

Environmental Sources, Formation, And Biotransformation Pathways And Health Effects Of Polycyclic Aromatic Hydrocarbons: A Review

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Abstract: This paper critically reviews the current knowledge on Polycyclic Aromatic Hydrocarbons (PAHs), hazardous organic pollutants mainly produced by the incomplete combustion of organic matter. While PAH distribution in air, soil, and water is relatively well-documented, their behavior in complex systems such as post-wildfire environments and urban runoff remains poorly understood. Key gaps include limited knowledge on PAH transport, transformation, and partitioning among particle sizes, as well as their long-range atmospheric transport and deposition in pristine ecosystems. The review highlights the need to investigate PAH interactions with emerging carbon-based materials such as graphdiyne, particularly their adsorption and desorption dynamics for potential remediation applications. Another critical research gap lies in understanding the bioavailability of both parent and alkylated PAHs in soils and sediments, especially using in vitro digestion models or bioaccumulation studies in aquatic organisms. Additionally, the transformation of PAHs into toxic metabolites for example, hydroxylated PAHs, and their health and ecological impacts remain underexplored. The role of microbial communities in degrading high-molecular-weight PAHs under diverse environmental conditions, both aerobic and anaerobic, also requires further study. Addressing these gaps would provide novel insights into PAH persistence, fate, and risk. The review concludes that effective environmental management and policy formulation depend on identifying PAH sources and adopting multifaceted approaches, including regulatory measures, continuous monitoring, cleaner technologies, public awareness, and community participation.

Keywords: polycyclic aromatic hydrocarbons, environmental sources, formation and biotransformation pathways, health effects

1.0 INTRODUCTION

PAHs are a large class of persistent organic pollutants, recognized for their ubiquity, chemical stability, hydrophobicity, and strong association with adverse health outcomes. Ravindra et al (2008) described PAHs as a group of organic compounds containing two or more benzene rings in a linear, angular, or clustered arrangement. They are formed primarily as a result of incomplete combustion or pyrolysis of organic matter, including fossil fuels and biomass (Honda & Suzuki, 2020). According to the United States Environmental Protection Agency (US EPA), PAHs are defined as a class of chemicals that occur naturally in the environment and are also produced as a result of the incomplete combustion of organic matter, such as coal, oil, gas, and biomass (Dandajeh *et al.*, 2021). They are widespread in the atmosphere, soils, sediments, water bodies, and biota.

PAHs can be sourced from natural sources such as forest fires, volcanic eruptions, and diagenesis of organic matter, as well as anthropogenic sources like incomplete combustion of fossil fuels, industrial processes, vehicle emissions, and waste incineration (Abdel-Shafy & Mansour, 2016). They are generated from various sources, including wildfires, volcanic activity, and industrial activities (Ortega-Calvo & Gschwend, 2010). The global impact of PAHs is significant, as they can

be absorbed into air, water, soils, and sediments, causing long-term contamination in aquatic environments (Tang & Wang, 2024). Once released, PAHs undergo photolysis, oxidation, adsorption to particulates, and microbial degradation. Biotransformation leads to oxy-, nitro-, and hydroxy-PAHs, which can be even more toxic and persistent. The human exposure pathways include inhalation (ambient/indoor air), ingestion (contaminated food/water), and dermal absorption (soils, occupational settings). Long-term exposure to PAHs can lead to cancer, developmental issues, immune system suppression, and reproductive harm (Guan *et al.*, 2023). Environmental impacts include toxic effects on aquatic life, particularly benthic organisms, which can bioaccumulate in the food web, affecting fish, amphibians, birds, and mammals (Abbasi *et al.*, 2024).

Their low water solubility leads to partitioning into sediments and biota, which can persist in the environment (Mitchell *et al.*, 2023). Many PAHs are carcinogenic, mutagenic, and teratogenic to humans and wildlife, and can bioaccumulate in the food chain, causing adverse effects on aquatic organisms. PAHs have a cyclic, planar structure with a conjugated system of π -electrons, allowing for electron delocalization and enhanced compound stability (Kingputtpong *et al.*, 2022). The number of fused rings can vary, resulting in different structures, such as naphthalene or coronene. The fused aromatic rings create a planar molecular structure, stabilized

by π -electrons (Kadri *et al.*, 2017). PAHs' rigidity is due to strong carbon-carbon bonds and the absence of rotatable bonds (Berger *et al.*, 2015). They are hydrophobic, meaning they are non-polar, due to the presence of carbon-hydrogen bonds and the absence of polar functional groups. This hydrophobic nature contributes to their solubility in non-polar solvents and their tendency to accumulate in lipid-rich environments (Ghosh & Mukherji, 2023).

In Africa, PAHs are increasingly recognized as a growing environmental concern due to rapid industrialization, urbanization, and oil and gas exploration (Dietrich *et al.*, 2022). In Uganda, the Albertine Graben region faces significant challenges related to PAH contamination due to oil exploration, urbanization, and traditional biomass burning. Collaboration with international organizations and environmental agencies could help enhance Uganda's capacity to monitor and mitigate PAH pollution (Li, 2024). Despite decades of research, gaps remain in understanding new/emerging sources, for example, e-waste burning, wildland-urban interface fires, secondary formation, environmental transformation, and combined exposure risks, as climate change and rapid urbanization are altering emission profiles, exposure pathways, and risk patterns, calling for updated assessment.

2.0 METHODOLOGY

The data for this study were gathered from original, peer-reviewed papers published in scientific journals with an emphasis on PAHs as well as their sources and health risks to the ecosystem using a narrative literature review technique. To locate the available peer-reviewed data, we conducted a thorough search of electronic literature databases from reliable sources, such as Research Gate and Google Scholar, among others. "Sources of PAHs", "environmental and health risks associated with PAHs pollution," and "Physical and chemical properties of PAHs. We checked the data we had read and downloaded, and we resolved any discrepancies that surfaced throughout the draft write-up by having a lengthy conversation that was governed by the review's guidelines. Taking into account the information from the evaluated literature, the conclusion was drawn.

