Polyaromatic Hydrocarbons (PAHs): Sources, Distribution, and Health Impacts in Aquatic Vertebrates

Sukhendu Dey, Tridib Mondal, and Palas Samanta

1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) are just one of the xenobiotics discharged into the nature as a consequence of the countless anthropogenic activities brought on by rapid urbanization and industrialization (Mojiri et al. 2019). Sixteen PAHs have been listed by the United States as priority pollutants for the twenty-first century (USEPA 2012). According to the International Agency for Research on Cancer, seven of them, including benz[a]anthracene, chrysene, benzo[a]pyrene (B(a)P), benzo[b]fluoranthene (B(b)F), benzo[k]fluoranthene (B(k)F), dibenz[a,h]anthracene (DbA), and indo[1,2,3-cd]pyrene, are extremely carcinogenic to humans (Li et al. 2018). A very recent study identified four PAHs (benzo[a]pyrene, benz[a]anthracene, benzo[b]fluoranthene, and chrysene) as primary markers of the existence of mutagenic/genotoxic PAHs, particularly in food (Montuori et al. 2022). Since PAHs are tenacious contaminants with a variety of biological hazards owing to their inherent characteristics, remediation has become a worldwide concern. PAHs are widespread, found in both terrestrial and aquatic habitats, as well as the atmosphere (Adeniji et al. 2019). Owing to their greater hydrophobic nature and low water solubility, it was discovered that PAH deposition rates accelerated in the aquatic

S. Dey
Department of Environmental Science, The University of Burdwan, Bardhaman, West Bengal, India

T. Mondal
Department of Chemistry, Sukanta Mahavidyalaya, University of North Bengal, Dhupguri, West Bengal, India

P. Samanta (✉)
Department of Environmental Science, Sukanta Mahavidyalaya, University of North Bengal, Dhupguri, West Bengal, India
e-mail: psamanta@sukantamahavidyalaya.ac.in

R. Singh et al. (eds.), *Xenobiotics in Urban Ecosystems*,
https://doi.org/10.1007/978-3-031-35775-6_9

ecosystem. The aquatic ecosystem turns as an utmost sink for PAHs because they are ultimately entering into aquatic body (Kuppusamy et al. 2017). PAH's introduction into watercourses increased significantly in the twentieth century due to rapid population growth and economic expansion. In aquatic ecosystem, generally three kinds of water PAH contamination are identified: uncontaminated (PAHs < 200 ng/g), mildly contaminated (PAHs, 200–600 ng/g), and substantially contaminated (PAHs > 1000 ng/g) (Wu et al. 2019).

About 80,000 tons of PAHs are thought to be released annually into aquatic environments on a global scale (Wright and Welbourn 2002). PAHs upon entry into waterways either might bind to dissolving organic material or persist in the water's free dissolved phase, or they might adsorb to dispersed particulate matter or silt (Qin et al. 2014). Their ecological fate and possible impacts on the aquatic biota are greatly influenced by interchangeable PAHs between sediment and water. This distribution is basically determined by partition coefficient of water-sediment (Yang et al. 2019) and is very dynamical. Resuspension is generally used to move sediment-bound PAHs into the water column; this process is also applicable with smaller molecular weight (Dong et al. 2016).

Human health and welfare, together with the well-being and health of other organisms worldwide (collectively called ecosystem health), are being negatively impacted by PAH contamination, either indirectly or directly (Patel et al. 2020). Numerous studies were carried out in different watercourses to appraise and measure the PAH concentrations in water/suspended matter and soil particles. Toxic consequences also were evaluated to confirm the negative impact on the ecosystem and the potential biotic threats for living creatures in the water bodies. Still there is dearth of data available. Accordingly, the present book chapter addressed the frequency of polycyclic compounds considering the effects of aromatic hydrocarbons on aquatic ecosystems to the dangers brought on by its contact with aquatic life. This book chapter's objective is to highlight the state of the art and most recent advancements in PAH status in aquatic ecosystem. This chapter also thoroughly discusses the attributes, sources, dosages, toxicology, and health impacts of PAHs and challenges encountered during PAH toxicity assessment.

