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REVIEW ARTICLE

Polycyclic Aromatic Aydrocarbons (PAHs) Pollution Approaches in Aquatic Ecosystems: Perils and Remedies Using Green Technologies

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Abstract

One of the most persistent environmental pollutants known as polycyclic aromatic hydrocarbons (PAHs), are pervasive throughout the world. Polycyclic aromatic hydrocarbons pose a serious health threat to a variety of life forms because of their mutagenic, teratogenic, immuno-toxicogenic, and/or carcinogenic properties. The majority of PAHs production comes from both natural and human sources, such as forest fires, volcanic emissions, coal, oil, and petroleum-based goods like gasoline. Because PAHs show very high persistence, aquatic and non-aquatic animal species can easily acquire their residues in the environment, either directly from the water or indirectly through their food. Because of this, the current review focuses on the main PAHs emission sources, transformations, occurrences in ecosystems, and harmful effects on aquatic animals, with an emphasis on fish. Also, eco-friendly biological treatment methods for PAHs remediation are thoroughly discussed. These methods include microbial remediation (bacterial-remediation, myco-remediation, and vermi-remediation) and Phyto-remediation techniques (active carbons, rhizo-remediation, and medicinal plants).

Keywords: Bacterial degradation, Behavioral alterations, Immuno-toxicity, PAHs, Phyto-remediation

Introduction

Contaminants can enter aquatic environments and accumulate over time [1-3]. A variety of pollutants such as pesticides, heavy metals, and hydrocarbons released due to extensive industry and agricultural operations have contaminated freshwater environments [4]. One of the most prevalent environmental pollutants that are highly problematic globally is polycyclic aromatic hydrocarbons (PAHs). Polycyclic aromatic hydrocarbons have been discovered as a general cause of aquatic ecosystem degradation in recent decades [5, 6].

Polycyclic aromatic hydrocarbons are a class of organic chemicals that are common potentially dangerous pollutants detected in soil, air, water, sediments, and biota. These compounds are made up of only hydrogen and carbon atoms that are organized in the form of two or more benzene rings that are combined in cluster, angular, or linear configurations. The family of hydrocarbons that includes PAHs is varied, with over one hundred identified compounds, all of which include at least two aromatic rings. Polycyclic aromatic hydrocarbons have a low vapor pressure and very low hydrophilicity in general [7, 8]. Coal, crude oil, and gasoline are all examples of materials that naturally include PAHs.

Due to their hydrophobic nature, PAHs have a propensity to build up in aquatic sediments, which over time causes bioaccumulation and high concentrations [9, 10]. In addition to their well-documented effects on human mutagenesis and cancer, they pose serious risks to aquatic life. Polycyclic aromatic hydrocarbons cause pervasive concerns because of their negative effects on the environment and human health [11]. Initially, they are constantly discharged into the environment because they are used and generated in modern society's daily routines (e.g., by using fossil fuels), potentially over time leading to an increased environmental aspect [12]. Secondly, they have very significant environmental persistence, which is due to their high resistance to biodegradation as well as their chemically stable structure [13]. Finally, their health consequences include carcinogenicity, genotoxicity, and teratogenicity [14]. Furthermore, humans can be exposed to PAHs directly or indirectly in aquatic ecosystems through skin exposure to sediment and ingestion of aquatic food [15, 16]. Although there are hundreds of PAHs in the environment overall, most research continues to concentrate on 16 major pollutants, such as probable human carcinogens and mutagens [17-19]. However, benzo(a) pyrene (BaP) has been found to be extremely carcinogenic, causing increased concern about the concentration of these health-threatening chemicals in the environment [20-23]. In industry and the environment, BaP is frequently employed as an indicator of total PAHs exposure [24].

Numerous reviews have been written in response to the significant eco-toxicity of PAHs and their hazards, each of which focuses on a different element of this worldwide contaminant [25-29]. To date, rising public and environmental health concerns about PAHs in the environment have prompted many countries to enforce a variety of initiatives and restrictions to monitor, control, or limit their release into the environment. Further investigation into PAHs' impact on sediment and water pollution, as well as an assessment of the risks to human health, are necessary for these reasons. Considering this, it is essential for resource management to understand the sources of PAHs as well as the possible threats to biodiversity they represent. However, effective management of PAHs necessitates a comprehensive strategy that combines in-depth knowledge of their physico-chemical characteristics, modes of environmental diffusion and bioaccumulation, effective detection, and bioremediation strategies [6, 26]. Consequently, we provide insight into the PAHs the physico-chemical characters, origin, transformations, and occurrence in ecosystems, impacts on aquatic animals' health with a focus on fish as well as their bioremediation strategies in this review paper as the aquatic environment is the most considerable contributor to the toxicity of PAHs.

Polycyclic aromatic hydrocarbons physicochemical characters, classification, and sources

Polycyclic aromatic hydrocarbons are a chemical group of petroleum with two or more condensed aromatic rings that are ubiquitous in water, air, and soil [25, 30]. Petroleum is made up of saturated and branching alkanes, alkenes, and homo and heterocyclic naphthene; aromatics made up of heteroatoms like heavy metal complexes and nitrogen, oxygen, sulfur; hydrocarbons made up of diverse functional groups like ethers, carboxylic acids, and so on; and big aromatic molecules like asphaltenes, resins, and naptheno-aromatics [29]. The structure becomes more resistant as molecular weight increases due to changes in hydrophobicity/lipophilicity, water solubility, vapor pressure, and hydrophobicity/lipophilicity.

There are about 16 priority PAHs (Table, 1) are listed based on frequency of occurrence, toxicity, and potential for human exposure rather than being a list of the "most toxic" compounds [31]. Naphthalene, chrysene, benzo(b) flouranthene, benzo(k) flouranthene, BaP, dibenz (a, h) anthracene, dibenzo (a.e) pyrene, and dibenzo(a,l)pyrene anthanthrene are of particular interest because of their mutagenic and carcinogenic properties [20, 21].

Incomplete combustion of organic matter and its slow maturation stored in deep sedimentary environments are the main causes of PAHs formation (Figure 1). The sources of PAHs included three main sources according to different papers such as petrogenic, pyrolytic, and biological sources.

Petrogenic sources of PAHs are small, 2-3 rings, emanating from petroleum and petroleum products. They are acute toxic, genotoxic, and low carcinogenic compounds [27]. An oil spill is one of the most common sources of PAHs. Oil spills, primarily caused by mishaps on oil platforms and ships, are required for the transportation of hydrocarbons [32, 33]. Polycyclic aromatic hydrocarbons can be found in coal, oil, and petroleum-based goods like gasoline. Additionally, they are produced intentionally by human activities like the burning of oil, waste coal, etc. [33, 34].

Pyrogenic PAHs are mainly larger, 4-6 ring compounds. They have lower acute toxicity, higher carcinogenicity, and mutagenicity [27]. Pyrolytic PAHs pollution interferences in harbors have been observed due to fuel combustion emissions from ships alongside quays and deliveries of petroleum products [35]. According to a report by Siudek [36], pyrolytic PAHs deposition from the atmosphere regulates the concentrations of the majority of PAHs. However, the presence of naphthalene, phenanthrene, and perylene in high amounts in plants, termite nests, and soils supports the biological origin theory [37].