3.0 Results and Discussion

SOURCES AND EMISSION PATHWAYS OF POLYCYCLIC AROMATIC HYDROCARBONS

PAH analysis involves collecting water, soil, and sediment samples, using techniques like GC-MS or HPLC, and determining the concentrations of various PAH compounds (Aziz *et al.*, 2021). The PAH profile, which represents the relative abundance of different PAH compounds, can be used to identify potential sources, such as petrogenic, pyrogenic, or biogenic sources (Feng *et al.*, 2023). The spatial distribution of PAH concentrations and source contributions within the study area can identify localized or regional trends, while temporal variations can provide insights into changes in emission patterns, environmental transport, and deposition processes over time (Nguyen *et al.*, 2020). These methods help

to understand the impact of PAHs on water and sediment quality and their potential sources.

a) Petrogenic sources of Polycyclic Aromatic Hydrocarbons

Petrogenic sources of Polycyclic Aromatic Hydrocarbons (PAHs) are derived from petroleum-based products, such as crude oil, oil spills, and refined petroleum products (Canli, 2022). These sources are distinct from pyrogenic sources, which are produced through incomplete combustion of organic matter (Güzel *et al.*, 2022). Key characteristics of petrogenic PAH sources include lower molecular weight PAHs, such as naphthalene, phenanthrene, and dibenzothiophene, with higher relative abundance. They also have higher phenanthrene/anthracene and lower fluoranthene/pyrene ratios compared to pyrogenic sources. Additionally, petrogenic PAHs often contain a higher proportion of alkylated PAH homologs, which can be used as a signature for these sources (Ravanbakhsh *et al.*, 2023).

Petrogenic PAHs are more resistant to weathering and biodegradation processes compared to pyrogenic PAHs and can persist in the environment, particularly in sediments, and may be transported long distances through aquatic systems (Farhat *et al.*, 2023). Examples of petrogenic PAH sources include oil spills from tanker accidents, leaks or discharges from petroleum refineries, runoff from roads and urban areas containing petroleum-based products, and inputs from industrial processes involving petroleum-based products (Güzel *et al.*, 2022).

Petrogenic sources of Polycyclic Aromatic Hydrocarbons (PAHs) can be released into water and sediments through various pathways (Nawrot *et al.*, 2023). These pathways include oil spills and leaks, stormwater and urban runoff, wastewater and industrial effluents, atmospheric deposition, sediment resuspension, and groundwater discharge. Oil spills and leaks from oil refineries, pipelines, and storage facilities can introduce PAHs into aquatic environments, which can be transported and distributed through water currents, sediment transport, and adsorption onto suspended particles (Wang *et al.*, 2023).

Petrogenic PAHs accumulated on urban surfaces can be washed off and carried into nearby water bodies through stormwater and surface runoff (Rokhbar *et al.*, 2023). Wastewater and industrial effluents from industrial facilities can also contribute to the contamination of surface water, groundwater, and sediments (Rocha *et al.*, 2021). Atmospheric deposition occurs through processes like volatilization, combustion of fuels, and industrial activities, which can deposit PAHs onto water surfaces and sediments through wet and dry deposition. Sediment resuspension occurs when PAHs accumulated in aquatic sediments are resuspended into the water column due to physical disturbances (Abdel-Shafy & Mansour, 2016). Understanding the emission pathways for PAHs is crucial for identifying primary sources, assessing environmental fate and transport, and developing targeted mitigation strategies to minimize their impact on aquatic ecosystems and water quality.

b) Pyrogenic sources of Polycyclic Aromatic Hydrocarbons

Polycyclic Aromatic Hydrocarbons are produced through incomplete combustion or pyrolysis of organic matter, such as fossil fuels, biomass, and other carbon-rich materials (Okechukwu *et al.*,2021). These sources are distinct from petrogenic sources, which are PAHs derived from petroleum-based products (Cui *et al.*,2022). Key characteristics of pyrogenic PAH sources include a higher molecular weight PAH profile, isomer ratios, and a lower proportion of alkylated PAH homologs (Maslov & Podkovyrov, 2023). Pyrogenic PAHs are more susceptible to degradation and transformation processes, such as photolysis and microbial degradation, compared to petrogenic PAHs (Christensen *et al.*,2022). However, they can persist in the environment, particularly in sediments and soils, due to their strong adsorption to organic matter and low bioavailability (Adu *et al.*,2023). Examples of pyrogenic PAH sources include combustion of fossil fuels in power plants, biomass burning in forest fires, incomplete combustion of organic matter in residential and industrial activities, and emissions from high-temperature industrial processes (Yang *et al.*,2019). Pyrogenic sources of Polycyclic Aromatic Hydrocarbons into water and sediments are primarily emitted from incomplete combustion or pyrolysis of organic matter (Radomirović *et al.*,2023). These sources can be found in atmospheric deposition, surface runoff and erosion, effluent discharges, spills and accidental releases, atmospheric deposition on land and subsequent runoff, and resuspension of contaminated sediments (Najurudeen *et al.*,2023). Atmospheric deposition occurs during combustion processes like power generation, industrial operations, and residential burning, which can deposit PAHs onto water surfaces and sediments through wet and dry deposition (Moskovchenko *et al.*,2023). Surface runoff and erosion, as well as soil erosion and the mobilization of PAH-contaminated soil and sediment, contribute to the introduction of PAHs into aquatic environments (Anders *et al.*,2023).

