

**Polycyclic Aromatic Hydrocarbons (PAHs) Persistence, Transformation, Bioaccumulation, and Fate in Different Waste-Impacted Environmental Matrices: A mini review**

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**ABSTRACT:** This paper provides an in-depth analysis of polycyclic aromatic hydrocarbons (PAHs), focusing on their chemistry, sources, distribution, biotransformation, magnitude, and environmental fate, as well as their bioaccumulation and bioconcentration in humans, animals, and plants. PAHs are a group of hazardous organic compounds consisting of multiple fused aromatic rings that have significant negative impacts on human health and ecosystems. The paper highlights the various sources of PAHs, including waste combustion processes, industrial activities, and natural occurrences, and discusses their distribution in different environmental compartments such as air, water, and soil. The complexity of PAH degradation processes, which can lead to the formation of potentially toxic transformation products, is also examined. The bioaccumulation and bioconcentration of PAHs in living organisms are explored, along with the mechanisms involved in their secretion and removal. Given the close association of PAHs with solid waste, sludge, and wastewater effluents, this review also emphasizes their significance within waste management contexts and the need for improved control and treatment strategies. Additionally, the exposure limits of these persistent organic pollutants were presented in accordance with the regulatory standards and permissible limits established by various global environmental and chemical regulatory agencies.

**KEYWORDS:** Polycyclic Aromatic Hydrocarbons (PAHs), waste-impacted matrices, environmental fate, bioaccumulation, waste management

### 1. Introduction:

In recent years, the significant growth in industrial and human activities, particularly in the petrochemical, pharmaceutical, urban, and agricultural sectors, has led to an increase in environmental contamination with persistent organic pollutants (POPs). The widespread and unregulated use of fertilizers and insecticides, combined with the growth of pharmaceutical and petrochemical industries, has raised serious concerns about the environmental and public health implications of POPs. According to the United Nations Environment Program (UNEP), the chemical industry is the world's second-largest manufacturing sector [1]. Since 1950, its global output has increased 50-fold, and forecasts predict that production will triple again by 2050 compared to 2010 levels [1]. The World Health Organization (WHO) reports that environmental chemical contamination causes about 2 million deaths, with health effects including poisoning, heart problems, chronic breathing issues, and cancer [2]. Furthermore, chemical pollution negatively impacts many parts of the ecosystem, which can then harm human well-being. This definitely includes exposure to toxic chemicals such as POPs. Among these hazardous compounds, Polycyclic Aromatic Hydrocarbons (PAHs) have emerged as a major group of concern due to their widespread occurrence, persistence, and potential health effects.

Polycyclic Aromatic Hydrocarbons (PAHs) are comprised of several hundred ubiquitous pollutants found throughout the environment. These toxic molecules are not only omnipresent in the environment but also in the interstellar medium. The chemical structure of PAHs consists of two or more fused benzene (aromatic) rings made up of shared pairs of carbon and hydrogen. Among this set of pollutants, 16 priority PAHs were identified by the U.S. Environmental Protection Agency (EPA) as being the parent PAHs [3]. The term "parent PAHs" is often used to refer to these sixteen priority PAHs because they serve as the basis for assessing the potential health and environmental impacts of PAHs in general. These parent PAHs are the most well-studied and well-known among the hundreds of PAH compounds, and they have been found to be the most toxic and prevalent in the environment. By focusing on these sixteen compounds, researchers and regulatory agencies can better understand and monitor the overall impact of PAHs on human health and the environment [4]. Figure 1 shows the chemical structure of these 16 parent PAHs [5].