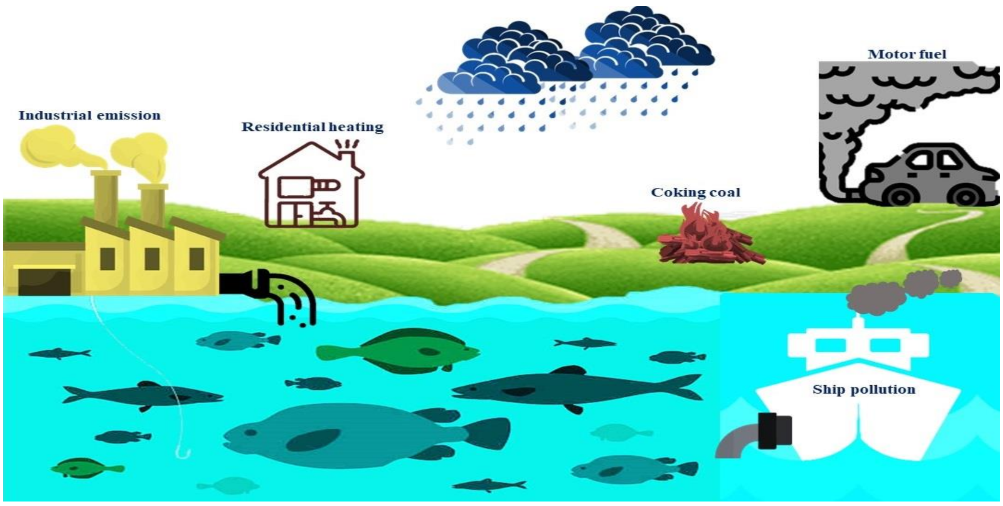
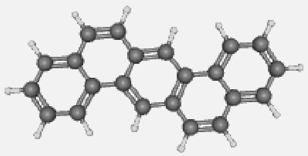
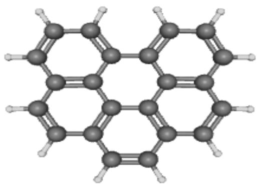
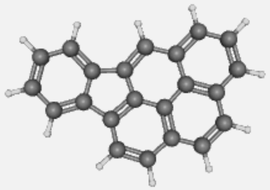
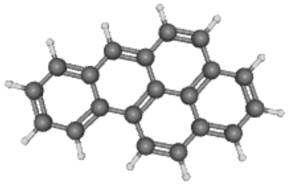
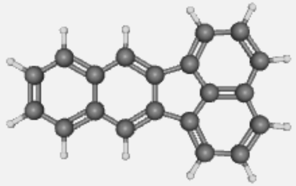
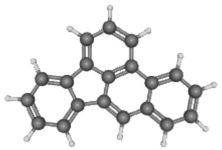
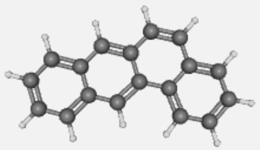


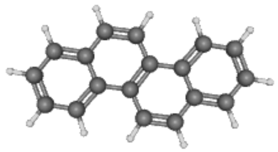
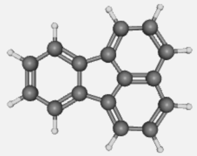
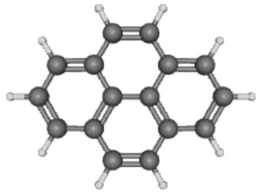
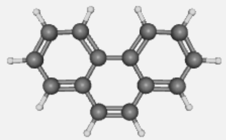
Figure 1: The different sources of polycyclic aromatic hydrocarbons.

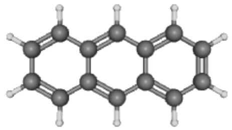
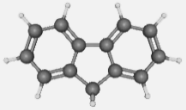
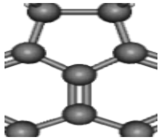
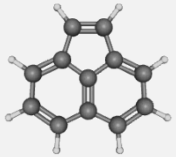
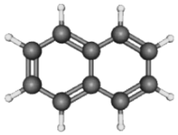
Microorganisms can also create PAHs from biogenic precursors including steroids, quinones, pigments diterpenes, and triterpenes. These precursors could come from biological tissues in either water or on land (animals, plants, macro- and microalgae, bacteria) [38].

Table 1: Sixteen priority polycyclic aromatic hydrocarbons (PAHs) as highly potential hazards in the environment listed by the United States Environmental Protection Agency (USEPA)

Name	*Compound PubChem CID*	*Molecular formula*	*3D Chemical structure*	*Molecular weight (g mol^{-1})*	*Biodegradation half-Life (days)*	*Fish biotransformation Half-Life (Km) days*
Dibenzo(a,h) anthracene	5889	$C_{22}H_{14}$		278.3	419.95	1.62
Benzo(ghi) perylene	9117	$C_{22}H_{12}$		276.3	561.95	-
Indeno(1,2,3-cd) pyrene	9131	$C_{22}H_{12}$		276.3	329.99	-

Benzo[a]pyrene	2336	$C_{20}H_{12}$		252.3	223.98	1.12
Benzo(k)fluoranthene	9158	$C_{20}H_{12}$		252.3	350.99	0.87
Benzo(b)fluoranthene	9153	$C_{20}H_{12}$		252.3	281.97	-
Benz(a)anthracene	5954	$C_{18}H_{12}$		228.3	286.02	1.05

Chrysene	9171	$C_{18}H_{12}$		228.3	378.01	3.89
Fluoranthene	9154	$C_{16}H_{10}$		202.25	146.99	0.95
Pyrene	31423	$C_{16}H_{10}$		202.25	236.97	2.09
Phenanthrene	995	$C_{14}H_{10}$		178.23	42	5.01

Anthracene	8418	$C_{14}H_{10}$		178.23	123	4.47
Fluorene	6853	$C_{13}H_{10}$		166.22	44	5.01
Acenaphthene	6734	$C_{12}H_{10}$		154.21	39	-
Acenaphthylene	9161	$C_{12}H_8$		152.19	38	3.31
Naphthalene	931	$C_{10}H_8$		128.17	3	2.57

The data was obtained from https://pubchem.ncbi.nlm.nih.gov/ [39].

Polycyclic aromatic hydrocarbons transformations (degradation and biotransformation) in ecosystems

Polycyclic aromatic hydrocarbons are a type of organic pollutant that are widespread, carcinogenic, and persistent. They damage not only the immediate area where they are released but also migrate from place to place as persistent contaminants. They degrade slowly and can react with other pollutants in the environment to create even worse toxins [27]. Researchers are currently interested in the degradation of PAHs as a result of their awareness of their detrimental effects on both the ecosystem and human health. Bioremediation, or the degradation of PAHs using bacteria, is emerging as an effective and viable alternative to the expensive and energy-intensive physico-chemical treatment of PAHs [40]. Most research on BaP biodegradation has been on the co-metabolization of BaP in the presence of one or more other carbon sources because of BaP 's resistance to degradation. During the hydrolysis of BaP, the activities of the fungal enzyme (*Lasiodiplodia theobromae*) were investigated. BaP can be used by *L. theobromae* as its exclusive carbon source, with a degradation ratio of up to 53% during a 10-day period after being isolated from a soil sample contaminated with PAHs that was obtained from the Chinese Beijing coking plant [41].

Biotransformation may greatly lower the extent to which a chemical accumulates; however, the enzymes responsible for this activity are sensitive to a range of combination effects including induction and inhibition. Through biotransformation, which increases the hydrophobic PAHs' solubility in water, one significant route of removal is achieved. Phase I enzymes from the cytochrome P450 (CYP450) enzyme family and a few phase II enzymes have been found in marine polychaetes [42].

Toxic-kinetic models are in silico tools used to evaluate the uptake, biotransformation, and elimination of environmental contaminants such as BaP. Gall bladder and liver samples from fathead minnows (*Pimephales promelas*), which were exposed to BaP through water, were used to create toxic-kinetic models. There was a noticeable rise in BaP metabolites [43].

Occurrence of PAHS in aquatic systems

The industrialization and technological development processes caused the introduction of chemicals that are hazardous to the environment which include agrochemicals, herbicides, hydrocarbons, and halogenated PAHs. These compounds become potential hazards if they escape during the production process into the environment or in industrial effluents [44].

In aquatic ecosystems, participating PAHs first float in the water column for a while before precipitating and accumulating in the sediment. It has been noted that organisms residing in the water column and sediment, including vertebrate and invertebrate animals, plants, and microorganisms, may contain PAHs, even at very low ambient concentrations [45]. Fish could obtain PAHs through their gills, water, food consumption, or sediment [25].