2 Sources of PAHs in Aquatic Ecosystem

Polycyclic aromatic hydrocarbon (PAH) contamination in aquatic ecosystem is generally originated from two prime sources, namely, human-made sources and environmental sources (Mojiri et al. 2019). Natural forest fires, moorland fires, biological deterioration, and volcanic eruptions are examples of environmental and/or natural sources of PAH contamination in aquatic ecosystems, although the causes of lightning bolts are negligible or less relevant (Abdel-Shafy and Mansour 2016). The primary determinants of anthropogenic PAH contamination in aquatic ecosystem are generally of four different types, i.e., emissions from transportation, industry, households, and agriculture sources (Patel et al. 2020). Incomplete combustion is prime industrial origin of PAHs which includes garbage burning, the manufacturing

of iron/steel, manufacture of aluminum, cement, coal-tar pitch production, rubber tire making, bitumen industry manufacture, manufacturing of fungicides and insecticides, and exhaust from power plants and refineries (Gupte et al. 2016; Mojiri et al. 2019; Patel et al. 2020). Coal gasification, blast/oxygen furnaces, diesel engines, and gasoline-powered engines of big machinery are further industrial emission sources (Patel et al. 2020). Aircraft, trains, ships, and off-road heavy- and lightweight vehicles are only a few examples of the various vehicles whose vent is a producer of mobile emissions (Patel et al. 2020). The sources of domestic emissions are things like rubbish burning, coal burning, wood burning, and cooking. Other domestic heating methods include oil/gas burners, kerosene/wood stoves etc. (Gupte et al. 2016). Open feedstock burning and incineration of agricultural waste when done so in less-than-ideal combustion conditions are contributors of agricultural emissions (Patel et al. 2020). Rural areas with high PAH contamination are mostly affected by agricultural and residential sources; however, in an urban setting, PAH contamination originated from household, transport, and industrial sources. Figure 1 presents various sources of PAH contamination in aquatic ecosystem.

In addition, depending upon origin of their formation, the sources of PAH contamination in aquatic ecosystem is categorized into three groups, namely, pyrogenic (smaller than two to three rings), petrogenic (molecules with 4–6 rings and a greater size), and biogenic origin (Mojiri et al. 2019). Pyrogenetic PAHs are created when organic matter accidentally burns imperfectly at very extreme temperatures (350–1200 °C) with minimal or without oxygen present. Pyrogenic PAHs are also generated by some intentional pyrolysis processes, such as thermal conversion of coal into coal tar and coke and thermal disintegration of complicated hydrocarbons in petroleum. In addition to this, the phenomenon of pyrolysis, which takes place whenever organic compounds are exposed to extreme temperatures while being oxygenated or not, results in the formation of pyrogenic PAHs. The prime origin of pyrogenic PAHs is industrialized operations, the burning of wood/fossil fuels, wildfire, and volcanic activity (Abdel-Shafy and Mansour 2016).

The most prevalent and widespread ambient PAHs, especially in freshwater environments, are pyrogenic PAHs (Li et al. 2019; Jesus et al. 2022). According to Mojiri et al. (2019) and Patel et al. (2020), metropolitan areas typically have greater quantities of pyrogenic PAHs. Owing to the storage, transportation, utilization, and leaking of crude oil or its derivatives, petrogenic PAHs are found in large quantities in petroleum and its byproducts (Patel et al. 2020). High molecular weight (HMW) PAHs are the predominant PAHs in pyrogenic sources, while low molecular weight (LMW) PAHs are the predominant PAHs in petrogenic sources (Marris et al. 2020). In particular, when petroleum hydrocarbons are extracted offshore, the PAHs of petrogenic origin are discharged into the ecosystem as petroleum-based products/crude oil. They are also discharged during the transportation, storing, and usage of petroleum and related byproducts (Jesus et al. 2022). Petrogenic PAHs molecules with 4–6 rings and a greater size has acute toxicity, significant mutagenic and carcinogenic potential.

Biogenic/diagenetic PAHs are produced by living things, namely, microbes, planktons, microalgae, and plants as well as when organic compounds undergo a slow biological conversion (Mojiri et al. 2019). In addition, the diagenetic PAHs

Fig. 1 Drivers of polycyclic aromatic hydrocarbon (PAH) contamination in aquatic ecosystem

autonomously develop from bioactive substrates like plant terpenes during the breakdown of organic substances, a phenomenon that frequently takes place in sedimentary conditions (Jesus et al. 2022).

