007) 855–874.
- [4] J. Latimer, J. Zheng, The sources, transport, and fate of PAH in the marine environment, in: P.E.T. Douben (Ed.), *PAHs: an ecotoxicological perspective*, John Wiley and Sons Ltd, New York, 2003.
- [5] A.C. Menzie, B.B. Potocki, J. Santodonato, *Environ Sci Technol* 26 (1992) 1278–1284.
- [6] J. Arey, R. Atkinson, Photochemical reactions of PAH in the atmosphere, in: P.E.T. Douben (Ed.), *PAHs: an ecotoxicological perspective*, John Wiley and Sons Ltd, New York, 2003, pp. 47–63.
- [7] D.M. Di-Toro, J.A. McGrath, D.J. Hansen, *Environ Toxicol Chem* 19 (2000) 1951–1970.
- [8] IARC (International Agency for Research on Cancer), Some non-heterocyclic polycyclic aromatic hydrocarbons and some related exposures, *Monogr Eval Carcinog Risks Hum* 92 (2010) 765–771.
- [9] Alf Bjorseth, *Handbook of polycyclic aromatic hydrocarbons*, Marcel Dekker Inc, New York (NY), 1983.
- [10] J. Masih, R. Singhvi, K. Kumar, V.K. Jain, A. Taneja, *Aerosol Air Qual Res* 12 (2012) 515–525.
- [11] J. Masih, A. Masih, A. Kulshrestha, R. Singhvi, A. Taneja, *J Hazard Mater* 177 (2010) 190–198.
- [12] M. Akyuz, H. Cabuk, *Sci Total Environ* 408 (2010) 5550–5558.
- [13] N.E. Kaminski, B.L. Faubert Kaplan, M.P. Holsapple, 7th ed., in: Curtis D. Klaassen (Ed.), *Casarett and Doull's Toxicology, the basic science of poisons*, vol. 526, Mc-Graw Hill, Inc, 2008.
- [14] I. Tolosa, J.M. Bayona, J. Albaiges, *Environ Sci Technol* 30 (1996) 2495–2503.
- [15] WHO (World Health Organization). Polynuclear aromatic hydrocarbons in drinking-water. Background document for development of WHO Guidelines for Drinking-water Quality; 2003 [WHO/SDE/WSH/03.04/59].
- [16] A. Masih, A. Taneja, *Chemosphere* 65 (2006) 449–456.
- [17] J.S. Seo, Y.S. Keum, R.M. Harada, Q.X. Li, *J Agric Food Chem* 55 (2007) 5383–5389.
- [18] Y. Zhang, S. Tao, *Atmos Environ* 43 (2009) 812–819.
- [19] Z. Wang, C. Yang, Z. Yang, J. Sun, B. Hollebone, C. Brown, M. Landriault, *J Environ Monit* 13 (2011) 3004–3017.
- [20] D.S.N. Parker, F. Zhang, Y. Seol Kim, R.I. Kaiser, A. Landera, V.V. Kislov, et al, *PNAS* 109 (2012) 53–58.
- [21] I. Tolosa, M.B. Josep, A. Joan, *Environ Sci Technol* 30 (1996) 2495–2503.

- [22] Z. Wang, C. Yang, J.L. Parrott, R.A. Frank, Z. Yang, C.E. Brown, B.P. Hollebhone, M. Landriault, B. Fieldhouse, Y. Liu, G. Zhang, L.M. Hewitt, *J Hazard Mater* 271 (2014) 166–177.
- [23] M.J. Suess, *Sci Total Environ* 6 (1976) 239–250.
- [24] K. Ravindra, R. Sokhi, R.V. Grieken, *Atmos Environ* 42 (2008) 2895–2921.
- [25] Z. Wang, P. Ren, Y. Sun, X. Ma, X. Liu, G. Na, *Environ Sci Pollut Res: China* 20 (2013) 5753–5763.