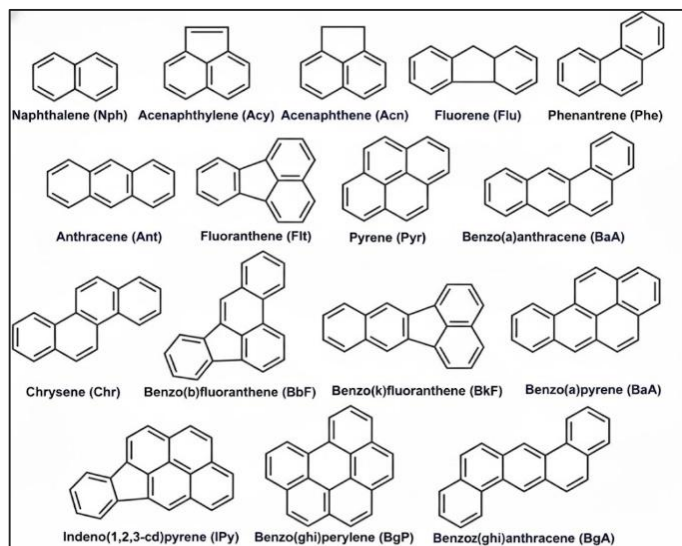


Figure 1. 2D representation of the 16 priority PAHs or "parent PAHs" (Reproduced from [5])

The parent PAHs are grouped together according to the profile provided by the Agency for Toxic Substances and Disease Registry (ATSDR) [6]. They are generally found in various environmental matrices, including air, soil, and water. PAHs are organic compounds that are typically colorless and odorless solids, exhibit diverse structures and varying levels of toxicity, and are classified based on their structure [4]. The UV spectrum plays a crucial role in identifying specific PAHs, as each ring possesses a unique UV spectrum, resulting in distinct absorption spectra for each isomer [7]. PAHs exhibit lipophilic properties (hydrophobic nature), making them insoluble in water but soluble in biological solvents. Factors such as low water-holding capacity, vapor pressure, and high melting and boiling points contribute to their classification as recalcitrant compounds. As their molecular weight increases, their aqueous solubility and vapor pressure decrease, and vice versa. Therefore, the addition of further aromatic rings to their structure leads to the complete loss of their aqueous solubility [8]. PAHs, as persistent organic pollutants, exhibit various properties, including heat resistance, conductivity, light sensitivity, and corrosion resistance, as well as diverse physiological effects [9]. PAHs are

also classified as substituted or unsubstituted compounds. Substituted PAHs are PAHs that have one or more of their hydrogen atoms replaced by another atom or group of atoms (i.e., a substituent). This can alter their chemical and physical properties, potentially affecting their toxicity and environmental fate. On the other hand, unsubstituted PAHs are PAHs that have no substituents, meaning that all of the hydrogen atoms on their aromatic rings are present. They are often considered to be more toxic than substituted PAHs because they are more readily absorbed by living organisms and can be more difficult to degrade in the environment [9]. Numerous questions remain unanswered in the field of POPs research, particularly concerning PAHs, due to their limited scope and complex chemical nature. This type of research is highly needed, as PAHs are a significant source of concern due to their harmful effects and persistence in the environment. To bridge the gap between current knowledge of technologies and the significant concerns surrounding PAH pollution, including its degradability and potential ecotoxicological impacts, further research in this area is necessary. This review aims to study the different aspects of PAHs, including their magnitude in the environment according to the recent statistics and limitation standards; their chemistry, analysis technologies, and quantification; recent knowledge about their distribution in the environment, bioaccumulation, biotransformation, and fate in the environment; their secretion and removal from the living organisms and the environment.

## 2. Magnitude of PAHs in the Environment:

The global release of PAHs into the environment is expected to increase from 85 million barrels in 2016 to 106.6 million barrels by 2030. In aquatic environments, approximately 209,000 tons of PAHs are discharged [10]. According to [11], around 520,000 tons of PAHs are emitted annually into the environment from various sources, including 56.9% from biofuels, 17% from wildfires, and 6.9% from consumer products. China and India led the list of PAH emitters with 114 Gg  $y^{-1}$  and 90 Gg  $y^{-1}$ , respectively, followed by the USA at 32 Gg  $y^{-1}$  in third place. Nigeria ranked fourth, Indonesia fifth, Brazil sixth, Pakistan seventh, the Democratic Republic of Congo (DRC) eighth, and Russia ninth. These nine countries collectively account for approximately 60% of global PAH emissions. PAH emissions were reported from all seven continents, with Asia emerging as the largest contributor, responsible for 53% of total worldwide PAH emissions [12].