Effluent discharges from facilities that use or produce high-temperature processes, such as power plants, refineries, and metal smelters, can also introduce PAHs into surface water bodies and sediments. Accidental spills or releases of materials containing PAHs can also lead to contamination of water and sediments (Wang *et al.*,2024). The specific emission pathways and their importance vary depending on location, land use, and the nature of the pyrogenic sources in the surrounding environment (Bwala & Sabiu Imam, 2023). The idea of these pathways is crucial for identifying sources, assessing environmental fate and transport, and developing effective mitigation strategies to reduce their impact on aquatic ecosystems and water quality.

c) Biogenic sources of Polycyclic Aromatic Hydrocarbons

Polycyclic Aromatic Hydrocarbons (PAHs) are naturally produced by living organisms like plants, bacteria, and fungi

through various biological processes (Drooge *et al.*,2022). Key characteristics of biogenic PAH sources include a lower molecular weight PAH profile, specific PAH compounds, and a lack of alkylated PAHs (Gao *et al.*,2022). These sources are more susceptible to degradation and transformation processes, such as microbial degradation and photolysis, and may have a more localized distribution and shorter residence time in the environment. Examples of biogenic PAH sources include natural production by microorganisms in soil, sediments, and aquatic environments, biosynthesis by higher plants and algae, especially in coastal and marine environments, and the diagenetic transformation of organic matter in sediments and soils (Mardoñez *et al.*,2023). However, anthropogenic activities can also introduce biogenic PAHs into the environment, such as the application of organic fertilizers or disturbance of natural ecosystems (Imai *et al.*,2023). Identifying biogenic PAH sources is crucial for understanding the natural background levels of these compounds in the environment and differentiating them from anthropogenic sources, which is essential for assessing environmental impacts and developing appropriate mitigation strategies (Aziz *et al.*,2021).

These PAHs can be released into water and sediments through various pathways. These pathways include aquatic organism excretion and decomposition, terrestrial plant litter and soil organic matter, bioturbation and sediment mixing, hydrothermal vents and seeps, and atmospheric deposition (Hou *et al.*,2023). Aquatic organisms, like phytoplankton, algae, and bacteria, can synthesize and release PAHs as part of their natural metabolic processes. These PAHs can also be transported into aquatic systems through surface runoff, erosion, and groundwater discharge (Biradar *et al.*,2024). Bioturbation and sediment mixing can resuspend and mix biogenic PAHs, making them available for release into the water column (Hou *et al.*,2023). In marine environments, biogenic PAHs can be released from natural seeps and hydrothermal vents, where they are produced by chemosynthetic microorganisms (Gidley *et al.*,2022). These PAHs can then be dispersed in the water column and deposited in nearby sediments. Atmospheric deposition can also release PAHs through biological processes, such as volatilization from plants or microorganism emission (Cousins *et al.*,2022). This helps to distinguish them from anthropogenic sources, assess natural background levels of PAHs in aquatic environments, and also evaluate the ecological impacts and cycling of biogenic PAHs in the ecosystem (Okechukwu *et al.*,2021).

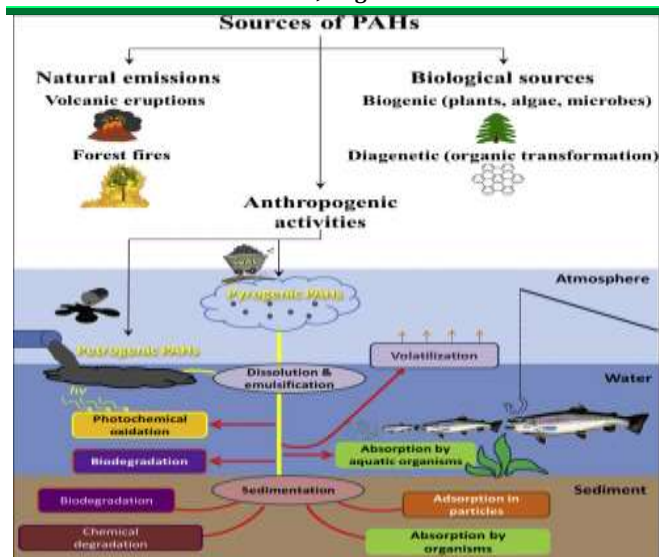


Figure 1: shows the different sources and transportation of PAHs and PFAS (Behera *et al.*, 2018)

Despite of this studies, significant research still exists on sources of PAHs such as a study that aims to reduce uncertainty in PAH source attribution and emissions by (i) developing isomer- and isotope-based source signatures for dominant and emerging sources, (ii) quantifying emission factors and source behaviors under real operating conditions, and (iii) integrating these data into source-to-exposure models that propagate uncertainty to inform mitigation is serious research gap.

PAHs often co-occur in contaminated environments with perfluoroalkyl substances (PFAS) (e.g., firefighting foam sites, post-wildfire areas), but their combined toxicological effects are rarely studied. The potential for additive, synergistic, or antagonistic interactions is a significant knowledge gap. Advanced research that investigates the toxicological interactions of PFAS and PAHs in human cell lines or animal models, focusing on endpoints like liver function or immune response, would address this gap. Additionally, the development of risk assessment models for PFAS-PAH mixtures in contaminated sites can reveal interesting data. Furthermore, a study of the combined environmental fate of PFAS and PAHs in complex systems like wildfire-affected sediments is needed.

There also exist analytical challenges for complex matrices for these pollutants. Detecting and quantifying PFAS and PAHs in complex environmental matrices (e.g., sediments, biota) is challenging due to their diverse chemical structures and low concentrations. Semi-quantitative and non-targeted analytical methods need further development. Another study that develops advanced analytical methods (e.g., high-resolution mass spectrometry, electrochemical detection) for simultaneous detection of PFAS and PAHs in environmental samples, creates standardized protocols for non-targeted analysis of PFAS and PAH mixtures in complex matrices, and validates passive sampling techniques for monitoring PFAS and PAHs in air, water, or soil is very coersing. Lastly, conduct comparative studies on PFAS and PAH

contamination in developing vs. developed regions, focusing on exposure pathways and health impacts