3 Salient Features of PAHs

Organic contaminants, falling under PAH category, are made up of two or more aromatic carbon fusion rings and predominantly colorless, white, and pale yellow which are solid chemicals. The configurations of aromatic molecule space have

angular (e.g., dibenz[a,h]anthracene), clustered (e.g., pyrene), as well as linear (e.g., anthracene) rings (Abdel-Shafy and Mansour 2016). Except for naphthalene, which was historically utilized as "moth balls," PAHs are hydrophobic and do not easily solubilize in water or vaporize into air. The strong adsorption efficiency, lower water solubility, and chemical resistance of all PAHs significantly increase their environmental persistence (Jesus et al. 2022). These compounds are hydrophobic in nature, chemically and thermodynamically very stable, highly resistant to biodegradation, have very low solubility in aqueous medium, have low vapor pressure, are soluble in an organic solvent, and have very high solubility in lipid vesicle. As PAHs have a very high affinity toward lipid vesicles, these compounds are absorbed by the mammalian gastrointestinal tract. Absorbed PAHs are immediately distributed among the various tissues and localized within the lipid body. Since most of the PAHs have carcinogenic or mutagenic properties, they may cause apoptosis and endocrine disruption, which overall suppresses the immune system (Wootton et al. 2003). The physicochemical attributes of 16 PAHs are shown in Fig. 2.

4 Classification and Types of PAHs

Polycyclic aromatic hydrocarbons (PAHs) are classified based on their molecular weight, structure, source, and process of formation. In terms of quantity of rings in compounds, more specifically molecular weight, PAHs are divided into two groups: high molecular weight (HMW) PAHs (e.g., pyrene, dibenz[a,h]anthracene, benzo[a]pyrene, chrysene), which have four or more aromatic rings, and low molecular weight (LMW) PAHs (e.g., naphthalene, acenaphthene, fluorene, phenanthrene (Phe)), which have two or three aromatic rings. HMW PAHs tend to be less water soluble, have lower Henry's constants and vapor pressures, and partition more readily into organic materials than LMW. As the molecular weight increases from low to high, these compounds are emitted into the environment as a gaseous form to a particulate form. Furthermore, PAHs are categorized into two classes based on their ring structures: alternant PAHs, which only have 6-carbon aromatic ring, and non-alternant PAHs, namely, fluorene, which fuse 6-carbon aromatic ring plus a second ring with less than six carbons (Gupte et al. 2016). The overall PAH structure has an aromatic character and very high π-electron density, which is behind the reason for its very high thermodynamic stability and reluctance to nucleophilic attack (Patel et al. 2020).

Depending upon sources, PAHs are divided into two categories, naturally emitted PAHs and anthropogenically originated PAHs (Mojiri et al. 2019). Based on formation, these compounds are also categorized into pyrogenic PAHs, petrogenic PAHs, digenetic PAHs, and biogenic PAHs. The formation process of the pyrogenic PAHs is called pyrolysis, generally occurring in 350–1200 °C temperature range, some of which may occur even higher than this temperature range. Petrogenic PAHs are formed at the time of crude oil maturation (Marris et al. 2020). Diagenetic PAHs