Polycyclic aromatic hydrocarbons with a lipophilic nature have a tendency to accumulate in fatty tissues, similar to some organochlorine chemicals [46]. As a result, oily fish, such as bluefish (*Pomatomus saltatrix*), catfish, some salmon (*Oncorhynchus gorbuscha*), and carp, have higher PAHs concentrations than lean fish, such as some sunfish (*Lepomis sp.*) and European sea bass (*Dicentrarchus labrax*) [47]. Passive transport through cellular membranes is the main mode of uptake for bioavailable PAHs due to their non-polar nature and overall considerable lipophilicity [48]. Benthic animals can take PAHs in nutrients in one of two ways: (i) through contact of the skin or respiratory surfaces with water; or (ii) through ingestion of PAH-contaminated sediment or food, with absorption largely occurring through the gut wall [49, 50].

Research has shown that the biomagnification of PAHs in the aquatic food chain is a highly complex process. For instance, biomagnification studies of BaP and benzo(a)anthracene, across the food chain of *Dunaliella tertiolecta* (a microalga), *Mytilus galloprovincialis* (a mussel), and *D. labrax* revealed higher accumulation of these PAHs in mussels than in fish [51]. Similar findings were made in another study [52], where it was discovered that PAHs concentrations decreased with increasing trophic levels in fish and decapods but increased in mollusks. Zhang *et al.* [53] found a direct correlation between the concentration of PAHs in aquatic plants and the bioaccumulation of PAHs in fish.

In certain Mediterranean coastal sediments, the sources and distribution of PAHs were investigated. The results showed that pyrolysis is the main source of these compounds in the Mediterranean coastal sediments at this location. The results also show that Lazaret Bay, which is close to Toulon Harbour, has high PAHs contamination [54].

The total PAHs content in a sample of soil, water, and sediment near a riverbank of the Qiantang River, Zhejiang Province, China was 85.2-676.2 ng/g, 91.3 - 1835.2 ng/g, and 70.3 -1844.4 ng/g, respectively. The findings demonstrated that PAHs contamination in this source of drinking water grew over time [55].

About 10 samples of surface soil and 11 different fish species taken from the Gulf of Suez, Egypt, and 16 PAHs were examined by Younis *et al.* [56]. The range of the overall average levels in sediments is 1667.02 to 2671.27 ng/g. The 11 fish species' PAHs residues revealed a prevalence of high molecular weight PAHs (4–6 rings). The reticulated filefish (*Stephanolepis diaspros*) had the lowest overall PAHs concentration (621.9 ng/g), whereas Brush tooth lizardfish (*Saurida undosquamis*) had the highest levels (4207.5 ng/ g). A pyrogenic was the primary source of PAHs discovered in the investigation, according to the results and diagnostic ratios.

In a different investigation, El-Kady *et al.* [57] tracked the aliphatic and PAHs profile in lake Manzala, one of Egypt's biggest wetlands. Aliphatic and PAHs were evaluated in sediment and tilapia fish samples. Except for acenaphthylene, fluorine, and ∑45PAHs in Bahr Al-Baqar drain sediments, PAHs were below the effect range when compared to sediment quality requirements. A total of 45 PAHs levels in tissue samples were moderate, ranging from 302.5 ng/g west of Bashteer to 596 ng/g in Legam. The ultimate finding was that the levels of PAHs residues in sediment and tilapia fish samples taken from Lake Manzala were low or below the threshold that would raise an environmental concern.

Mechanism of PAHS toxicity

Hydrocarbons are a significant cause of pollution in the environment, and their toxicity varies depending on the number of exposure sources on the one hand and their toxicity on the other (Figure 2).

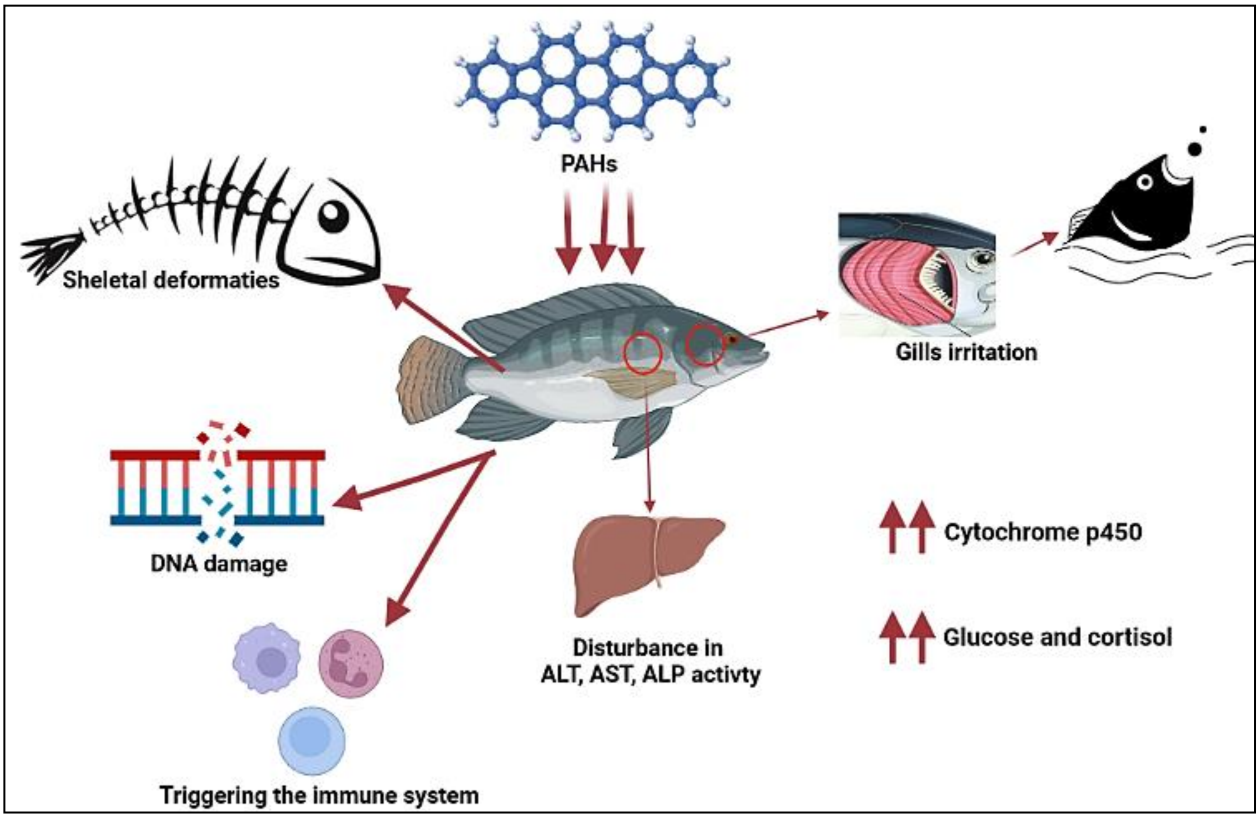


Figure 2: Mechanism of PAHS toxicity. PAHs: Polycyclic aromatic hydrocarbons, ALT: alanine transaminase, AST: aspartate transaminase, ALP: alkaline phosphatase.

After absorption, PAHs are dispersed across tissues, where the toxicity of PAHs inevitably depends on how well these tissues can metabolize and detoxify PAHs [48, 58, 59]. Polycyclic aromatic hydrocarbons metabolization is mediated by a large family of heme proteins that are membrane-bound, such as the CYP450 superfamily. These proteins take part in phase I reactions by "functionalizing" PAHs, for example, by oxidation, so that other phase I and II enzymes can further transform them into metabolites that are more soluble and extractable [60]. Moreover, PAHs have the power to alter the aryl hydrocarbon hydroxylase receptor (AHR) transcription factors-mediated metabolic pathway of the CYP1 family upstream of CYP1 induction. Most PAHs are known to activate the AHR pathway (AHR-agonists), which encourages CYP1A1 transcription and increases PAHs metabolism [61]. Many reviews [48, 62-64] have discussed further information regarding the mechanisms of action of PAHs through the AHR pathway, which is considered a hallmark of PAHs toxicity.

Some of the PAHs-derivatives can bind covalently to DNA and proteins, generating DNA and protein adducts, which may be responsible for teratogenesis, mutagenesis, and carcinogenesis [65]. Moreover, PAHs change DNA integrity (DNA methylation) and the way it is repaired, which causes genomic integrity to change and increases the risk of cancer and/or death [66]. Additionally, PAHs decrease cell regeneration by raising the levels of receptors that inhibit stem cell development and differentiation [67].