Different global regulatory agencies, such as the *Occupational Safety and Health Administration (OSHA)*, the National Institute for Occupational Safety and Health (NIOSH), the U.S. Environmental Protection Agency (EPA), the U.S. Department of Health and Human Services, the *Agency for Toxic Substances and Disease Registry*, the *European Chemical Agency (ECHA)*, and the *World Health Organization (WHO)* established exposure limits for PAHs in various environmental matrices, such as air, water, soil, and sediments. These limits vary depending on the specific PAH compound, taking into account its unique properties, transport mechanisms, and potential health effects. Monitoring and enforcing these exposure limits are crucial for mitigating the adverse impacts of PAHs on humans and the environment.

The Occupational Safety and Health Administration (OSHA) has established a threshold of 0.2 milligrams of PAHs per cubic meter of air (0.2 mg/m<sup>3</sup>). Additionally, OSHA's Permissible Exposure Limit (PEL) for mineral oil mist containing PAHs is set at 5 mg/m<sup>3</sup>, averaged over an 8-hour exposure duration [13].

The National Institute for Occupational Safety and Health (NIOSH) advises that average workplace air concentrations for coal tar products should not surpass 0.1 mg/m<sup>3</sup> during a 10-hour workday within a 40-hour workweek. There are also additional limits in place for workplace exposure to substances containing PAHs, including coal, coal tar, and mineral oil [13].

In 2011, the US EPA established ambient water quality guidelines, setting the maximum concentration level for benzo(a)anthracene at 0.0001 mg/l. For other PAHs, such as benzo(a)pyrene, chrysene, benzo(k)fluoranthene, and benzo(b)fluoranthene, the limit is 0.0002 mg/l. For dibenzo(a,h)anthracene and indeno(1,2,3-c,d)pyrene, the maximum concentration levels are 0.0003 mg/l and 0.0004 mg/l, respectively [14].

Monitoring occupational exposure to PAHs typically involves assessing workplace air (both static and personal air), and increasingly, biological monitoring is also employed. Air samples commonly focus on the 16 EPA PAHs, particularly BaP, while 1-OHP, a metabolite of pyrene, is monitored in workers' urine. Biomonitoring is conducted because dermal exposure plays a significant role in total PAH exposure, taking into account the effectiveness of personal protective equipment (PPE), including respiratory and skin protection. Some studies have measured dermal exposure using semi-quantitative methods [15].

## 3. PAHs Distribution in the Environment:

PAHs, as prevalent environmental organic pollutants, exhibit characteristics like bioaccumulation in mammalian tissue, which are associated with mutagenic and carcinogenic effects. These pollutants also have adverse effects on the environment, leading to the uptake and accumulation of toxic substances through food chains and respiration, and in some instances, causing genetic defects and severe health problems in humans. The following section provides details on the distribution of PAHs in various environmental components.

3.1 PAHs distribution in air. The concentration and presence of PAHs in the air vary by location, with higher levels detected in urban, industrial, and residential areas, and lower levels in rural areas. For example, industrial areas have PAHs concentrations ten times higher than rural areas, while urban areas have levels five times higher. PAH concentrations in rural areas primarily increase due to biomass burning, causing a 9.7-fold increase compared to non-biomass burning periods [16]. Two types of emission sources contribute to the distribution of PAHs in the air: stationary and mobile. Stationary sources include industrial area emissions (waste incinerators, coking plants, power plants, boilers, and asphalt plants), agricultural burning (organized or unorganized), and residential combustion (cooking, heating, and tobacco smoking). Mobile emissions come from shipping, motor vehicles, railways, and aircraft. The particulate size differs between stationary and mobile sources, with stationary sources having considerably smaller particles [17]. In the troposphere, low molecular weight PAHs are typically found in vapor form or occasionally in particulate form after condensation. High molecular weight PAHs predominantly exist in the particulate phase [18].