3.2.1 Physical properties of polycyclic aromatic hydrocarbons

PAHs, or polyhydroxy compounds, have various properties that are influenced by their molecular structure, weight, volatility, solubility, and environmental behavior (Berger *et al.*,2015). The number of aromatic rings in PAHs can be linear, angular, or clustered, affecting their stability, reactivity, and environmental behavior (Liu *et al.*,2024). The molecular weight of PAHs ranges from low-molecular-weight (LMW) compounds like naphthalene to high-molecular-weight (HMW) compounds like coronene (Zoveidadianpour *et al.*,2023). Volatility is inversely related to the number of aromatic rings, with LMW PAHs being more volatile than HMW PAHs. PAHs are generally hydrophobic and have low water solubility, which is crucial in determining their bioavailability and environmental fate (Piccolo *et al.*,2024). PAHs have relatively high melting and boiling points compared to other organic compounds of similar molecular weight, which influence their fate and transport under environmental conditions (Roslan *et al.*,2023). The Log Octanol-Water Partition Coefficient (Log Kow) measures the hydrophobicity and lipophilicity of PAHs, indicating greater partitioning into organic matter and lipids, which can lead to bioaccumulation in living organisms (Kang *et al.*,2016). Photochemical reactivity of PAHs is also important, as many are susceptible to photochemical degradation, particularly lighter, more volatile compounds. This can lead to the formation of more polar and water-soluble metabolites, with different environmental fates and toxicological profiles (Gong *et al.*,2021)

3.2.2 Chemical properties of polycyclic aromatic hydrocarbons

PAHs, or polyhydroxy acids, have an aromatic structure due to their delocalized π -electron system, which provides stability and influences their reactivity (Thacharodi *et al.*,2023). This makes them resistant to chemical and biological degradation, ensuring their persistence in the environment. PAHs can undergo various chemical reactions, including oxidation, reduction, electrophilic addition, and photochemical reactions, influenced by factors like aromatic rings and substituents. Oxidation reactions can lead to more polar and potentially toxic metabolites (Liu *et al.*,2024).

PAHs have a strong tendency to adsorb to organic matter, such as soil, sediments, and suspended particulates, influenced by factors like organic carbon content, pH, and ionic strength of the environment (Radomirović *et al.*,2023). Adsorption affects the bioavailability, mobility, and persistence of PAHs in the environment (Patel *et al.*,2020). PAHs can be degraded by microorganisms like bacteria and fungi through enzymatic processes, with rates and pathways varying based on the compound, environmental conditions, and microbial metabolic capabilities (Wang *et al.*,2022).

PAHs can also be bioaccumulated in living organisms due to their hydrophobic nature, with bioaccumulation influenced by factors like lipid content, metabolism, and trophic level (Gondwal & Mandal, 2023). Biomagnification can occur when PAHs are transferred and concentrated through the food web, posing a risk to higher-level consumers (Cara *et al.*, 2022).

Summary for Physical and Chemical Properties of Polycyclic Aromatic Hydrocarbons

Table 1: Chemical and physical properties of the 16 SEPA priority pollutant PAHs. abbreviations: Kow - octanol-water partitioning coefficient, Koc - organic carbon partitioning coefficient

Name	Formula	Molecular weight (g/mol)	Solubility in water (mg/L)	Phase distribution	Melting point (°C)	Boiling point (°C)	Vapor pressure (mm Hg)	Log Kow	Log Koc	Toxicity (LD ₅₀)	Fluorescence	Partition coefficient	Other properties
Naphthalene	C ₁₀ H ₈	128.17	31.00	Gas	80.26	218	0.087	3.29	2.97	2B	Fluorescent	Par	254 448 6.4×10 ⁻⁹ 5.90 No data 2B
Acenaphthene	C ₁₀ H ₈	154.21	3.80	Gas	95	96	4.47×10 ⁻³	3.98	3.66	3	Benzo(a,h,i)perylene	Par	156 393 2.5×10 ⁻⁵ 4.88 4.58 3
Acenaphthylene	C ₁₀ H ₈	152.20	16.10	Gas	92-93	265-275	0.029	4.07	1.40	3	Dibenz(a,h)anthracene	Par	179 495 5.6×10 ⁻⁹ 6.06 4.58 1
Anthracene	C ₁₄ H ₁₀	178.23	0.045	Par	218	340-342	1.75×10 ⁻⁶	4.45	4.15	3	Indeno(1,2,3-c)pyrene	Par	168 No data 5.0×10 ⁻⁷ 6.04 6.74 2B
Phenanthrene	C ₁₄ H ₁₀	178.23	1.10	gas	100	340	6.8×10 ⁻⁴	4.45	4.15	3	Benzo(a)anthracene	Par	215 480 9.59×10 ⁻¹¹ 6.06 5.74 2B
Fluorene	C ₁₃ H ₁₀	166.22	1.90	Gas	116-117	295	3.2×10 ⁻⁴	4.18	3.86	3	Benzo(a)anthracene	Par	262 No data 1.0×10 ⁻¹⁰ 6.84 6.52 2A
Fluoranthene	C ₁₄ H ₁₀	202.26	0.260	Par	110.8	375	5.0×10 ⁻⁶	4.90	4.58	3	Benzo(a)anthracene	Par	273 550 1.03×10 ⁻¹⁰ 6.50 6.20 3
Benzo(a)anthracene	C ₁₂ H ₁₂	288.29	0.011	gas	158	438	2.5×10 ⁻⁶	5.61	5.30	2B	Benzo(a)anthracene	Par	276 530 10 ⁻¹⁰ - 10 ⁻¹⁸ 6.58 6.20 2B

These properties are, however, not updated, a validated, isomer-resolved property database and predictive framework for PAHs and common substituted/oxidized derivatives (vapor pressure, solubility, partition coefficients, photochemical and oxidative reactivity, sorption kinetics), and quantify implications for fate, bioavailability, and exposure would develop the PAH knowledge about its chemical and physical properties.

3.3 Formation of Polycyclic Aromatic Hydrocarbons in the environment, their Fate and Transport in complex systems

PAHs are formed in the environment through various processes, including incomplete combustion of organic matter, pyrolysis and thermal degradation, petroleum and oil spills, and natural geological processes (Praveenkumar *et al.*, 2024). The incomplete combustion of fossil fuels and biomass produces PAHs like benzo[a]pyrene, fluoranthene, and pyrene (Honda & Suzuki, 2020). The industrial processes, like coke production, metal smelting, and power generation also generate PAH emissions. Pyrolysis and thermal degradation of organic matter at high temperatures can lead to the formation of PAHs, such as charcoal production, wood burning, and waste treatment (Praveenkumar *et al.*, 2024). The PAH profile in these cases is influenced by factors such as organic matter composition, temperature, and oxygen presence (Yang *et al.*, 2019).