The occurrence of oxidative stress brought on by derivatives of parent substance metabolic pathways or by photo activation of parent chemicals by ultraviolet light is another established mechanism of PAHs toxicity [68, 69]. Furthermore, PAHs have been found to have endocrine-disrupting effects and to depress immune responses in exposed organisms [70-72]. This is due to the stimulation of programmed cell death (apoptosis) in lymphocytes and phagocytes [73]. During the development of all organs and systems, the PAHs can pass the brain barrier. They can affect the development and have long-term consequences [74, 75].

Polycyclic aromatic hydrocarbons can alter reproductive health, thus endangering the species survival. One of the main ways they act is disruption of the normal metabolism of gonadotropins and other sex hormones in aquatic animals even at very low quantities. Due to decreased fertility, altered sexual behavior, decreased survivability of progeny, and decreased hatch rate, causes the reproductive system to become dysfunctional [76-78].

Impacts of PAHs on aquatic animals' health status

Aquatic ecosystems represent the last environmental context in which PAHs are present [6]. It is well-known that PAHs, which are pollutants released to the environment at escalating concentrations, build up in aquatic creatures [19]. Persistent pollution by PAHs may be damaging the upper trophic levels of tropical creatures in the food chain [79]. The impact of PAHs that pose the highest ecological danger varies depending on the location because the ecological risk provided by PAHs depends on ambient concentrations and is thus specific to each aquatic system. Notably, if chronic toxicity data were considered instead of acute toxicity data, more PAHs that pose a concern to aquatic animals would probably be discovered [26].

Marine creatures, such as fish, have the capacity to collect PAHs concentrations that are many times higher than the water around them [80]. According to Perugini *et al.* [81], Perugini *et al.* [82], and Conti *et al.* [83], PAHs are ingested both directly through the skin and gills, which have direct contact with the environment and indirectly through the digestion of tainted food and drink.

Lethal effects of PAHS

About 206 findings pertained to LC_{50} (median lethal concentration 50) values of PAHs discovered by water exposures out of the 298 data values. The endo-benthic midge (*Chironomus riparius*) and the epi-benthic amphipod (*Hyalella azteca*) were the two species that were most frequently investigated [26].

Depending on the kind of PAHs and the organism, PAHs have moderate to substantial acute toxicity in aquatic species [6]. In general, PAHs are found to be extremely toxic to zooplankton, with LC_{50} values approaching parts per billion (ppb or mg/L) concentrations. For instance, BaP was reported to exhibit LC_{50} values against *Eurytemora affinis* and *Daphnia pulex* of 58 mg/L and 5 mg/L, respectively. *Ceriodaphnia reticulate* (LC_{50} = 4.3 mg/L) and *Daphnia magna* (LC_{50}= 4.7 mg/L) both showed similar ppb level toxicity [84].

Aquatic creatures exposed to PAHs can have reduced survival during acute exposures. For instance, *O. gorbuscha*) that were exposed to PAHs had lower survival rates [85]. In Puffer Fish (*Takifugu obscurus*), chrysene (1.5 μg/L; 96-h LC_{50}) had the highest acute toxicity of all PAHs compounds, while pyrene (65 μg/L), fluoranthene (158 μg/L), phenanthrene (432 μg/L), and naphthalene (8690 μg/L) had the lowest [86].

A study was conducted to assess the toxicity of two PAHs (naphthalene and anthracene) on freshwater fish (*Rasbora daniconius*) for 24-96 h. The LC_{50} values for naphthalene ranged from 3.6 to 4.4 mg/L, while for anthracene ranged from 0.5 to 2.4 mg/L. The study revealed that anthracene exhibited more toxicity to this fish species compared to naphthalene

[87]. In another study, the Probit analysis method was employed to analyze the results of acute toxicity tests. The 96-hour LC_{50} values for milkfish (*Chanos chanos*) exposed to anthracene and BaP were determined to be 0.030 mg/L and 0.014 mg/L, respectively [88].

Impacts on behaviors, survival, and growth

The behavior allows for the discrimination of many integrating factors from the effects of PAHs. Swimming activity, as well as other factors such as lethargy, anxiety, social communication, eating behavior, flight response, learning, and reproductive behavior, can all be assessed [89].

In juvenile gilthead seabream (*Sparus aurata*) exposed to three PAHs compounds, fluorene (EC 10 = 0.29 mM), phenanthrene (EC 10 = 0.56 mM), and pyrene (EC 10 = 0.031 mM), there were changes in their locomotor activities and social behaviors. Also, following the exposure, the fish showed decreased swimming activity, as well as an increase in lethargy and a decrease in the number of surface rolling. These characteristics can also be used to assess a contaminant's neurotoxic potential. It has been demonstrated that exposure to phenanthrene reduces social interactions [90].

Impairment in survival has been observed in *O. gorbuscha* after exposure to crude oil [91], in minnow (*P. promelas*) that was exposed to polluted sediment [92], in *C. chanos* and capelin (*Mallotus villosus*) exposed to dissolved PAHs (anthracene, BaP, pyrene, and heavy fuel oil) [93].

Acute exposure to commercial petroleum fuels such as gasoline, kerosene, or diesel (12 mL) drastically decreased its growth performance and adversely damaged its physiological status [94]. The F1-F3 generation of medaka (*Oryzias latipes*) larvae have been reported to have skeletal abnormalities as a result of ancestral BaP exposure (1 μg/L, 21 days) [95].

Impacts on hematology and biochemical indices

For two reasons, hematological parameters provide information on the fish's physiological response to environmental stressors. The first is that the circulatory system is strongly related to the external environment, and the second is that fish blood is readily available [96, 97].

In Rockfish (*Sebastes schlegeli*), over the 30 days of receiving the highest BaP dose (2.0 mg/kg), a substantial drop in red blood cells (RBCs), hematocrit, and hemoglobin was recorded [98]. *Lepomis sp.* showed a decreased white blood cell count (WBCs), often known as lymphopenia [99]. After 96 h, exposure of streaked prochilod (*Prochilodus linestus)* to 2.4 μg/L endosulfan dramatically increased the number of WBCs and plasma glucose while decreasing hemoglobin concentration, mean cell hemoglobin, and total plasma protein. In addition, more thrombocytes and monocytes and fewer lymphocytes and neutrophils were seen in exposed fish, indicating a change in the differential leukocyte count [100].

The physiological factors of Nile tilapia exposed to commercial petroleum fuels, such as RBCs and hemoglobin concentration, changed over time. Hemoglobin content and RBCs count in the blood of exposed fish increased suddenly after their exposure to commercial petroleum fuels decreased with time and reached control levels at the end of the experiment (4 weeks) [94]. In climbing perch (*Anabas testudineus*), the WBCs count increased during naphthalene exposure (0.71 and 1.42 mg/L) for 5 days compared to the control, and this increase was relatively greater under 1.42 mg/L dose [101].

Blood biochemistry test indicates what is happening in the fish body after exposure to pollutants. When different tissues are injured, the damaged cells release specific enzymes into plasma, and we can recognize their abnormal levels in blood. Then, it helps to locate the lesions [102]. For instance, mummichog (*Fundulus heteroclitus*) subjected to naphthalene (4 mg/L) had higher blood cortisol and glucose levels, which resulted in an imbalance in the osmo-regulatory system [103].

In the experiment with acute stress, rainbow trout (*Oncorhynchus mykiss*) were intraperitoneally injected with 10 mg/kg of oil containing naphthalene, β-naphthoflavone, or BaP, and 72 h after injection, fish were severely stressed by chasing for 15 min. After acute stress, naphthalene and β-naphthoflavone treatments elevated plasma levels of cortisol. On the other hand, cortisol levels in fish exposed to long-term stress for 3 days showed a definite tendency to fall after treatment with β-naphthoflavone and BaP. Stress increased plasma glucose levels, which were unaffected by PAHs in acutely stressed fish but decreased in fish exposed to long-term stress [104].