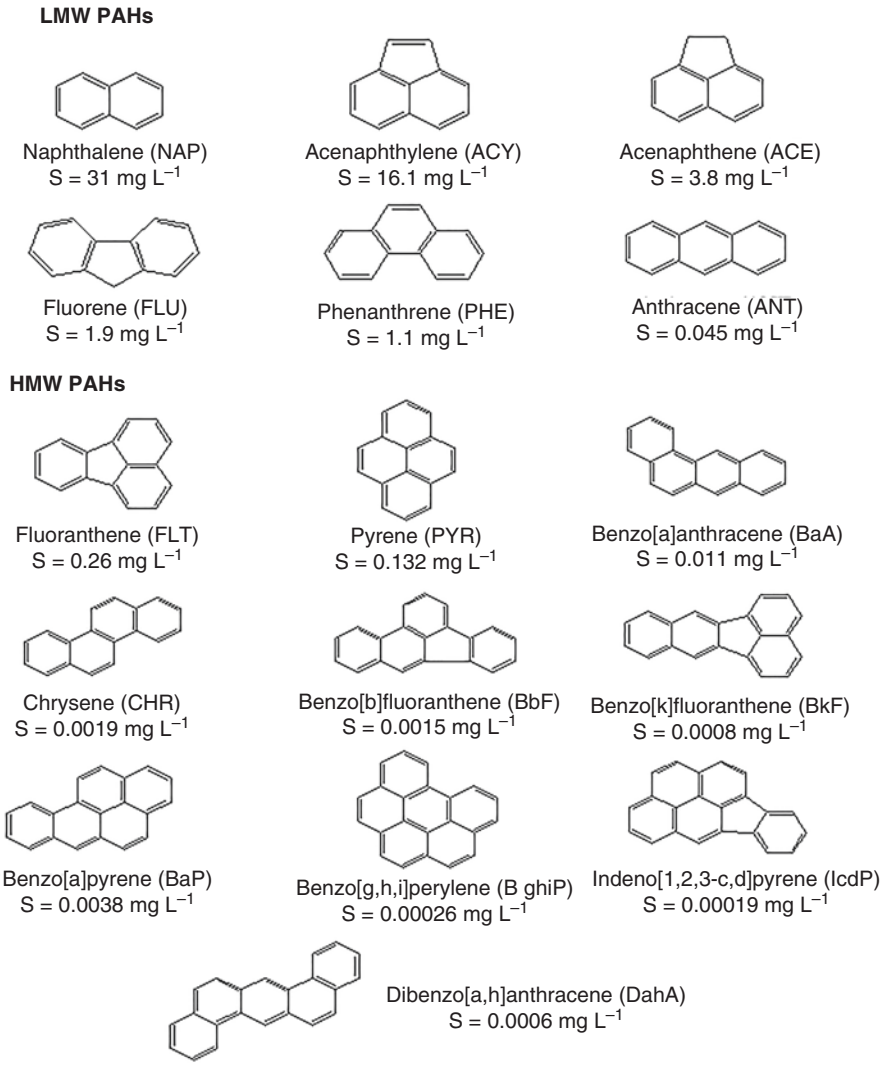

Fig. 2 Structural representation and water solubility at 25 °C of 16 priority PAHs according to the US Environmental Protection Agency. LMW low molecular weight, HMW high molecular weight

are generated spontaneously from biogenic precursors of terrestrial plants (e.g., terpenes) in an anoxic sedimentary environment, and the process is known as the diagenetic process (Bouloubassi and Saliot 1993). There is a contradiction whether higher plants, unicellular algae, or bacteria can synthesize such PAHs or organisms just accumulate these PAHs instead of synthesis (Wilcke 2000). Climate conditions (e.g., temperature, wind, humidity, etc.) and types of fuel clouds play a dominant factor in the production of these natural PAHs.

5 Distribution of PAHs in Environmental Segments

Polycyclic aromatic hydrocarbons (PAHs) generated from diverse origins are dispersed all over the environment (soil, terrestrial, and aquatic environment) through air and water motion. The urban area or near-urban region has more PAH pollutant concentration than the rural sector due to industrialization. Emitted PAHs from different sources break up in the atmosphere either into vapor phase or solid phase and the solid phase sorbeting into particulate matter (PM) (Lin et al. 2018). It was noted that PAH compounds having high molecular weight or low vapor pressure favored sorbet into particulate (e.g., benzo[a]pyrene) while preferring vapor phase compounds having low molecular weight or high vapor pressure (e.g., naphthalene) (Kameda 2011). Dust particles in the air influence the stability of the particulate phase; thus in the summer season and tropical region, PAH distribution in the vapor phase is more dominant over the particulate phase; opposite trends are observed in the arctic region and winter season (Lai et al. 2011). PAHs are absorbed into PM depending on the humidity and suspended particles (e.g., dust particles, fly ash, soot, etc.). Emitted meteorological PAHs are distributed in diverse environmental compartments (earth soil surface, terrestrial and aquatic ecosystem) through dry deposition and wet deposition. In the aquatic ecosystem, in addition to the above process, these pollutants move by water, river stream, sewage system, ocean wave, and particularly industrial and urban effluents (Huang et al. 2019; Li et al. 2019).

5.1 Deposition of PAHs in Soil Surface

Polycyclic aromatic hydrocarbons (PAHs) are deposited on the earth's crust through the processes of dry deposition and wet deposition, as was previously indicated. Part of these soil surface aromatic pollutants are coming from neighboring sources (e.g., transport vehicles, industry, etc.), and the remaining portion came from far away through wind flow. The deposited PAHs over the earth's surface can be static or mobile depending upon the nature of adsorbate and sorbent. A bulk portion of the adsorbed PAHs are bound to the soil particles; thus, this pollutant mobility depends upon the size of the sorbent soil and its pore size (Cachada et al. 2012). Mobility became restricted if PAH could not pass through the sorbet soil pore size. To determine PAH concentration with significant accuracy in soil, combined solvent extraction and mass spectrometry (pseudo-multiple reaction mode gas chromatography (GC)/MS/MS) techniques were mostly used (Shang et al. 2014).