Petroleum and oil spills release PAHs into the environment during oil spills or weathering of petroleum products. The specific PAH profile depends on the composition of the original petroleum source and weathering processes (Guma *et al.*, 2021). Weathering of crude oil can release lighter PAHs, while heavier PAHs like benzo[a]pyrene may be more persistent (Qiao *et al.*, 2021). Natural geological processes, such as the thermal maturation of organic matter in sedimentary rocks, can also produce PAHs in certain geological formations like coal and shale deposits (Yilmaz *et al.*, 2023). The PAH profile in these sources is influenced by the composition of the original organic matter and the thermal history of the geological formation (Nakajigo *et al.*, 2023). While PAH fate in the environment has been studied, the interaction of PAHs with emerging materials is not well known. Therefore, a study that investigates PAH transport and transformation in reactive matrices such as post-wildfire sediments or urban aquatic systems, focusing on partitioning between coarse, fine, and ultrafine particles. Conduct exposure assessments for PAHs in urban communities near sources like asphalt sealcoating or industrial emissions. Evaluate the effectiveness of PPE in reducing PAH exposure in firefighters, focusing on dermal and inhalation pathways. Develop biomarkers (e.g., urinary OH-PAHs) for assessing PAH exposure in diverse populations.

3.3.1 Hydrogen abstraction and acetylene or carbon addition (HACA)

The best standard reaction mechanisms for polycyclic hydrocarbon formation in HACA involve hydrogen abstraction and acetylene addition (Zhao *et al.*, 2018). This 2-step route involves continuous hydrogen abstractions to initiate the aromatic grain, followed by acetylene addition to a radical site formed in the hydrogen abstraction step (Kusumawati & Mangkoedihardjo, 2021). The HACA mechanism is a process that involves the sequential addition of acetylene or other small carbon-containing species to aromatic molecules, coupled with hydrogen abstraction steps. This leads to the growth and formation of larger particulate

air (PAH) structures (Khan *et al.*, 2024). The key steps in the HACA mechanism include hydrogen abstraction, where an aromatic molecule is transformed into an aromatic radical (Asiwaju *et al.*, 2023). This radical then reacts with acetylene or other small carbon-containing species, resulting in the addition of the carbon-containing species to the aromatic structure (Asiwaju *et al.*, 2023).

The adduct formed in the previous step may undergo rearrangement and cyclization reactions, leading to the formation of a new aromatic ring or the expansion of the existing aromatic structure (Bauer *et al.*, 2022). The process of hydrogen abstraction and acetylene or carbon addition can repeat, allowing for the sequential growth of the PAH structure and the formation of larger and more complex PAHs (Mallah *et al.*, 2022). Understanding the HACA mechanism is crucial for developing strategies to mitigate the formation of harmful PAHs and soot in combustion systems and designing clean and efficient combustion technologies (Verma *et al.*, 2023). The best standard reaction mechanisms for polycyclic hydrocarbons formation in HACA involve hydrogen abstraction and acetylene addition (Khan *et al.*, 2024). This 2-step route involves continuous hydrogen abstractions to initiate the aromatic grain, followed by acetylene addition to a radical site formed in the hydrogen abstraction step (Zhao *et al.*, 2018).

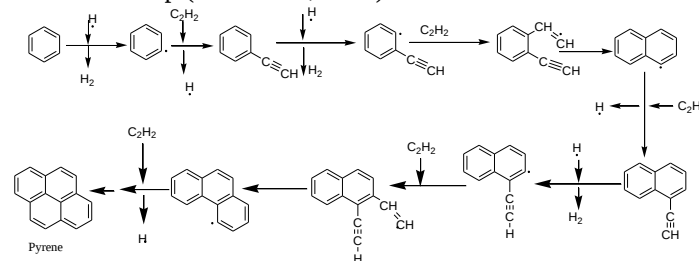


Figure 2: Showing HACA reaction path representation of the HACA reaction mechanism (Reizer *et al.*, 2022)

This pathway however poses a challenge that there is lack of isomer-resolved formation yields to support source apportionment and toxicology. Also, HACA derived at very high temperature; environmental low-temperature regimes and oxygen-limited flames may favor other routes (radical-mediated carbon addition, surface polymerization). Additionally, upscaling molecular mechanisms to emissions and fate models, i.e., mechanistic parameters, are rarely implemented in reactive-transport or atmospheric models with proper uncertainty. A study that measures yields and kinetics of PAH formation from controlled precursor mixtures under variable temperature (400–1400 °C), Oxygen, pressure, and residence time is important.

3.3.2 Bittner Howard's reaction route

The Bittner-Howard reaction is a process that involves the addition of acetylene to an aromatic radical, resulting in the formation of a linear, unsaturated intermediate (Kislov *et al.*, 2005). This intermediate then undergoes cyclization,

forming a new carbon-carbon bond, leading to the closure of a new aromatic ring (Jin *et al.*, 2021). The cyclic intermediate then undergoes hydrogen abstraction, resulting in the loss of hydrogen and the formation of a fully aromatic PAH structure. This sequence can repeat, allowing for the growth and formation of larger PAH structures (Altarawneh & Altarawneh, 2022).

The acetylene addition step is fast and exothermic, providing driving force for the reaction (Y. Wang *et al.*, 2014). The cyclization step is often rate-limiting due to the need to overcome kinetic barriers and form new carbon-carbon bonds (Kislov *et al.*, 2013). The dehydrogenation step stabilizes the aromatic structure and drives the reaction forward. The Bittner-Howard reaction route is particularly relevant for the formation of larger PAHs, such as pyrene, benz[a]anthracene, and chrysene, which are important soot precursors in combustion systems (Kislov *et al.*, 2005). Its ability to efficiently convert linear or open-chain aromatic intermediates into more stable, condensed aromatic structures makes it an important pathway for soot formation (Bao *et al.*, 2023).

Understanding the Bittner-Howard reaction route is crucial for developing strategies to mitigate the formation of harmful PAHs and soot in combustion systems (Yilmaz *et al.*, 2023). Extensive experimental and computational modeling studies have provided valuable insights into the kinetics, thermodynamics, and importance of the Bittner-Howard reaction route in the formation and growth of PAHs and soot in combustion environments (Mancera *et al.*, 2020).