The biochemical composition of the himri (*Barbus luteus*) blood serum was discovered to be altered in petroleum hydrocarbon-polluted locations, with decreased total protein and albumin concentrations, indicating a likely case of blood loss to the tissues or ineffective liver function [105]. In *S. schlegeli*, total protein and albumin concentrations were reduced after exposure to dimethylbenz (a) anthracene at 2.4 and 4.8 mg/kg for 8 weeks [106]. In a similar manner, the total protein and albumin levels of the mrigal carp (*Cirrhinus cirrhosis*) fish were dramatically reduced after being exposed to 1% water-soluble fractions of crude oil [107]. On the contrary, the total protein and albumin indices were significantly increased in African catfish (*Clarias gariepinus*) exposed to 10% aqueous extract of Nigerian crude oil for 30 days [108].

PAHs from a diesel-polluted environment were discovered to alter enzymatic activity in the liver, which could change the physiological functioning of *Labeo bata*, *L. rohita*, and *C. mrigala* [109]. Because PAHs bio-accumulate in the fish liver, it is one of the organs that PAHs attack [110]. The exposure of *A. testudineus* to naphthalene different concentrations (4.4, 4.6, 4.8, and 5 mgL^{-1}) for 72 h inhibited enzyme activity in liver tissues [aspartate and alanine transaminases (AST&ALT), acid phosphatase, and alkaline phosphatase (ALP)] compared to the control group [111]. Contrariwise, the hepatic enzyme activity (ALT, AST, and ALP) of Klunzinger's mullet (*Liza klunzingeri*) that was intraperitoneally injected with BaP (5, 10, and 50 mg/kg) was increased after 1^{st}, 3^{rd}, 7^{th}, and 14^{th} days [112].

Similarly, the liver enzymes (ALT, AST, ALP, lactate dehydrogenase (LDH)) were significantly increased in hepatocytes of orange-spotted grouper (*Epinephelus coioides*) exposed to 10^{-5}, 2×10^{-5}, 3×10^{-5} mol/L BAP for 24 h [113]. In addition, after 14 and 21 days of exposure to 200 μg/L naphthalene, the activity of ALT, AST, and ALP in Goldfish (*Carassius auratus*) was elevated [114]. Also, the results showed that pyrene significantly elevated plasma levels of glucose, AST, ALP, and triglyceride while total protein, albumin, ALT, and cholesterol were significantly reduced in common carp (*Cyprinus carpio*) after exposure to the intermediate and high dose (50 and 100 μgL^{-1}) for 35 days [115].

Impacts on immune response

The innate immune system is crucial in fish. Antibacterial peptides, lysozymes, lectins, acute-phase proteins, and complement system molecules are among the components of humeral innate immunity that are primarily identified in fishes. Meanwhile, macrophages, neutrophils, and eosinophils are the most well-studied innate immune cells [116]. Fish immune systems can be changed by exposure to environmental pollutants [1, 2, 117-120]. When fish are exposed to environmental stress, lysozyme and complement elements C3 and C4 are frequently utilized to assess the immunological status of the fish [121]. Additionally, immunoglobulin M is a critical marker for fish health and humoral immune activity [122].

Polycyclic aromatic hydrocarbons impair the specific and non-specific immunity in fish. However, the effects of both specific and non-specific immunity are incompatible, which rely on the manner of exposure, the dose of exposure, and the species investigated [123, 124]. For instance, some studies have proven that exposure to heavy oil, which contains high levels of PAHs and alkyl-PAHs, affects the expression of immune-related genes, and macrophage colony-stimulating factors in the kidney, as well as leads to the suppression of antibacterial activity in serum [125, 126]. T-cell and B-cell proliferation were significantly reduced in *O. latipes* 48 h following injection of 2, 20, or 200 µg/g BW BaP [127]. Experiments on rainbow trout by intraperitoneal injection of 25 or 100 mg/kg BaP showed that the absolute number of myeloid cells, B cells, or T cells in the blood, head kidney, or spleen decreased in a dose- and time-dependent manner [128].

A significant increase in lysozyme concentration of *D. labrax* was recorded after a 24 h in vitro incubation with anthracene at 7.00 ± 0.24 mg/L, while benzo[a] pyrene altered the hemolytic alternative complementary activity after 4 h of in vitro incubation at dose 5.30 ± 0.26 mg/L [129].

Impacts on oxidant/antioxidant response

According to earlier research, oxidative stress reactions may also affect aquatic organism's immune systems, especially when exposed to harmful chemicals, and result in a number of diseases that endanger their ability to grow and reproduce [130, 131]. Because antioxidant enzymes react to diverse chemical substances in different ways, the activity of a single antioxidant enzyme cannot be used as a general indicator of oxidative damage. As a result, various antioxidant values are frequently evaluated together to show total oxy-radical scavenging capacity, which has been found to offer a higher indicative value [132, 133].

In temperate scallop (*Pecten maximus*) hemolymph, oxidative stress was caused by phenanthrene exposure at 200 µg/L for 7 days resulting in significantly reduced levels of total glutathione and significantly greater levels of lipid peroxidation [134]. Similarly, Malonaldehyde (MDA) levels increased, and antioxidant defense enzyme activity reduced in the gill and liver tissues of juvenile *C. gariepinus* after exposure to benzene (0.017 ml/L), xylene (0.086 ml/L), toluene (0.398 ml/L), and crude oil (2.219 ml/L) [135].

A significant increase in glutathione-S-transferase (GST) activity was detected in the digestive gland of *M. galloprovincialis* exposed to 100 µg/L of benzo[a] pyrene for seven days in pelagic or benthic conditions. While MDA levels in the gills and digestive gland of clams (*Ruditapes decussatus*) exposed to benzene[a] pyrene increased significantly after seven days at 100 µg/L [136]. Furthermore, the glutathione peroxidase (GPx), 7-ethoxyresorufin-o-deethylase (EROD), and MDA activities were up after the mitten crab (*Eriocheir sinensis*) crabs were exposed to phenanthrene (50 g/L) for 14 days at pH 7.8, while the superoxide dismutase (SOD), catalase (CAT), and GST activities were lowered

[137]. Contrarily, in *L. klunzingeri* exposed to three concentrations of benzene[a] pyrene 10^{-6}, 2×10^{-6}, 3×10^{-6} mmol/L) for 2 weeks, SOD, CAT, and GPx increased considerably, while lipid peroxidation (LPO), total antioxidant power, and total protein decreased dose-dependently [138].

Impacts on CYP 450 molecular level

Cytochromes P450 (CYP450) enzymes have a role in fish responses to pollution as well as the detoxification and bio-activation of environmental contaminants. The cytochrome P4501A (CYP1A) enzyme, is a protein that catalyzes the oxidation of a variety of organic compounds and is recognized as a sensitive biomarker for oil pollution [139, 140]. The cytochrome genes have recently garnered interest as biomarkers for environmental biomonitoring in marine organisms.

The cytochrome P1 gene family, including *CYP1A*, *CYP1B*, *CYP1C*, and *CYP1D*, was primarily focused on the metabolic activation of dioxins and PAHs in fish [141]. The bioavailability of PAHs and the amount to which particular PAHs are converted into more hazardous metabolites by CYP enzymes account for most of their toxicity [142]. Polycyclic aromatic hydrocarbons exposure raised the amounts of PAHs metabolites in the bile and stomach and induced hepatic CYP1A activity in juvenile chinook and chum fish [143].

In Antarctic fish (*Trematomus bernacchii*) treated for 7 days with 10 μg/g of BaP, it was evident that oxidative processes were perturbed, and the decreased capacity to absorb peroxyl and hydroxyl radicals revealed various oxidative routes through which this substance can subtly affect the biotransformation efficiency of CYP [144]. Because of their hydrophobicity, PAHs are carried into cells and trigger gene expression in the CYP enzyme group [145]. The cytochrome 1A gene displayed a potential correlation with benzo[a]anthracene (BaA) in *Forsterygion capito* samples obtained from Auckland, New Zealand, indicating that the expression of this gene may be related to this chemical [146]. *Gambusia affinis* adult male exposed to 100 μg/L BaP for 5 days resulted in dramatically increased expression level of CYP1A in the muscle, testis, brain, liver, and gut. Additionally, at relatively low exposure concentrations of 1 μg/L, CYP1A expression grew with exposure time [147].