5.2 Sediments in Water

In addition to wet and dry deposition, the aquatic systems can be contaminated by different paths (river streams, sewage systems, ocean waves, and particularly industrial and urban effluents) as mentioned earlier. PAHs tend to be adsorbed by the

adsorbent and ultimately sediments at the bottom of the aquatic environment owing to their hydrophobic property and limited solubility in an aqueous medium. The concentration of a PAH pollutant in bulk water is determined by partition coefficient of sediment-water (K_{sw}, μg Kg^{-1}/μg L^{-1}) (Yang et al. 2019), also known as octanol-water partition coefficient (K_{ow}):

$$K_{sw} = \frac{C_s}{C_w} \tag{1}$$

where C_s indicates the PAH concentration in sediments (μg kg^{-1}) and C_w (μg L^{-1}) indicates the PAH concentration in bulk water above the sediment. Some physical parameters like total organic carbon (TOC) in sediment, particle size, and sediment surface are also modified by the equilibrium distribution. The partition coefficient of sediment-water (Table 1) indicates that much higher soluble in water as that of HMW. By contrast, HMW PAHs have more affinity to be adsorbed by the sediment particle or organic matter owing to their lower solubility and higher hydrophobicity (Lee et al. 2021). Many authors represent the sediment-water partition coefficient by the function of carbon content known as normalized partition coefficient of organic carbon (K_{oc}) (Gou et al. 2019; He et al. 2020) and in situ organic carbon

Table 1 Partition coefficient of PAHs in between sediment and water

PAH	Log K_{sw} ± SD[a]	Log K_{oc}[b]	Log $K_{oć}$	ff[c]
NAP	2.601 ± 1.127	3.11	3.25	0.05
ACY	1.985 ± 1.949	3.51	3.78	0.10
ACE	2.638 ± 1.080	3.43	4.15	0.06
FLU	2.655 ± 1.160	3.70	3.58	0.04
PHE	2.860 ± 1.037	3.87	4.22	0.06
ANT	2.745 ± 1.337	3.40	4.00	0.06
FLT	3.585 ± 1.018	3.70	4.79	0.09
PYR	3.322 ± 1.076	4.66	3.88	0.08
BaA	3.132 ± 1.780	5.30	4.29	0.12
CHR	3.854 ± 1.300	5.43	4.05	0.18
B(b)F	3.883 ± 1.300	5.36	1.21	0.27
B(k)F	3.635 ± 1.572	5.57	1.18	0.23
B(a)P	4.131 ± 1.415	5.61	2.22	0.12
Bghip	4.097 ± 1.146	6.64	0.41	0.28
IcdP	4.284 ± 1.336	6.62	2.10	0.10
DahA	4.415 ± 1.338	6.90	0.83	0.05

For details of abbreviated names of different polyaromatic hydrocarbons, refer to Fig. 2
[a]Jesus et al. (2022)
[b]Guo et al. (2009)
[c]Montuori et al. (2022)

coefficient ($K_{oć}$) (Fakhradini et al. 2019; Zhao et al. 2020). In situ carbon coefficient is defined by the following equation:

$$K_{oc'} = \frac{K_{\mathrm{d}}}{f_{oc'}} \tag{2}$$

where $f_{oć}$ indicates proportion of organic carbon (OC) resuspended in sediment particles. In an aquatic condition, the values of log K_{oc} and log $K_{oć}$ are the indicators of the PAHs equilibrium state (Zhao et al. 2020). PAHs are in a more adsorbed state than the water exchange state when the value of log $K_{oć}$ is lower than log K_{oc}. The fugacity parameter determines the motion of PAHs from one region to another region, defined as (ff):

$$ff = \frac{K_{oc}}{K_{oc} + K_{oc}} \tag{3}$$

A lower value of fugacity (ff < 0.3) for a PAH suggested that sediment behaves as a sink for it and has a very high affinity toward sediment particles, and a high value of fugacity (ff > 0.7) describes the wavering toward water from sediment. A value between 0.3 and 0.7 denotes that PAH remains in equilibria between water and sediment. Montuori et al. (2022) reported that in Sele River, Italy, most of the PAHs tend to be adsorbed by the sediment particle from water except B(b)F, B(k)F, and IcdP (Table 1).