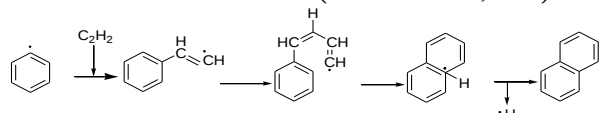


Figure 3: Showing the Reaction of acetylene with benzene to form a two-benzene ring PAH (Khan *et al.*, 2024)

A study that characterizes the formation of PAHs via the Bittner-Howard route under environmentally relevant conditions, determines how surfaces and aging processes alter the B-H product distributions, and quantifies fate & transport implications in complex media (air → aerosol → water/soil) would contribute greatly to this field.

3.3.3 Diels-Alder mechanism

The Diels-Alder reaction is a crucial organic chemistry reaction that plays a significant role in the formation of polycyclic aromatic hydrocarbons (PAHs) and soot in combustion processes (Wu *et al.*, 2023). The process involves the cycloaddition of a conjugated diene and an alkene (dienophile) to form a cyclohexene derivative (Matamba *et al.*, 2021). The key steps in the Diels-Alder mechanism include diene activation, dienophile addition, cyclization, aromatization, and dehydrogenation (Hernández-Mancera *et al.*, 2023). In combustion processes, the Diels-Alder mechanism can lead to the formation and growth of PAHs, particularly larger, more condensed structures (Wu *et*

al., 2023). For example, the Diels-Alder reaction between a conjugated diene and an alkene can result in the formation of cyclic intermediates that can be further reacted with to produce PAHs like naphthalene, anthracene, or phenanthrene (Altarawneh & Altarawneh, 2022). The Diels-Alder mechanism is often considered in conjunction with other PAH formation pathways, such as the Hydrogen Abstraction and Acetylene or Carbon Addition (HACA) mechanism and the Bittner-Howard reaction route (Vaitheeswaran *et al.*, 2013). Experimental and computational studies have investigated the kinetics, thermodynamics, and importance of the Diels-Alder mechanism in various combustion environments, including flames, engines, and industrial processes (Vermeeren *et al.*, 2020).

The Diels-Alder mechanism is essential for developing strategies to mitigate the formation of harmful PAHs and soot in combustion systems and designing cleaner and more efficient combustion technologies (Medvedev *et al.*, 2017). Factors such as the nature of the diene and dienophile, the presence of substituents, and reaction conditions can influence the kinetics and thermodynamics of the Diels-Alder reaction (Gancedo *et al.*, 2022).

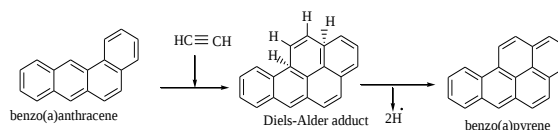


Figure 4: Showing Reaction of acetylene with a five membered ring (Kislov *et al.*, 2013)

Despite of this knowledge, mechanistic pathways to high-MW PAHs and alkyl/oxy/nitro derivatives from biomass, solid fuels, and wildfires at 500–900 °C are missing. Also, a study that quantifies the contribution of Diels-Alder mechanisms to PAH formation under environmental and engineered combustion/pyrolysis regimes, determines how surfaces and aging modify D-A products, and assesses fate & transport implications in air/aerosol–water–soil systems is lacking.

3.4 Polycyclic aromatic hydrocarbons emission pathways

The evaluation of emission pathways involves identifying and quantifying industrial sources of pollutants, such as heavy metals, organic compounds, and nutrients (Kaur *et al.*, 2022). This literature aims to assess the treatment and disposal methods used by industries, as well as the effectiveness of pollution control measures, which can provide insights on to the potential for industrial discharges contribution to environmental contamination. Regulatory compliance and enforcement measures play a crucial role in mitigating industrial emissions (Wang *et al.*, 2024).

Urban runoff from urban areas can transport a wide range of pollutants, including sediments, heavy metals, hydrocarbons, and nutrients, into surface water bodies and groundwater (Ouro-Sama *et al.*, 2023). The evaluation the sources and loading of pollutants in urban runoff is necessary to understand their impact on the environment (Stephansen *et*

et al.,2020). The effectiveness of stormwater management practices, such as green infrastructure, detention basins, and constructed wetlands, in reducing pollutant loads should be assessed to guide on possible exposure pathways (Yan *et al.*,2023). Atmospheric deposition is another important aspect of environmental pollution that facilitates movement of PAHs. It is also important to identify the sources of atmospheric pollutants, such as industrial emissions, transportation, and agricultural activities, is important in understanding their contribution to environmental contamination (Machate *et al.*,2022). The modeling of atmospheric transport and deposition patterns can help in quantifying the impact of atmospheric deposition on different environmental compartments (Cousins *et al.*,2022).

Though the PAH distribution in air, soil, and water is well-documented, their behavior in complex systems like post-wildfire environments and urban runoffs is less understood. The interaction of PAHs with emerging materials like graphdiyne or other carbon allotropes also warrants further exploration. Furthermore, the bioavailability of PAHs in different environmental matrices (e.g., soil, sediment) and their biotransformation into toxic metabolites (e.g., hydroxylated PAHs) are not fully understood, particularly for alkylated PAHs. The role of microbial communities in PAH degradation also needs further exploration. A study that investigates PAH transport and transformation in post-wildfire sediments or urban aquatic systems, focusing on partitioning between coarse, fine, and ultrafine particles and models the long-range atmospheric transport of PAHs and their deposition in pristine ecosystems would make interesting research. Additionally, the study on adsorption and desorption dynamics of PAHs on novel carbon-based materials (e.g., graphdiyne) for potential use in remediation would give additional novel data. Quantify the bioavailability of parent and alkylated PAHs in sediments or soils using *in vitro* digestion models or bioaccumulation studies in aquatic organisms.