Impacts on DNA damage

The Comet assay is increasingly being used in a variety of domains, from genetic toxicology to epidemiology because it is well recognized as a cheap, sensitive, and quick method for evaluating DNA damage and repair in individual eukaryotic and some prokaryotic cells [148].

Large *et al.* [149] discovered the different levels of DNA strand breaks (alkaline COMET assay) in gill and digestive gland nuclei following chronic field and acute laboratory (14 days) exposure to PAHs in mussels (*Mytilus edulis*). Moreover, the level of DNA damage in freshwater bivalve mollusk (*Corbicula fluminea*) gill tissue was quite high, maybe because the gills are the organ that is most directly exposed to environmental contaminants, methyl methane sulfonate, and mutagenic agents [150]. The comet assay results in swan mussel (*Anodonta cygnea*) hemocytes exposed to 0.25, 0.5, and 1.0 ppm crude oil for 10 days demonstrated a significant increase in DNA damage and micronuclei [151]. Microscopic plastic can alter the genotoxic potential of PAHs, BaP, and 3-nitrobenzanthrone in *O. mykiss* cells, as shown by the significant increase in DNA damage in the intestinal cell line as measured by the comet assay [152].

Impacts of PAHs on histological architecture of gills and liver as vital organs

Multiple studies have used the pathologies of fish liver and gills as an important environmental indicator, where various lesions were noted as histological biomarkers of response to xenobiotic chemical exposure generally and to PAHs exposure specifically as pacific degenerative/necrotic lesions, non-neoplastic proliferative, and neoplasms lesions [153-155]. Acute and chronic exposure to organic pollutants, heavy metals, and complex mixtures can all result in diseases that can manifest as morphological abnormalities in target organ tissues [156].

In marine Pejerrey larvae (*Odontesthes argentinensis*), after exposure to petroleum water-soluble fraction with sub-lethal concentrations (2.5, 5, 10, and 20 %) for 21 days, the gills of *O. argentinensis* showed several histological alterations, including edema, necrosis, hyperplasia, and aneurisms [157]. Martins *et al.* [158] examined the effects of two model PAHs, phenanthrene and benzo[b]fluoranthene, alone or in combination, at equitoxic and realistic concentrations for 28 days on the *D. labrax* gills. The results revealed that benzo[b]fluoranthene, alone or mixed with phenanthrene caused the most significant gills histopathological changes such as interlamellar hyperplasia of epithelial cells with originating foci of lamella fusion. The branchial lamellae of oysters (*Pinctada radiate*) subjected to PAHs contamination on Kuwait's Al-Khiran coast showed signs of necrosis and edema, significant gill filament degeneration, loss of normal shape, inflammation, and hemolysis [159].

In the similar manner, the most severe lesions in the gill of Caspian white fish (*Rutilus frissi* kutum) were reported at a concentration of 200 ppb BaP after 21 days of exposure, which induced hyperplasia, cartilage hypertrophy, epithelial lifting, curvature, fusion of lamellae, and clubbed tips in the gill tissue [160].

Lipid accumulation, necrosis, bile stagnation, megalocytosis, cholangitis, and spongiosis hepatitis were the most common changes seen in the liver of rabbit fish (*Siganus canaliculatus*) that exposed to acute crude oil and dispersed oil for 3 and 21 days with different concentrations 3 and 100% water accommodated fraction [161].

In marine *O. argentinensis*, after exposure to petroleum water-soluble fraction with sub-lethal concentrations (2.5, 5, 10, and 20 %) for 21 days, the liver of *O. argentinensis* showed several histological alterations (e.g., hypertrophy, karyopyknosis, and karyorrhexis) [157].

Strategies for PAHs control using green technologies

Due to its negative consequences, pollution brought on by PAHs is a serious concern on a global scale. There is an urgent need for sustainable technologies to quicken the elimination of PAHs given their tremendous toxicity across the entire ecosystem. If the ongoing buildup of PAHs in aquatic resources is not promptly addressed, in the unique context of the aquatic ecosystem, these highly persistent compounds would progressively eliminate the biodiversity of fish and aquatic plankton. This will ultimately influence the population's ability to support itself and meet its nutritional needs [6, 34, 162].

The remediation of PAH-contaminated settings has been made possible by a number of promising methods; each method has its advantages and disadvantages, as shown in Table 2. . They include soil washing, thermal desorption, land farming, soil vapor extraction, bioremediation, and other developing technologies [162]. Unfortunately, most of these technologies will encounter implementation difficulties in the context of inland aquatic environments. Bioremediation may provide a promising, affordable, sustainable, and efficient method of removing PAHs from inland aquatic ecosystems without severely affecting the surrounding environment. As a result, the present review has only looked at potential bioremediation methods for removing PAHs.

Green technologies based on biological energy involving microbes (bioremediation) and plants (phytoremediation) have emerged in recent years [163]. Phytoremediation is a type of method that uses phyto-extraction, phyto-degradation, and rhizosphere biodegradation to completely remove organic pollutants from locations of contamination. Phytoremediation has the advantages of being relatively less expensive, causing less environmental disruption, and allowing natural resources to be reused [164, 165].

Table 2: The principles, advantages, and disadvantages of different technologies used to quicken the elimination of polycyclic aromatic hydrocarbons (PAHs)

Technology	Principles	Advantages	Disadvantages	References
Bioremediation	Utilizing microorganisms (bacteria, fungi) to degrade PAHs.	- Sustainable, cost - Effective, in-situ treatment. - Effective for low to moderate PAH contamination.	- Slower than some other methods. - Sensitive to environmental conditions.	[28, 166, 167]
Chemical oxidation	Employing oxidizing agents (ozone, Fenton's reagent) to break down PAHs.	- Rapid degradation, effective for diverse PAHs. - Can be applied in-situ or ex-situ.	- Potential toxicity of byproducts. - High cost for large-scale applications.	[168-170]
Thermal desorption	Heating contaminated soil to volatilize PAHs for capture and treatment.	- Efficient for high - Concentration contamination. - Relatively quick turnaround time.	- Energy-intensive, generates air pollution if not properly managed. - May not be suitable for all soil types.	[171, 172]
Soil washing	Extracting PAHs from soil using solvents or surfactants.	- Effective for removing readily mobile PAHs. - Can be combined with other technologies for improved results.	- Generates contaminated wastewater requiring treatment. - Potential for soil erosion and leaching.	[173-175]
Electrokinetic remediation	Applying electric current to mobilize and separate PAHs in soil.	- Can target specific PAH types. - Potentially applicable to deep soil contamination.	- High energy consumption, complex setup. - Limited effectiveness for highly bound PAHs.	[175, 176]

Microbial bioremediation (bacterial-remediation, myco-remediation, and vermi-remediation)

The primary goal of bioremediation is to speed up the biodegradation process by creating the ideal environment for microbial development and favoring the use of PAH as a feedstock for their metabolic processes. In order to achieve this, a variety of microorganisms, such as fungi and bacteria, have been isolated and characterized and can break down a variety of PAHs [177]. The inherent metabolic flexibility of bacteria allows them to degrade PAHs contaminants [178]. In contrast to bacterial anaerobic PAHs degradation, which employs a completely different strategy to break and open the aromatic ring depending on the reductive reaction type and alternative final electron acceptors, bacterial aerobic PAHs degradation uses oxygen as the final electron acceptor and as a co-substrate for the hydroxylation and oxygen-mediated cleavage of the aromatic ring [40, 179, 180]. Also, bacteria plan for the degradation of PAHs either anaerobically under nitrate and sulfate-reducing circumstances or via the CYP450-assisted pathway with the generation of trans-dihydrodiols [181-183]. The existence of anoxic conditions in various environmental niches, including the phreatic zone, deep aquatic sediment, and water-flooded soil, is causing anaerobic PAH degradation to receive more attention these days despite the fact that aerobic PAH degradation is traditional and preferred [40, 180].