- [26] T. Kameda, *J Health Sci* 57 (6) (2011) 504–511.
- [27] C.Y. Kuo, P.S. Chien, W.C. Kuo, C.T. Wei, R.J.Y. Jui-Yeh, *Environ Monit Assess* 185 (7) (2012) 5749–5761.
- [28] R.P. Schwarzenbach, P.M. Gschwend, D.M. Imboden, *Environmental organic chemistry*, John Wiley and Sons, Inc, 1993.
- [29] EPRI (Electric Power Research Institute). Literature review of background polycyclic aromatic hydrocarbons. Final report; March 2000.
- [30] I.C. Lai, C.L. Lee, K.Y. Zeng, H.C. Huang, Seasonal variation of atmospheric polycyclic aromatic hydrocarbons along the Kaohsiung coast, *J Environ Manage* 92 (8) (2011) 2029–2037.
- [31] Mohanraj R, Dhanakumar S, Solaraj G. Polycyclic aromatic hydrocarbons bound to PM_{2.5} in urban Coimbatore, India with emphasis on source apportionment. *Sci World J*; 2012.
- [32] X. Li, P. Li, L. Yan, J. Chen, T. Cheng, S. Xu, *J Environ Monit* 3 (11) (2011) 2988–2993.
- [33] S.K. Pandey, K.-H. Kim, R.J.C. Brown, *Trends Anal Chem* 30 (11) (2011) 1716–1739.
- [34] A. Cachada, P. Pato, T. Rocha-Santos, D.S.E. Ferreira, A.C. Duarte, *Sci Total Environ* 430 (2012) 184–192.
- [35] C. Riccardi, P. Di Filippo, D. Pomata, M. Di Basilio, S. Spicaglia, *Sci Total Environ* 450 (2013) 13–21.
- [36] D. Shang, M. Kim, M. Haberl, *J Chromatogr A* 1334 (2014) 118–125.
- [37] G.M. Tehrani, R. Hshim, A.H. Sulaiman, S.S.B. Tavakoly, A. Salleh, *Environ Protect Eng* 15 (2012) 115–128.
- [38] C. Dong, C. Chen, C. Chen, *Int J Environ Res Public Health* 9 (2012) 2175–2188.
- [39] K. Veltman, M.A.J. Huijbregts, H. Rye, E.G. Hertwich, *Integr Environ Assess Manage* 7 (2012) 678–686.
- [40] J. Beyer, G. Jonsson, C. Porte, M.M. Krahn, F. Ariese, *Environ Toxicol Pharmacol* 30 (2010) 224–244.
- [41] M.A. Tudoran, M.V. Putz, *Chem Bull “Politehnica” Univ (Timisoara)* 57 (71) (2012) 1.
- [42] Y. Inomata, M. Kajino, K. Sato, T. Ohara, J.I. Kurokawa, *Environ Sci Technol* 46 (2012) 4941–4949.
- [43] Z.Y. Zhao, Y.I. Chu, J.D. Gu, *Ecotoxicology* 21 (2012) 1743–1752.
- [44] D.H. Phillips, *Mutat. Res.* 443 (1999) 139–147.
- [45] Standing Committee on Foodstuffs, 2001. Outcome of the expert group meeting on 3 October on ways to prevent contamination of olive residue oil and other oils with polycyclic aromatic hydrocarbons (PAH). Summary record of the 85th meeting of the Standing Committee on Foodstuffs, 25th October 2001, agenda item 9. http://europa.eu.int/comm/food/fs/rc/scfs/rap09_en.pdf.
- [46] K. Speer, E. Steeg, P. Horstmann, Th. Kühn, A. Montag, *J High Res Chrom* 13 (1990) 104–111.
- [47] Y.F. Jiang, X.T. Wang, M.H. Wu, G.Y. Sheng, J.M. Fu, *Environ Monit Assess* 183 (2011) 139–150.