The aromatic pollutants in the aqueous phase especially at the top of the aqueous layer are degraded by photooxidation in the presence of intense radiation, higher oxygen concentration, and temperature (Xiao and Shao 2017). In the aqueous phase, LMW PAHs are further degraded by specific algae, fungi, and bacteria (e.g., NAP, ACY, etc.), but HMW PAHs that are in sediment mainly remain unaffected (e.g., B(a)P, DahA, etc.) by these organisms. Although water PAH value depends upon the sediment-water partition coefficient (K_{sw}), many dynamic processes (water flow, bioturbation) and the timescale of these processes (Dong et al. 2016) alter the equilibrium distribution. Frequent PAH resuspension phenomenon elevated the risk to aquatic species by direct contamination with these pollutants mainly those living species at the water-sediment boundary (Dong et al. 2016).

Very low solubility in aqueous media, negligible photobleaching phenomenon, and an anoxic environment within sediments increase the PAH potential flux. Adsorbed PAHs are observed within the pore water of sediment particles; thus, concentrations of these pollutants are significantly more in pore water in comparison to bulk water in the aquatic environments. The adsorbed PAHs are not entirely insoluble and immobilized, especially the low molecular weight pollutants. Reduced polarity in pore water elevated the dissolved PAH concentration and diffused across the sediments. Consequently, the bioavailability and mobility of PAHs increase within sediments (Dong et al. 2012) and lead to a high threat to the benthic community (Ha et al. 2019).

Table 2 Total PAH concentration in the river experimentally obtained from different locations of the world (N represents PAH quantity, i.e., sampling size)

	Location	*N*	WDP (ng/L)	SPM (ng/L)	Sediment (ng/g)
River water[a, b, c]	Daliao River Estuary, China	16	139–1718	227–1405	–
	Yellow River Delta, China	16	65–335	66–675	–
	Yellow River Beach, China	16	144–2366	507–10,510	–
	Susquehanna River, USA	36	17–150	–	–
	Gaoping River, Taiwan, China	16	10–9400		
	Weihe River, China	16	351–2321	3557–147,907	362–15,667
	Sarno River Estimate, Italy	16	124–2321	6–779	
	Sele River, Italy	16	10.1–567.2	121.2–654.4	331.8–872.0
	Tianjin River, China	16		938–64,200	787–1,943,000
	Athabasca River, Canada	16	–	–	10–34,700
	Soltan Abad River, Iran	16	–	–	246–442

WDP water dissolved phase, *SPM* suspended particulate matter
[a]Chen et al. (2015)
[b]Kafilzadeh (2015)
[c]Montuori et al. (2022)

Industry and cities around the world are primarily developed near the riverside. Thus, rivers are considered as a prime object for discharge of sewage sludge, industrial/domestic wastes, degraded waste materials containing ample loads of PAHs, heavy metals, petroleum hydrocarbon, etc. River water containing a high level of PAHs and heavy metals significantly damages the river ecosystem as well as public health via food chain. So, monitoring and maintaining levels of PAHs and heavy metal concentration in river ecosystems are essential all over the world. Table 2 reported the total PAH values in water-dissolved phase (WDP), suspended particulate matter (SPM), and sediment experimentally from different rivers around the globe. The reported value of total PAH level in SPM in Weihe River, China, and sediment in Tianjin River, China, was highest than the world's major rivers even Sarno River, Italy, which is widely recognized as "the most polluted river in Europe" (Montuori and Triassi 2012). Susquehanna River in the United States had the lowest overall PAH concentration in WDP out of all the rivers listed in Table 2. Rivers have very high concentrations of total PAHs in SPM and WDP, but relatively lower sediment concentrations suggested that pollution might be due to the fresh addition of pollutants.

Scientific community has imposed their attention to evaluate the levels of PAH concentration in marine environments as these compounds have very high detrimental effects on marine organisms (Nasher et al. 2013). Table 3 reported the total PAH concentration at different coastal regions around the world. Pollutant contamination in the coastal region partly arises from far away by ocean waves, river water, and other part affected by nearby land site activities. Gerlache Inlet Sea, Antarctica,

Table 3 Total PAH levels (ng/L) in subsurface marine water around the various locations of the earth (*N* represents the number of PAHs included during the study)