3.2 PAHs distribution in water. The origins of PAHs in marine ecosystems can generally be classified into three groups: petrogenic PAHs (derived from fossil fuels), pyrogenic PAHs (resulting from organic matter combustion), and biogenic PAHs (formed through diagenetic processes). The primary sources of petrogenic PAHs in offshore sediments include natural oil seeps, oil spills, and offshore oil and gas operations. Apart from their pyrogenic origin, nitrogen and oxygenated derivatives of PAHs have an additional emission source, which involves the degradation of PAHs through biological, chemical, and photochemical processes in the environment [19]. PAHs are typically found in combination with other pollutants in wastewater, crustaceans, sediments, and water sources. They originate from industrial waste byproducts, as well as emissions from the burning of agricultural waste and domestic fuel combustion products. PAHs, particularly those with four to five rings like chrysene and benzo[a]pyrene, have negligible solubility in water [3]. This property enables them to easily adhere to the surface of particulate matter, which is believed to be the primary mechanism for transferring these pollutants from air and land to aquatic systems, as well as from the sea surface to deeper depths. Common pathways for PAHs to enter the environment include wet and dry deposition, leaching from creosote-treated wood, road runoff, industrial wastewater, fossil fuel combustion, and petroleum spills [3].

Numerous studies have reported the presence of these contaminants in aquatic environments. In treated potable water, PAH concentrations range from 1.33 ng/L for benzo[a]pyrene in Tehran, Iran, to 139,000 ng/L for phenanthrene in untreated potable water in Lagos, Nigeria [20]. PAH concentrations in rivers and lakes range from 0.5 ng/L for benzo[a]pyrene in northeastern China to 1,138,000 ng/L for pyrene in Southern Italy [21]. In domestic wastewater, fluorene concentration was found to be 14 ng/L in Jordan, while benzo[b]fluoranthene concentration reached 8,310,000 ng/L in South Africa [22].

3.3 PAHs distribution in soil & sediments. PAHs are commonly found in soils due to various sources such as coal and aluminum production, petrochemical activities, contaminated water irrigation, wood preservation, waste incineration, cement manufacturing, bushfires, traffic emissions, rubber tire manufacturing, power plant treatments, and asphalt constituents contribute to soil contamination by pollutants like PAHs [23]. Being hydrophobic, PAHs are typically found in the non-aqueous phase and are adsorbed by organic matter, soil particles, oily phases, and crystals. Various studies in India have revealed varying concentrations of PAHs in soil, depending on the specific location, with some areas exhibiting higher concentrations due to the presence of industrial sites, thermal power plants, or bus stops [23].

## 4. PAHs Bioconcentration, Bioaccumulation, Biotransformation, and Fate:

Polycyclic aromatic hydrocarbons (PAHs) enter the environment through various sources, including industrial activities, transportation, and natural processes. Once PAHs enter the environment, they undergo a series of transformations that can alter their chemical structure, toxicity, and fate. In this section, the various transformations of PAHs in the environment, their bioaccumulation in living organisms, and their fate in the environment will be discussed.

### 4.1 PAHs bioconcentration, bioaccumulation

Bioconcentration and bioaccumulation are two processes by which PAHs can accumulate in living organisms and the environment.

Bioconcentration refers to the process by which a substance, such as a PAH, is taken up and accumulated in an organism directly from the environment, primarily through the gills or skin in aquatic organisms or through the lungs or skin in terrestrial organisms. Bioconcentration factor (BCF) is a measure of the concentration of a chemical in an organism relative to the concentration in the surrounding environment [24]. The BCF for a PAH is dependent on its physicochemical properties,

such as molecular weight, solubility, and lipophilicity. Generally, higher molecular weight PAHs with low water solubility and high lipophilicity have higher BCF values. Bioaccumulation, on the other hand, is the process by which a substance, such as PAH, is taken up and accumulated in an organism over time through multiple exposure pathways, including food, water, and air [24]. Bioaccumulation occurs when an organism is repeatedly exposed to a substance, and the substance accumulates in the organism's tissues and organs, resulting in higher concentrations than in the surrounding environment. The bioaccumulation factor (BAF) is a measure of the concentration of a chemical in an organism relative to the concentration in its food or the surrounding environment.