- [48] A.M. Kipopoulou, E. Manoli, C. Samara, *Environ Pollut* 106 (1999) 369–380.
- [49] T. Nielsen, H.E. Jørgensen, J.C. Larsen, M. Poulsen, *Sci Tot Environ* 189 (190) (1996) 41–49.
- [50] P. Baumard, H. Budzinski, P. Garrigues, *Environ Toxicol Chem* 17 (1998) 765–776.
- [51] H. Chen, Y. Teng, J. Wang, *Sci Total Environ* 414 (2012) 293–300.
- [52] B.H. Chen, Y.S. Lin, *J Agric Food Chem* 45 (1997) 1394–1403.
- [53] K. Kim, S.A. Jahan, E. Kabir, R.J.C. Brown, *Environ Int* 60 (2013) 71–80.
- [54] ACGIH (American Conference of Governmental Industrial Hygienists). Polycyclic aromatic hydrocarbons (PAHs) biologic exposure indices (BEI) Cincinnati, OH: American Conference of Governmental Industrial Hygienists; 2005.
- [55] E. Lannerö, M. Wickman, M. van Hage, *Thorax* 63 (2008) 172–176.
- [56] M. Ciecierska, M.W. Obiedziński, *Food Chem* 141 (2013) 1–9.
- [57] Y. Wang, Z. Tian, H. Zhu, Z. Cheng, M. Kang, C. Luo, *Sci Total Environ* 439 (2012) 187–193.
- [58] K. Ravindra, R. Sokhi, R.V. Grieken, *Atmos Environ* 42 (2008) 2895–2921.
- [59] M. Benedetti, G. Martuccio, D. Fattorini, A. Canapa, M. Barucca, M. Nigro, F. Regoli, *Aquat Toxicol* 85 (2007) 167–175.
- [60] A. Tarantini, A. Maitre, E. Lefebvre, M. Marques, A. Rajhi, T. Douki, *Toxicology* 279 (2011) 36–44.
- [61] L. Campo, F. Rossella, S. Pavanello, D. Mielzynska, E. Siwinska, L. Kapka, P. Alberto Bertazzi, S. Fustinon, *Toxicol Lett* 192 (2010) 72–78.
- [62] J. Unwin, J. Cocker, E. Scobbie, H. Chambers, *Ann Occup Hyg* 50 (4) (2006) 395–403.
- [63] IPCS (International Programme On Chemical Safety). Polycyclic aromatic hydrocarbons, selected non-heterocyclic; 2010. <<http://www.inchem.org/documents/ehc/ehc/ehc202.htm>>.
- [64] P.B. Bach, M.J. Kelley, R.C. Tate, D.C. McCrory, *Chest* 123 (2003) 72–82.
- [65] D.L. Diggs, A.C. Huderson, K.L. Harris, J.N. Myers, L.D. Banks, P.V. Rekhadevi, *J Environ Sci Health C Environ Carcinog Ecotoxicol Rev* 29 (4) (2011) 324–357.
- [66] A.C. Olsson, J. Fevotte, T. Fletcher, A. Cassidy, A. Mannetje, P. Brennan, *Occup Environ Med* 67 (2010) 98–103.
- [67] US EPA (Environmental Protection Agency). Polycyclic aromatic hydrocarbons (PAHs) — EPA fact sheet. Washington (DC): National Center for Environmental Assessment, Office of Research and Development; 2008.
- [68] S.W. Burchiel, M.I. Luster, *Clin Immunol* 98 (2001) 2–10.
- [69] M. Miyata, M. Furukawa, K. Takahashi, F.J. Gonzalez, Y. Yamazoe, *Jpn J Pharmacol* 86 (2001) 302–309.
- [70] I.N. Pessah, C. Beltzner, S.W. Burchiel, G. Sridhar, T. Penning, W. Feng, *Mol Pharmacol* 59 (2001) 506–513.