	Location	*N*	Subsurface concentration (ng/L)	Sediment concentration (ng/gm)
Subsurface water from various marine sites around the world[a]	Chesapeake Bay, USA	17	20–66	
	Baltic Sea	14	300–594	3.96–22,100
	Alexandria coast, Egypt	–	13–120	–
	Daya Bay, China	16	4228–29,320	115–1134
	Northern Spanish	25	190–28,800	–
	Saronikos Gulf (Greece)	17	425–459	–
	Gerlache Inlet Sea (Antarctica)	–	5–9	–
	Deep Bay, South China	15	24.7–69	353.8–128.1
	Mumbai Harbour Line, India	15	866–46,740	17–134,134
	Kitimat harbor, Canada	15	–	310–52,800
	Northern Adriatic Sea	22	–	30–600
	Cienfuegos Bay, Cuba	–	–	180–5500

[a]Dhananjayan et al. (2012)

subsurface water has the lowest level of PAH concentration (~ 5–9 ng/L) as there is no nearby human civilization. On the other hand, the Mumbai Harbour Line, India, marine subsurface water has the highest level of contamination (~ 860–46,740 ng/L), which is significantly higher than the water quality recommended by various statutory agencies (Zhu et al. 2015). Chesapeake Bay, USA, and Alexandria coast, Egypt, coastal area subsurface seawater has the least contamination with PAHs close to the human civilization (Table 3).

6 Impact of PAHs on Aquatic Invertebrates

6.1 Impact on Fishes

Despite the rarity of large-scale fish deaths caused by the contamination of freshwater or saline watercourses with PAH pollutants, there is ample data to conclude that such substances have detrimental effects on fish's survival. PAH metabolism in fish has resulted in the generation of reactive chemical species with the potentiality to

attach covalently with proteins and deoxyribonucleic acid (DNA), similar toward the majority of research examining the PAH metabolism in vertebrate. Fish might suffer major health implications from toxins like PAH because of the extremely porous structure of their gills and skin. Bussolaro et al. (2019) observed no cytotoxic effect in the gill and intestine of rainbow trout (*Oncorhynchus mykiss*) exposed to 3-nitrobenzanthrone (3-NBA) and B(a)P and no DNA alteration in gill epithelial cells for both the exposures, but in intestinal cells, there was increasing DNA damage under 3-NBA exposure. Ezenwaji et al. (2013) recorded the liver enzyme activity in *Clarias gariepinus* to diesel exposure; the mean liver alanine aminotransferase (ALT) activity was reduced in control in comparison to treatment, but a totally opposite phenomenon was observed for liver aspartate aminotransferase (AST) activity. Kim et al. (2008) noticed the reduction of RBC count, Hb concentration, and hematocrit value and increasing value of AST activities and no significant changes in ALT activities, total protein, and calcium in B(a)P-exposed rockfish, *Sebastes schlegelii*. Santana et al. (2018) observed significantly increased activities of glutathione S-transferase (GST), ethoxyresorufin-o-deethylase (EROD), superoxide dismutase (SOD), glutathione peroxidase (GPx), lipid peroxide (LPO), and oxidized glutathione (GSSG) under PAH-exposed fish, but catalase (CAT), glutathione reductase (GR) activity, and reduced glutathione (GSH) levels remain unaltered. Nunoo et al. (2019) recorded the nutritional profile and PAH level in three marine fish species such as the yellow fin tuna, *Thunnus albacares*; barracuda, *Sphyraena sphyraena*; and the common white grouper, *Epinephelus aeneus*, which were smoked with a fuel wood smoker (Chorkor smoker) and a gas smoker (Abuesi Gas Fish Smoker). They observed that nutritional profiles such as total carbohydrate, protein, fat, moisture and the ash contents and PAH concentration were different and also observed that good-quality smoked fish was produced by the Abuesi Gas Fish Smoker than the Chorkor smoker.

Sunmonu et al. (2009) recorded the increasing gamma-glutamyl transferase (GGT), ALT, and AST levels in the stomach and liver of *Heterobranchus bidorsalis*, exposed to anthracene, and also postulated that GGT, AST, and ALT activities could be considered as biomarkers for anthracene exposure in *H. bidorsalis*. Tiwo et al. (2019) reported the effects in *Cyprinus carpio* and *Clarias gariepinus* on the nutritional value and PAHs after that showed the decreased amount of protein content and lipid content. Ekere et al. (2019) observed the PAH concentration, such as naphthalene, phenanthrene, anthracene, B(b)F, B(k)F, and B(a)P, in catfish and tilapias. Biuki et al. (2012) recorded the hepatocytic necrosis, blood sinusoid dilation, vacuolations, lipidosis, and bile stagnation in the liver of *Chanos chanos* exposed to PAHs. Vasanth et al. (2012) noticed the increasing lactate dehydrogenase (LDH), ALT, and AST levels in the liver compared with the kidney, gill, and muscle of *Labeo rohita* under anthracene exposure. Phalen et al. (2014) demonstrated that no significant changes occurred in erythrocyte/thrombocyte level of every tissue and showed decreased T cells, B cells, and myeloid cells in the blood, head kidney, or spleen of *Oncorhynchus mykiss* due to B(a)P exposure. Karami et al. (2016) strongly established that the increasing mRNA level, plasma ALT activity, LDH levels, lactate and glucose content, glycogen content, and no change occurred in triploid in