PAHs can bioaccumulate in various organisms in the food chain, including phytoplankton, zooplankton, fish, birds, and mammals, including humans. The bioaccumulation of PAHs in organisms can have adverse effects on their health, including developmental abnormalities, reproductive problems, and immune system dysfunction [25].

PAHs can undergo various complex transformations and accumulate in different concentrations within the bodies of living organisms [26], including humans, animals, and plants. Once PAHs enter the body, they can be metabolized and biotransformed by enzymes, predominantly in the liver. This process usually involves two main phases [26]:

a. Phase I: During this phase, PAHs are oxidized, reduced, or hydrolyzed by enzymes, such as cytochrome P450, to produce reactive intermediates. These intermediates can form DNA or protein adducts, leading to potential mutagenic or carcinogenic effects [26].

b. Phase II: In this phase, the reactive intermediates are conjugated with endogenous molecules, like glucuronic acid, sulfate, or glutathione, to form water-soluble compounds that can be easily excreted from the body through urine or bile [26].

PAHs tend to accumulate in lipid-rich tissues due to their lipophilic nature. They can be distributed throughout the body and stored in various organs, including the liver, kidneys, lungs, adipose tissue, and even the brain. The concentrations of PAHs in these tissues may vary depending on factors like exposure levels, duration, and the specific PAH compound [26]. In plants, PAHs can be absorbed from the soil, air, or water through the roots, leaves, or other plant parts. The processes of absorption, translocation, and metabolism of PAHs within plants can be affected by factors like plant species, environmental conditions, and the specific PAH compound [27]. Once absorbed, PAHs can be distributed to different plant tissues, including stems, leaves, fruits, or seeds. Some PAHs can be metabolized within plant tissues, while others may remain in their original form or be sequestered in plant compartments such as cell walls or vacuoles [27].

Overall, the transformation and concentrations of PAHs within living organisms are complex processes that depend on various factors like the exposure route, duration, metabolism, and the specific PAH compound involved.

#### 4.2 PAHs biotransformation and fate in the environment

PAHs predominantly enter the environment through air emissions from sources such as volcanic activity, forest fires, residential wood burning, and vehicle exhaust [39]. They can also infiltrate surface water via industrial plant discharges and wastewater treatment facilities or contaminate soils at hazardous waste sites if storage containers leak [28]. The environmental behavior of PAHs depends on factors like their solubility in water and their propensity to evaporate into the air. Generally, PAHs don't dissolve easily in water and can be found in the air as vapors or attached to tiny solid particles. They can travel great distances before being deposited back to the earth through precipitation or particle settling [28]. While some PAHs evaporate from surface waters, most adhere to solid particles and accumulate at the bottom of rivers or lakes. In soil, PAHs tend to bind strongly to particles, with some evaporating from the surface into the air. Some PAHs in soil can also contaminate groundwater. The PAH concentration in plants and animals can be significantly higher than that in soil or water. PAHs can degrade into longer-lasting products through reactions with sunlight and other chemicals in the air, typically over days to weeks. In soil and water, breakdown usually takes weeks to months, primarily due to microbial activity. The fate of PAHs in the environment is influenced by several factors, including their physicochemical properties, environmental conditions, and the presence of other substances. The primary processes affecting the fate and removal of PAHs in the environment include volatilization, photodegradation, biodegradation, and sorption [29].

The breakdown of PAHs in the environment takes place through biological, chemical, and photochemical pathways. This degradation can lead to various transformation products (such as methyl-PAHs, oxy-PAHs, and nitro-PAHs), some of which may accumulate. Both biological and chemical degradation processes can generate temporary intermediates or compounds that resist further breakdown. If these products are not further degraded, they may potentially build up during a remediation process. As a result, substituted PAHs may be present in the environment, similar to their parent PAHs. Many of these compounds exhibit toxicity and mutagenicity, making it essential to determine their presence in various environments [30].

- Volatilization: Low molecular weight PAHs with higher vapor pressures can evaporate from soil or water surfaces and enter the atmosphere. The extent of volatilization depends on factors like temperature, wind speed, and the compound's vapor pressure.