- [71] R.T. Gamboa, A.R. Gamboa, A.H. Bravo, W.P. Ostrosky, *Int J Environ Res Publ Health* 5 (5) (2008) 349–355.
- [72] J. Lewtas, Air pollution combustion emissions: characterization of causative agents and mechanisms associated with cancer, reproductive and cardiovascular effects, *Mutat Res/Rev Mutat Res* 636 (1–3) (2007) 95–133.
- [73] A. Tarantini, A. Maitre, E. Lefebvre, M. Marques, C. Marie, J. L. Ravanat, T. Douki, *Mutat Res* 671 (2009) 67–75.
- [74] D.C. Spink, S.J. Wu, B.C. Spink, M.M. Hussain, D.D. Vakharia, B.T. Pentecost, L.S. Kaminsky, *Toxicol Appl Pharmacol* 226 (2008) 213–224.
- [75] H. Yang, M. Mazur-Melnyk, J.G. de Boer, B.W. Glickman, *Mutat Res* 423 (1999) 23–32.
- [76] M.L. Miller, K. Vasunia, G. Talaska, A. Andringa, J. de Boer, K. Dixon, *Environ Mol Mutagen* 35 (2000) 19–27.
- [77] S.J. Wei, R.L. Chang, K.A. Merkler, M. Gwynne, X.X. Cui, B. Murthy, M.T. Huang, J.G. Xie, Y.P. Lu, Y.R. Lou, D.M. Jerina, A.H. Conney, *Carcinogenesis* 20 (1999) 1689–1696.

- [78] A.K. Prahalad, J.A. Ross, G.B. Nelson, B.C. Roop, L.C. King, S. Nesnow, M.J. Mass, *Carcinogenesis* 18 (1997) 1955–1963.
- [79] P. Hainaut, G.P. Pfeifer, *Carcinogenesis* 22 (2001) 367–374.
- [80] K.H. Jung, J.K. Kim, J.H. Noh, J.W. Eun, H.J. Bae, M.G. Kim, et al, Characteristic molecular signature for the early detection and prediction of polycyclic aromatic hydrocarbons in rat liver, *Toxicol Lett* 216 (1) (2013) 1–8.
- [81] IPCS (International Programme on Chemical Safety). Selected nonheterocyclic polycyclic aromatic hydrocarbons. *Environmental Health Criteria* 202. Geneva: WHO; 1998.
- [82] D.M. Wassenberg, R.T. Di Giulio, *Environ Health Perspect* 112 (17) (2004) 1658–1664.
- [83] P. Kristensen, E. Eilertsen, E. Einarsdóttir, A. Haugen, V. Skaug, S. Ovrebo, *Environ Health Perspect* 103 (1995) 588–590.
- [84] F. Perera, D. Tang, R. Whyatt, S.A. Lederman, W. Jedrychowski, *Cancer Epidemiol Biomarkers Prev* 14 (3) (2005) 709–714.
- [85] S.C. Edwards, W. Jedrychowski, M. Butscher, D. Camann, K. A. Agnieszka, E. Mroz, *Environ Health Perspect* 118 (9) (2010) 1326–1331.
- [86] H.I. Abdel-Shafy, A.M. Al-Sulaiman, M.S.M. Mansour, *Water Sci Technol* 71 (4) (2015).
- [87] H.I. Abdel-Shafy, A.M. Al-Sulaiman, M.S.M. Mansour, *J Water Process Eng* 1 (2014) 101–107.
- [88] F. Perera, S. Wang, J. Vishnevetsky, B. Zhang, K.J. Cole, D. Tang, *Environ Health Perspect* 119 (8) (2011) 1176–1181.
- [89] S.J.M. Delgado, N. Aquilina, S. Baker, S. Harrad, C. Meddings, R.M. Harrison, *Anal Methods* 2 (2010) 231–242.
- [90] Y. Zhong, L. Zhu, *Sci Total Environ* 444 (2013) 177–182.