It has been reported that a range of bacterial strains from the genera *Acidovorax, Arthrobacter*, *Brevibacterium, Burkholderia*, *Pseudomonas, Sphingomonas*, *Mycobacterium*, and *Aeromonas* can use phenanthrene as the only carbon and energy source. *Pseudomonas spp.* and *Brevibacterium spp*. metabolic pathways for phenanthrene degradation were compared, and the results showed that the two microorganisms may use notably different mechanisms for PAHs degradation [184].

Several bacterial species, though with various degrees of efficiency, including *Bacillus*, *Sphingomonas*, *Mycobacterium*, *Micrococcus*, and *Stenotrophomonas*, have been reported for their BaP degradation abilities. In addition to bacteria, filamentous fungi having the ability to break down BaP include, *Cladosporium cladosporioides*, *Aspergillus flavus, Talaromyces rotundus*, *Gliocladium viride*, *Paecilomyces farinosus*, and *Pleurotus ostreatus* [185].

Pyrene has been found to be degraded by several bacterial species, including *Mycobacterium*, *Sphingopyxis*, *Sphingomonas*, and *Pseudomonas*. *Mycobacterium* has been extensively reported to degrade pyrene [186]. Anthracene can be mineralized by bacteria from the genera *Sphingomonas*, *Mycobacterium*, *Pseudomonas*, *Nocardia*, *Corynebacterium*, *Rhodococcus*, and *Streptomyces* [187, 188].

A metabolically adaptable strain of *Rhodococcus spp*. was capable of using naphthalene as the only source of carbon and energy for growth [189]. In another investigation [190], naphthalene, anthracene, fluoranthene, and phenanthrene were all degraded by a Pseudomonas strain that was isolated from soil sediments of municipal garbage.

Using immobilized *Pseudomonas taiwanensis* PYR1 and *Acinetobacter baumannii* INP1 on cinder beads, Huang *et al.* [191] demonstrated increased pyrene and indeno[1,2,3-cd]pyrene breakdown (71 and 81%) in petroleum-contaminated soil. An intriguing study [192] found that phenanthrene contamination of plants might be prevented by inoculating them with an endophytic *Pseudomonas* strain isolated from clover (*Trifolium pratense*) cultivated in a PAHs-contaminated environment. These results highlight the significance of PAHs-resistant genes activating in lower and higher forms of organisms throughout time following long exposures to PAHs contaminated locations, and future possibility of studying these natural selection mechanisms for effective PAHs bioremediation.

In recent years, myco-remediation of PAHs using a variety of fungi species has been widely reported. All fungi, unlike bacteria, do not use PAHs as their only source of carbon; instead, they co-metabolize them to produce a variety of oxidation products, including carbon dioxide. The breakdown of PAHs by the fungus is mediated by the monooxygenase enzyme [193]. Polycyclic aromatic hydrocarbons are oxidized by CYP450 monooxygenase-like enzymes produced by fungi, which create arene oxide and water. Moreover, arene oxides undergo non-enzymatic rearrangement to create phenols, which bind to xylose, gluconeric acid, and glucose [40, 194]. Certain fungal species may also produce biosurfactants to get over the difficulty of less soluble PAHs, which leads to greater breakdown [195].

The most effective bio-remedial techniques have been shown to involve co-culturing techniques such as bacterial-fungal, bacterial–algal and fungal-algal co-cultures [196, 197]. Because algae provide a variety of extra polymeric and weighted compounds (including lipids, nucleic acids, proteins, fermentation products, etc.), which encourage bacterial and/or fungal growth and thereby enhance PAHs degradation, the bacterial-algal synergy is more advantageous than bacterial consortia and bacterial-fungal co-cultures [162].

Vermi-remediation is used alone or in combination with microbes or plants to remove PAHs from fine soil (porous soil with pores smaller than 0.1 mm). Polycyclic aromatic hydrocarbons in fine soil pores are neither bioavailable nor accessible to microorganisms (size 1–10 mm) and plant root hairs that can break them down (size 15–17 mm). Earthworms' burrowing activities during vermi-remediation increase the size of the soil pores, allowing degrading bacteria and plant roots to enter the soil, proliferate, and eventually be able to destroy buried PAHs [162]. Moreover, earthworms remove PAHs from the soil by intestinal digestion or cutaneous absorption that bio-transform or breakdown into innocuous substances [198].

Improved physical and biological soil quality, the excretion of nutrients as vermicasts, and the growth of advantageous soil microbes are all advantages of vermi-remediation [199]. Earthworms reproduce quickly and with little to no energy, which may speed up the removal of PAHs in a short amount of time, demonstrating how effective, sustainable, and environmentally beneficial vermi-remediation is [198].

After 5 weeks of pre-composting, the addition of earthworms (*Eisenia Andrei)* to the sewage sludge bioreactor resulted in increased PAHs elimination (86, 58, and 62% under three distinct pre-composting methods) [199]. The only limitation of vermi-remediation is that it only works in areas with low to moderate levels of pollution, where earthworms can develop and thrive [162].

Phytoremediation

The active carbon (AC) and biochar

One of the most popular techniques for the removal of PAHs is sorption. Polycyclic aromatic hydrocarbons have a high capacity for absorbing into solid medium and have a low solubility in water. The removal of PAHs from aqueous solutions and the immobilization of PAHs in contaminated soils have mostly been accomplished using a variety of adsorbent media, including AC, charcoal, and modified clay minerals. Past research [200] has shown that by utilizing adsorbents, extremely high removal efficiencies can be attained. For example, the removal efficiencies of activated carbon, modified clay minerals, and biochar were 100%, >99%, and 98.6%, respectively. The effectiveness of PAHs removal or the capacity for adsorption or absorption is greatly influenced by a number of factors, including the adsorbent's manufacture method, pH, temperature, solubility, and salinity [201-204].

The microporous kind of carbon known as AC has a high adsorption capacity due to its well-developed pore structure, internal surface area, and pore volume [205]. Owing to its widespread use in water treatment and purification, it has the potential to replace both traditional and cutting-edge water treatment technologies [206, 207]. There are two varieties of AC: granular activated carbons (GACs) and powdered activated carbons (PACs). The huge specific surface area and micro-porosity of PACs boost their adsorption capability [207]. Five PAHs (acenaphthylene, fluorine, naphthalene, and phenanthrene) were removed from water by adsorption onto GACs in a study by Eeshwarasinghe *et al.* [208]. The Thomas model successfully mimicked the adsorption of naphthene, acenaphthylene, and naphthene in fixed-bed columns containing a mixture of GACs (0.5g) and (24.5g).

Agricultural by-products are an appropriate raw material to produce AC due to their low cost. Thermo-chemical conversion of agricultural waste has attracted a lot of interest due to its availability and potential to produce energy in addition to AC with powerful adsorption characteristics [209]. Almonds, hazelnuts, apricot kernels, and walnuts which are used to make AC, are effective adsorbents [210, 211]. According to a prior study [212], water toxicants including PAHs could be frequently eliminated by AC. Also, three PAHs (acenaphthalene, naphthalene, and fluorene) were investigated using AC to remove them from aqueous solutions. The outcomes demonstrated that the hydrocarbons' molecular size had a significant impact on the rate of adsorption. In addition, the number of aromatic rings in PAH determines how favorable a contact between an adsorbate and a carbon is [213].

According to Inbaraj *et al.* [214], synthetization of a magnetic AC nanocomposite from green tea leaves (MNPs-GTAC) was performed to assess the effectiveness of PAHs' adsorption. With an MNPs-GTAC concentration of 50 or 60 mg/L, an ionic strength of 0.1–10%, and a pH of 2-4, PAHs adsorption achieved a plateau. The pseudo-second-order rate declined in the following order: BaP> chrysene> Benzo(b)fluoranthene> benzo(a)anthracene. Kinetics was quick, reaching 80% elimination in 5 min. According to isotherm modeling, the maximal adsorption capacities for benzo(b)fluoranthene, BaP, chrysene, and benzo(a)anthracene, respectively, were 28.08, 22.75, 19.14, and 15.86 mg/g. When applied to mineral water, PAHs spiking at 0.1 and 1 mg/L were removed 86-98% and 72-89%, respectively, while tap and river waters were completely removed.