- Photodegradation: PAHs can be degraded by sunlight, especially in the ultraviolet (UV) range. Photodegradation breaks down PAHs into smaller molecules or other degradation products.

- Biodegradation: Microorganisms, such as bacteria and fungi, can break down PAHs in the environment, especially in soil and water. The biodegradation rate depends on factors like PAH structure, nutrient availability, temperature, and microbial populations. Generally, smaller PAHs with 2-3 rings biodegrade more readily than larger PAHs with 4-6 rings.

- Sorption: PAHs can adsorb onto soil particles, sediments, or organic matter due to their hydrophobic nature. This process can reduce the mobility of PAHs in the environment and decrease their bioavailability to organisms. However, PAHs can also be desorbed from these surfaces under certain conditions, such as changes in pH or the presence of other organic compounds.

These processes are not mutually exclusive and can occur simultaneously in the environment. The relative importance of each process depends on the specific PAH compound and the environmental conditions.

#### 5. PAHs Secretion and Removal from Living Organisms:

The secretion and removal of PAHs from living organisms' bodies, including humans, animals, and plants, involve a variety of processes. PAHs can be metabolized, excreted, or sequestered in tissues. In this section, we'll discuss these processes in detail [31] & [32]:

- Metabolism: In humans and animals, PAHs are primarily metabolized in the liver by a group of enzymes known as cytochrome P450 (CYP) enzymes. These enzymes transform PAHs into more water-soluble metabolites, which can be more easily excreted from the body. The metabolism of PAHs often involves several steps, including oxidation, reduction, and hydrolysis, followed by conjugation with water-soluble compounds like glucuronic acid, sulfate, or glutathione.

- Excretion: In humans and animals, the water-soluble metabolites resulting from PAH metabolism can be excreted through urine or feces. Bile serves as a primary route for the elimination of PAH metabolites in the form of conjugates. Some PAH metabolites can also be excreted through sweat, saliva, and breast milk. In plants, the polar metabolites of PAHs can be transported to the vacuoles, where they may be stored or excreted into the surrounding environment via root exudates or transpiration [32].

- Sequestration: In some cases, PAHs and their metabolites can accumulate in tissues, such as fats in humans or animals, instead of being metabolized and excreted. This can lead to bioaccumulation and potential adverse health effects. In plants, PAHs can be stored in various tissues, such as leaves, stems, and roots, or bound to lignin and cellulose, making them less available for metabolism and excretion. Some plants can also produce specialized structures, such as glandular trichomes or resin ducts, that can store PAHs and reduce their toxic effects.

The efficiency of these processes varies among different organisms and depends on factors such as the specific PAH compound, the organism's metabolic capabilities, and the environmental conditions.

#### 6. Conclusion

In conclusion, this paper provides a comprehensive overview of polycyclic aromatic hydrocarbons (PAHs), covering their chemistry, sources, distribution, biotransformation, and environmental fate. PAHs are a group of hazardous organic compounds consisting of multiple fused aromatic rings, which are ubiquitous in the environment and have significant negative impacts on human health and ecosystems. The paper highlighted the various sources of PAHs, including combustion processes, industrial activities, and natural occurrences, and their distribution in different environmental compartments such as air, water, and soil. It also discussed the biotransformation and fate of PAHs in the environment, emphasizing the complexity of their degradation processes, which can lead to the

formation of potentially toxic transformation products. Furthermore, the paper explored the bioaccumulation and bioconcentration of PAHs in living organisms, including humans, animals, and plants, as well as their potential adverse health effects. It also addressed the mechanisms involved in the secretion and removal of PAHs from the bodies of humans, animals, and plants, underscoring the importance of understanding these processes to protect human health and the environment. In summary, understanding the complexities of PAHs is crucial for addressing the environmental and health risks they pose. By adopting the recommended measures and fostering collaborative efforts among researchers, policymakers, and industry stakeholders, we can work towards a cleaner and healthier future, not only in the UAE but also globally.

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