- [91] L. Zhu, H. Lu, S. Chen, T. Amagai, L. Zhu, T. Amagai, *J Hazard Mater* 162 (2–3) (2009) 1165–1170.
- [92] N. Nadarajah, H.J. Van, J. Pannu, A. Singh, O. Ward, *Appl Microbiol Biotechnol* 59 (2002) 540–544.
- [93] A.K. Haritash, *J Hazard Mater* 169 (2009) 1–15.
- [94] R.-H. Peng, A.-S. Xiong, Y. Xue, X.-Y. Fu, F. Gao, W. Zhao, Y.-S. Tian, Q.-H. Yao, *FEMS Microbiol Rev* 32 (2008) 927–955.
- [95] C.E. Cerniglia, Recent advances in the biodegradation of polycyclic aromatic hydrocarbons by *Mycobacterium* species, in: V. Sasek (Ed.), *The utilization of bioremediation to reduce soil contamination: problems and solutions*, Kluwer Academic Publishers, The Netherlands, 2003, p. 51–73.
- [96] C.E. Dandie, S.M. Thomas, R.H. Bentham, N.C. McClure, *J Appl Microbiol* 97 (2004) 246–255.
- [97] L. Fredslund, K. Sniegowski, L.Y. Wick, C.S. Jacobsen, R. De Mot, D. Springael, *Res Microbiol* 159 (2008) 255–262.
- [98] B.P. Hatzinger, A. Martin, *Environ Sci Technol* 29 (1995) 537–545.
- [99] S.-J. Kim, O. Kweon, R.C. Jones, J.P. Freeman, R.D. Edmondson, C.E. Cerniglia, *J Bacteriol* 189 (2007) 464–472.
- [100] S. Rappert, K.C. Botsch, S. Nagorny, W. Francke, R. Muller, *Appl Environ Microbiol* 72 (2006) 1437–1444.
- [101] C. Archana, G.O. Fazlurrahman, K.J. John Rakesh, *Indian J Microbiol* 48 (2008) 95–113.
- [102] M. Uyttebroek, S. Vermeir, P. Wattiau, A. Ryngaert, D. Springael, *Appl Environ Microbiol* 73 (2007) 3159–3164.
- [103] G. Cornelissen, H. Riegerink, M.M.A. Ferdinandy, P.C.M. Van Noort, *Environ Sci Technol* 32 (1998) 966–970.
- [104] W.A. Thorsen, C.W. Gregory, S. Damian, *Environ Sci Technol* 38 (2004) 2029–2037.
- [105] S.H. Chen, M.D. Aiken, *Environ Sci Technol* 33 (1999) 435–439.
- [106] C. Wang, H. Sun, J. Li, Y. Li, Q. Zhang, *Chemosphere* 77 (2009) 733–738.
- [107] Y. Teng, Y. Luo, M. Sun, Z. Liu, Z. Li, P. Christie, *Bioresour Technol* 101 (2010) 3443–3457.
- [108] E. Stanley Manahan, *Environmental chemistry*, CRC Press Inc., 1994.
- [109] B.J. Finlayson-Pitts Jr., J.N. Pitts, *Nature* 276 (1997) 1045–1052.
- [110] B.D. Thomas, A.H. Ronald, *Environ Sci Technol* 19 (1985) 1004–1006.
- [111] W.A. Korfmacher, E.L. Wehry, G. Mamantov, D.F.S. Natusch, *Environ Sci Technol* 14 (1980) 1094–1099.
- [112] J. Niu, P. Sun, K.-W. Schramm, *J Photochem Photobiol A: Chem* 186 (2007) 93–98.
- [113] H.I. Abdel-Shafy, M.S.M. Mansour, *Sustain Sanitation Pract* 17 (2013) 20–29.
- [114] A.S. Moursy, H.I. Abdel-Shafy, *J Environ Int* 9 (3) (1983) 165–171.