As hydrocarbon adsorbents, biochar made by pyrolyzing dead *Posidonia oceanica*, whether natural or chemically activated, has been studied. The adsorption tests were conducted using aqueous dispersions to simulate bilge waters that contained marine gas oil, a surfactant, and various sodium chloride concentrations. The reverse-phase high-performance liquid chromatography technique in combination with a fluorescence detector was used to directly evaluate the hydrocarbon concentrations prior to and following adsorption [215].

The use of rhizo-remediation

Plant-associated rhizosphere bacteria are used in one specific type of phytoremediation called rhizo-remediation used to treat contaminated soils [216]. Rhizoremediation is more intense for PAHs breakdown, and it depends on the right cooperation between the plant and bacteria that may degrade the substance [217, 218]. At 10 to 15 m underground in the soil, plants enormous root surfaces support microbial growth and help to clean up contaminants [219].

In rhizo-remediation, plant roots provide nutrients in the form of carbohydrates, amino acids, flavonoids, and organic acids for the growth and activities of PAHs degrading microbes, while microbes make up for this by helping the plants overcome stress brought on by pollutants and lower phytotoxicity [218, 219]. In the aged, polluted soil of 50-year-old coking plants, Kong *et al.* [220] conducted a field scale PAHs degradation investigation (3 m 1.2 m, 0.4 m depth, and 5 tonnes dirt) over 175 days. *Rhodococcus ruber* Em1 combined with *Orychophragmus violaceus*, which was used in the comparison of four distinct techniques, was shown to be superior to natural attenuation, bio-augmentation (*R. ruber* Em1), and phytoremediation (*O. violaceus*). In comparison to other approaches, *R. ruber* Em1 and *O. violaceus* greatly improved the removal of 16 PAHs, increasing it by 54% as opposed to 18, 30, and 36%. Microbe-associated phytoremediation approaches (55%) significantly outperformed natural attenuation (10%) and phytoremediation (20%) in the elimination of PAHs with 4-6 rings. García-Sánchez *et al.* [221] conducted pot tests using 5 kg of contaminated soil that had been aged for 180 days to examine four different PAHs bioremediation strategies. The most effective method was a microbe-associated phytoremediation technique involving maize plants, white rod fungus, and local microorganisms.

When compared to other methods, phytoremediation and rhizo-remediation have the following advantages: they preserve the soil's natural conditions; their energy source is primarily sunlight; their ability to achieve high levels of microbial biomass in the soil; and both their efficiency and environmental friendliness. However, sites where plants cannot grow, a large land requirement, only applicable for low-level polluted sites (plant tolerance level), limited remediation depth, a great deal of reliance on climatic and seasonal conditions, disposal of accumulated PAHs from plant parts, unknown effects of biodegradation products, risk for pollutants to enter the food chain, and uncertainty in treatment duration prediction are the main drawbacks of both methods [219, 222, 223].

The use of medicinal plants with an emphasis on cauliflower (Brassica oleracea var. botrytis)

Ideally, plants are chosen for their ability to thrive in contaminated environments and for their growth rate, biomass productivity, capacity to maintain an active soil microbial community, ability to breakdown pollutants, and capacity to adapt to their environment [224]. Phytoremediation with grass is preferred, according to an economic perspective due to fewer care requirements, low nutrient requirements, tolerance for cold, acidic, and sought environments, and grass's extremely fibrous root system that improves soil microbial activities [222, 224].

The species *B. oleracea* of the genus *Brassica*, which includes broccoli, cabbage, cauliflower, Brussels sprouts, kale, turnips, and collards, is the most widely consumed vegetable in the world. Brassica crops contain the largest quantities of glucosinolates (beta-thioglycoside-N-hydroxysulfates), which are powerful anti-carcinogens. When a plant's cells are damaged (e.g., cut, ground, or chewed), the plant enzyme myrosinase hydrolyzes glucosinolates into biologically active isothlocyanates. Glucoraphane (1-isothiocyannato-4-(methylsulfinyl) butane), which constitutes 35–50% of the glucosinolates in broccoli, is a potent mono-functional phase 11 enzyme inducer [225, 226].

Several animal studies have revealed that *Brassida* genus vegetables offer protection from many DNA-reactive carcinogens. They can minimize the growth of tumors brought on by chemicals, lessen the damaging effects of nitrosamines and polycyclic aromatic hydrocarbons, and guard against heterocyclic amines [227, 228].

Cauliflower is regarded as a strong source of dietary fibers, vitamin B_5 and B6, folic acid, and minerals, including potassium and phosphorus, as well as glucosinolates, which have powerful anti-carcinogenic properties against PAHs [229]. However, there are no previous reports regarding using Cauliflower against PAHs in fish.

Concluding remarks

This review concluded that PAHs could cause a significant economic loss by fish mortalities and rendering them unsuitable for human consumption providing health risks when consumed. Researchers from all over the world have studied the toxic effects of PAHs in fish, including ethological changes, histopathological alterations, haemato-biochemical changes, molecular alterations, immuno-depressive effects, and DNA damage. Also, there are variances in the sensitivity of various fish species to these contaminates that are expressed by the differences in response to them. A constant monitoring and surveillance program for PAHs in the fisheries industry must be implemented due to the toxicity and health concerns, particularly the genotoxicity and carcinogenic risks. To reduce the risk to consumers and the accumulation of PAHs in fish, it is crucial to implement an awareness campaign for fishermen, fish producers, and customers.

Additionally, as part of the goals at the national level, a strong analytical quality control procedure for the accurate assessments of PAHs should be implemented. Recent developments in integrated approaches, such as bioremediation of PAHs including microbial degradation or phyto-remediation, or both have significantly improved the effectiveness of removing PAHs contamination from the environment. Further studies and research addressing the worldwide distribution of PAHs in the different areas of aquatic environments. Also, the impacts of PAHs on various fish species and the introduction of new eco-friendly bio-remediation protocols with emphasis on medicinal plants together with microbial degradation to alleviate these hazards should be taken into consideration.

Conflict of Interest

No potential conflict of interest was reported by the author(s).

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الملخص العربى

التلوث بالهيدروكربونات العطرية متعددة الحلقات (PAHs) في النظم الإيكولوجية المائية: المخاطر والعلاجات بإستخدام التقنيات الخضراء

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تعد الهيدروكربونات العطرية متعددة الحلقات (PAHs)، واحدة من الملوثات البيئية الثابتة والمنتشرة في جميع أنحاء العالم. حيث تشكل الهيدروكربونات العطرية متعددة الحلقات تهديدًا صحيًا خطيرًا لمجموعة متنوعة من أشكال الحياة بسبب خصائصها المسببة للطفرات و/أو السمية المناعية و/أو المسببة للسرطان. يتم إنتاج الهيدروكربونات العطرية متعددة الحلقات بشكل طبيعي من مجموعة متنوعة من المصادر، مثل حرائق الغابات والانبعاثات البركانية. يمكن للأنواع الحيوانية المائية وغير المائية أن تكتسب بسهولة بقايا الهيدروكربونات العطرية المتعددة الحلقات في البيئة، إما مباشرة من الماء أو بشكل غير مباشر من خلال غذائها. ولهذا السبب، تركز المراجعة الحالية على مصادر انبعاث الهيدروكربونات العطرية المتعددة الحلقات الرئيسية، والتحولات، والأحداث في النظم البيئية، والآثار الضارة على الحيوانات المائية، مع التركيز على الأسماك. كما تم مناقشة طرق المعالجة البيولوجية الصديقة للبيئة لمعالجة الهيدروكربونات العطرية متعددة الحلقات بشكل مستفيض. وتشمل هذه الأساليب المعالجة الميكروبية (المعالجة البكتيرية، والمعالجة الفطرية، ومعالجة الديدان) وتقنيات المعالجة النباتية (الكربون النشط، ومعالجة الجذور، والنباتات الطبية).