More importantly, investigate microbial degradation pathways for high-molecular-weight PAHs under varying environmental conditions (e.g., anaerobic vs. aerobic). And assessing the toxicity of PAH metabolites (e.g., OH-PAHs) in human or ecological systems would enrich PAH knowledge base.

3.5 Health effects of exposure to Polycyclic Aromatic Hydrocarbons to humans, aquatic organisms and animals and plants

PAHs are known carcinogens, with numerous studies linking them to an increased risk of various types of cancer. These include lung, bladder, skin, and gastrointestinal cancers, as well as breast and prostate cancers (Dandajeh *et al.*,2021). Exposure to PAHs during pregnancy can lead to adverse reproductive outcomes, such as decreased fertility, increased risk of spontaneous abortion, and reduced fetal growth and development (Dai *et al.*,2023). PAHs can also cross the placental barrier, affecting the developing fetus and potentially leading to congenital abnormalities or developmental delays in children (Patel *et al.*,2020).

Inhalation of PAH-containing particles by firefighters can cause respiratory irritation, exacerbate asthma, and increase the risk of respiratory diseases (Sandeep *et al.*,2019). Chronic exposure to PAHs has been linked to reduced lung function and an increased incidence of respiratory infections. PAHs can also contribute to the development of oxidative stress and inflammation, leading to endothelial dysfunction and cardiovascular complications (Hou *et al.*,2023). Though firefighters and other occupational groups face significant PAH exposure, exposure levels and health risks in other high-risk groups like urban residents near industrial sites are less studied, and the role of personal protective equipment (PPE) in reducing PAH exposure is underexplored.

Neurological effects of PAHs include impaired neurological and cognitive development in children, including effects on learning, memory, and overall cognitive performance, though their long-term cardiometabolic, neurological, or epigenetic effects of such exposures are not well-characterized (Panwar & Mathur, 2023).

PAH exposure can modulate the immune system, increasing susceptibility to infectious diseases and autoimmune disorders. Alterations in immune function and inflammation have been observed in individuals exposed to PAHs, highlighting the potential for these pollutants to disrupt the body's defense mechanisms (Pahila *et al.*,2008). Most researches on PAHs focused on acute or high-level occupational exposures like firefighters and industrial workers but their chronic low-level exposure in the general population, particularly through air, water, or food, is less studied.

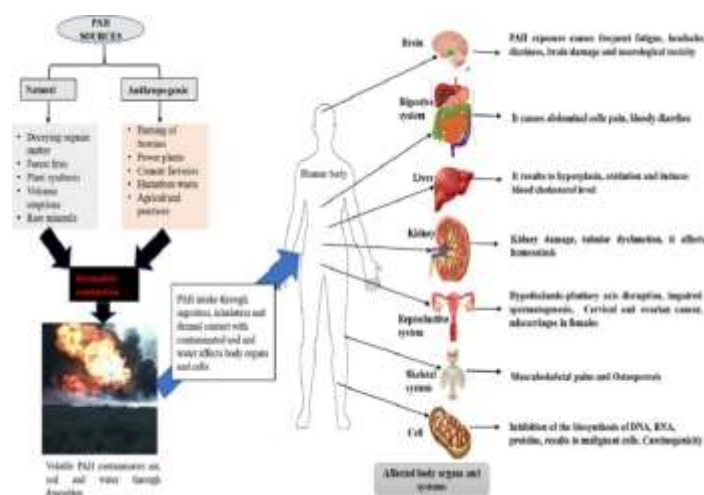


Figure 5: Showing different sources of PAHs and their corresponding effects on human health (Akinpelumi *et al.*, 2023)

High concentrations of polycyclic aromatic hydrocarbons (PAHs) can lead to direct mortality in aquatic organisms, particularly in early life stages (Sandeep *et al.*,2019). These chemicals disrupt critical physiological processes, causing organ failure, suffocation, and death. They also interfere with the normal growth and development of aquatic organisms, resulting in reduced survival, growth, and abnormalities

(Wright *et al.*,2018). PAHs can negatively impact reproductive capacity by disrupting endocrine systems, altering gonadal development, and interfering with spawning and mating behaviors, affecting fecundity, hatching success, and recruitment (Jaruga *et al.*,2017).

Genotoxicity and carcinogenicity are also potential consequences of PAHs. DNA damage and genetic mutations can lead to increased incidence of tumors and other neoplastic diseases, potentially impacting population-level effects (Jaruga *et al.*,2017). PAH exposure can suppress the immune function of aquatic organisms, making them more susceptible to infectious diseases and reducing their ability to respond to environmental stressors (de Pinho *et al.*,2022). Neurotoxicity can disrupt the normal functioning of the nervous system in aquatic organisms, affecting their behavior, sensory perception, and cognitive abilities (Xiang *et al.*,2022). This can impair their ability to navigate, detect prey, and perform essential functions, ultimately reducing their chances of survival (Jiang *et al.*, 2023).

Oxidative stress in aquatic organisms can lead to cellular damage, lipid peroxidation, and depletion of antioxidant defenses, resulting in tissue-specific effects like liver and kidney damage, gill and skin lesions, and overall physiological impairment (Martin-Folgar *et al.*,2024). Bioaccumulation and trophic transfer of PAHs can also occur, potentially impacting ecosystem-level processes and human health (Hou *et al.*,2023).

PAHs can disrupt plant growth and development, leading to reduced germination, root and shoot growth, and biomass production (Sandeep *et al.*,2019). They also negatively impact the photosynthetic apparatus, causing decreased chlorophyll content, reduced photosynthetic rates, and disruptions in the photosynthetic electron transport chain (Tarigholizadeh *et al.*,2024). Exposure to PAHs can induce oxidative stress, leading to overproduction of reactive oxygen species, membrane damage, and depletion of antioxidant defenses. This disrupts various metabolic pathways, affecting plant growth and development (Suszek *et al.*,2024). PAHs can also interfere with the uptake, translocation, and utilization of essential nutrients, resulting in nutrient deficiencies or toxicities, leading to suboptimal growth and physiological imbalances. They can adversely affect plant reproduction, reducing pollen viability, fertilization success, and the quality and quantity of seeds and fruits produced (Cihangir *et al.*,2023).