- [115] A. Alebic-Juretic, T. Cvitas, L. Klasinc, *Environ Sci Technol* 24 (1990) 62–66.
- [116] L. Zhang, P. Li, Z. Gong, X. Li, *J Hazard Mater* 158 (2008) 478–484.
- [117] Hassan SSM, El Azab WIM, Ali HR, Mansour MSM. In: *The 18th International conference on petroleum, mineral resources and development*. EPRI, Cairo, Egypt, 8–10 February; 2015.
- [118] Y. Wang, C.S. Liu, F.B. Li, C.P. Liu, J.B. Liang, *J Hazard Mater* 162 (2009) 716–723.
- [119] X.K. Wang, G.H. Chen, Z.Y. Yao, *Chin Chem Lett* 14 (2003) 205–208.
- [120] I.D. Manariotis, K.H. Karapanagioti, C.Y. Chrysikopoulo, *Water Res* 45 (2011) 2587–2594.
- [121] U.S. EPA. 2000. *Deposition of Air Pollutants to the Great Waters: Third Report to Congress*. Office of Air Quality Planning and Standards. EPA-453/R-00-0005; June 2000. <<http://www.epa.gov/air/oaqps/gr8water/3drprt/index.html>> .
- [122] K-F. Chang, G-C Fang, C. Lu, H. Bai, *Aerosol Air Qual Res* 3 (1) (2003) 41–51.
- [123] A. Bozlaker, A. Muezzinoglu, M. Odabasi, *J Hazard Mater* 153 (2008) 1093–1102.
- [124] S. Del Vento, J. Dachs, *Environ Sci Technol* 41 (2007) 5608–5613.
- [125] A.S. Shannigrahi, T. Fukushima, N. Ozaki, *Atmos Environ* 39 (2005) 653–662.
- [126] R.M. Harrison, D.J.T. Smith, L. Luhana, *Environ Sci Technol* 30 (1996) 825–832.
- [127] F. Esen, Y. Tasdemir, S.S. Cindoruk, *Atmos Res* 95 (2010) 379–385.
- [128] F. Esen, S.S. Cindoruk, Y. Tasdemir, *Environ Pollut* 152 (2008) 461–467.
- [129] R.M. Dickhut, K.E. Gustafson, *Environ Sci Technol* 29 (1995) 1518–1525.
- [130] Y. Wang, P.H. Li, H. Liu, X. Liu, W. Wang, *Atmos Res* (2010) 1–7.
- [131] X.M. Wu, Z.T. Fan, X. Zhu, K.H. Jung, P. Ohman-Strickland, C.P. Weisel, P.J. Lioy, *Atmos Environ* 57 (2012) 72–79.
- [132] W. Tsal, Y. Cohen, H. Sakugawa, I.R. Kaplan, *Environ Sci Technol* 25 (1991) 2012–2023.
- [133] N. Vardar, F. Esen, Y. Tasdemir, *Environ Pollut* 155 (2008) 298–307.
- [134] K.E. Gustafson, R.M. Dickhut, *Environ Sci Technol* 31 (1997) 1623–1629.
- [135] P.T. Franz, S.J. Eisenreich, *Environ Sci Technol* 32 (1998) 1771–1778.
- [136] Occupational Safety & Health Administration (OSHA) *Coal Tar Pitch Volatiles* [accessed 14.11.10].
- [137] NIOSH (National Institute for Occupational Safety and Health); 2010. <<http://www.cdc.gov/niosh/about.html>> .

[138] European Commission, Directive 2004/107/EC of the European Parliament and of the Council of 15 December 2004 relating to arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air, Off J L023 (2005) 0003–0016 [26/01/2005].

[139] Egyptian regulation: Egyptian Environmental Association Affair (EEAA), Law 48, No. 61–63, Permissible values for wastes in River Nile (1982) and Law 4, Law of the Environmental Protection; 1994.