PAHs can cause DNA damage and genetic alterations in plants, leading to increased incidence of tumor-like growths and cellular transformation. This has long-term implications for plant health and ecosystem stability (Li *et al.*,2022). Plants may exhibit stress-response mechanisms, such as the upregulation of secondary metabolites, to mitigate the adverse effects of PAH exposure. However, PAHs can also be taken up and accumulated in plant tissues, potentially leading to biomagnification in the food web (Ubong *et al.*,2023). In conclusion, PAH exposure can lead to disruptions in plant-

microbe symbioses, plant-herbivore relationships, and ecological interactions, resulting in reduced plant productivity and yield, which can have significant implications for food security and ecosystem services (Yang *et al.*,2022). Most PAH research focuses on acute or high-level occupational exposures (e.g., firefighters, industrial workers), but chronic low-level exposure in the general population, particularly through air, water, or food, is less studied. The long-term cardiometabolic, neurological, or epigenetic effects of such exposures are not well-characterized. Study on the chronic effects of low-level PAH exposure on cardiometabolic health (e.g., lipid profiles, liver function) in non-occupational populations. And investigates epigenetic changes (e.g., DNA methylation) induced by long-term PAH exposure and their role in disease development would reveal innovative studies on PAHs. Additionally, assessing the combined health effects of PAH and other pollutants such as PFAS co-exposure, as both are often present in contaminated environments would enrich the knowledge of PAHs and related contaminants.

3.6 Minimization of PAHs exposure into the environment

The U.S. government has established standards for controlling the concentration of polychlorinated aromatic hydrocarbons (PAHs) in the workplace and the environment. These standards include those for PAHs in drinking water and the workplace. The Occupational Safety and Health Administration (OSHA) has established standards for PAH exposures under OSHA's Air Contaminants Standard, which covers coal tar pitch volatiles (CTPVs) and coke oven emissions. The OSHA PEL for PAHs in the workplace is 0.2 mg/m³ for an 8-hour time-weighted average.

The National Institute for Occupational Safety and Health (NIOSH) recommends setting the workplace exposure limit for PAHs at the lowest detectable concentration, which is 0.1 mg/m³ for coal tar pitch volatile agents for a 10-hour workday, 40-hour workweek. The EPA established ambient water quality criteria in 2000 to protect human health from the carcinogenic effects of PAH exposure. The EPA developed a maximum contaminant level (MCL) for benzo(a)pyrene (BaP), which is the most carcinogenic PAH. The World Health Organization (WHO) has set the unit risk of lung cancer of BaP at 87×10^{-6} ng m⁻³ for lifetime exposure. The European Commission sets a target annual average concentration of 1 ng m⁻³ in PM₁₀ fraction, but this target has been exceeded in many locations, particularly in eastern countries. The Egyptian Environmental Association Affairs (EEAA) limits benzo(a)pyrene (BaP) at 0.7 µg/L. Current researches have generally established that polycyclic aromatic hydrocarbon originate primarily from incomplete combustion of organic materials such as fossil fuels, biomass burning, and vehicle emissions and are ubiquitous in air, water, soil, and food. Toxicologically, numerous PAHs have been shown to induce genotoxicity, mutagenicity, and carcinogenesis in humans and experimental models, with inhalation and dietary intake identified as the principal exposure routes. Epidemiological studies have consistently linked elevated ambient PAH levels to increased risks of respiratory diseases,

cardiovascular disorders, and certain cancers, particularly among urban populations and occupational cohorts. Despite these, many research gaps exist. Traditional PAH remediation methods (e.g., bioremediation, thermal desorption) are effective for some compounds but less so for high-molecular-weight or alkylated PAHs. The environmental impact of PAH-containing materials like coal tar sealants is also a growing concern. Mitigation strategy would involve developing novel bioremediation strategies using genetically engineered microbes or biochar for high-molecular-weight PAHs, investigating the efficacy of alternative sealants with lower PAH content for asphalt and pavement applications and assessing the environmental and health impacts of PAH-containing waste (e.g., coal tar sealants) in municipal water systems.

4.0 Conclusion and Recommendation

4.1 Conclusion

In conclusion, this review underscores the critical environmental and health challenges posed by polycyclic aromatic hydrocarbons (PAHs). Originating from diverse sources natural, petrogenic, pyrogenic, and biogenic PAHs are persistent, toxic pollutants found in air, water, soil, and biota. The research gaps outlined above provide numerous opportunities for impactful research studies on PAHs and associated pollutants. Key areas include the toxicology and environmental fate of emerging compounds, co-exposure risks, novel remediation strategies, and addressing global disparities in research. Despite regulatory efforts by agencies like OSHA, EPA, and WHO, PAH contamination remains a global concern. Effective mitigation requires integrated strategies including stricter regulation, improved monitoring, and international collaboration, particularly in developing regions. Future research should focus on innovative remediation technologies and sustainable policies to reduce exposure and safeguard environmental and public health.

4.2 Recommendations for environmental and ecosystem protection

This review recommends adopting mixture-based thresholds for air, soil, and water, expanding high-resolution surveillance systems, focusing on at-risk groups, fostering interdisciplinary consortia, and leveraging exposomics and systems-biology insights. By uniting environmental chemists, epidemiologists, toxicologists, and data scientists, these measures will refine exposure assessments, clarify toxic pathways, and guide evidence-driven policymaking. A multifaceted approach is needed to address PAH contamination, beginning with comprehensive regulations that enforce strict limits on emissions and discharges across industry, transport, and waste sectors, backed by penalties for violations. High-resolution monitoring employing advanced analytics will ensure accurate detection, while public outreach initiatives will raise awareness of pollution sources and health risks. Adoption of cleaner production and alternative energy technologies, alongside bioremediation and targeted soil-and-

water treatments, will reduce ongoing releases and remediate existing hotspots. Concurrently, ecosystem rehabilitation programs should be launched and their progress systematically evaluated. Sustained investment in novel detection, surveillance, and cleanup methods will promote rapid responses, and coordinated partnerships among agencies, researchers, and affected communities will enhance governance and empower local participation in decision-making.

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