Clarias gariepinus exposed to waterborne phenanthrene. Nyarko et al. (2011) measured PAH concentration in two fishes, *Sardinella maderensis* and *Galeoides decadactylus*, by using gas chromatography (GC) and recorded that the ratio of high molecular weight PAHs/low molecular weight PAHs was <1 which indicated the pyrogenic and anthropogenic origin of PAHs in Ghanaian coastal environment. Vehniäinen et al. (2019) recorded that retina has more adverse effects as action potentials (APs) than phenanthrene in *O. mykiss*; and both exposures affected the cardiac function of rainbow trout, and Na^+ and Ca^+ also increased. Jafarabadi et al. (2018) observed higher PAH concentration in the liver than muscle based on lipid content of *Scomberomorus guttatus*, *Lutjanus argentimaculatus*, and *L. microdon* from the Persian Gulf. Abdel-Shafy and Mansour (2016) reported PAH accumulation, and phase I and II biotransformation enzymes are highly effective in the livers and gills than muscle.

Manju et al. (2008) noticed the higher damage in the brain than the liver tissue in *Anabas testudineus* in the presence of thiobarbituric acid reactive substance (TBARS) content exposed to salicylcurcumin. It also revealed the decreasing level of CAT, GSH, and GPx and increasing level of the superoxide dismutase (SOD) activity but no change in glutathione reductase (GR). Patnaik et al. (2016) observed the decreasing value of protein, glycogen, acetylcholine esterase activity, adenosine triphosphate, and brain acetyl cholinesterase (AChE) activity in *Anabas testudineus* exposed through naphthalene. They also revealed that the blood cells of *Anabas testudineus* showed aggregation and chain formation for naphthalene toxicity. Ahmad et al. (2003) reported the increasing total cell count (TCC) value in phagocytes apart from the head kidney, gill, and peritoneum during short-term exposure to naphthalene in *Anguilla anguilla*, but the long-term exposure period showed decreased value of TCC and respiratory burst activity (RBA), increasing peroxidative damage, and persisted concentration in the gill and kidney and lipid peroxidation (LPO) activity. Hossain et al. (2014) measured the naphthalene concentration in some fish species like bata, puti, baim, chapilla, prawn, taki, and kakila and showed the permissible limit is under recommended value according to the US Environmental Protection Agency (EPA) and European Union. Among these fishes, bata fish consumed highest amount of naphthalene.

According to Dey et al. (2019), anthracene exposure on *Anabas testudineus* caused increasing count of white blood cells (WBC), lymphocyte count, mean corpuscular hemoglobin (MCH), mean corpuscular hemoglobin concentration (MCHC), and mean corpuscular volume (MCV) and decreasing content of hemoglobin, packed cell volume (PCV), red blood cell (RBC), and platelet (PLT). They also reported the increment of PRO, CHOLES, triglyceride (Trig), and ALB and reduction of GLU, low-density lipoprotein (LDL), high-density lipoprotein (HDL), glutamic pyruvic transmission (GPT), and Ca level. In another study, Dey and Ghosh (2019) reported the enhancing activity of ALP and GPT but decreasing value of PRO and ALB due to anthracene exposure on *Anabas testudineus*. Kim and Kim (2016) recorded increasing DNA damage along with EROD and vitellogenin (VTG) levels in *Cyprinus carpio* which was exposed by dibenz[a,h]anthracene (DbA) and acetyl cholinesterase (AChE). Kim et al. (2008) observed the decreasing of red

blood cell (RBC) count, hemoglobin, and hematocrit but increasing of AST activities and LDH concentration, and no effect was found in total PRO, ALT activities, and magnesium or calcium in rockfish, *Sebastes schlegelii*, due to B(a)P.

Haque et al. (2018) observed decreasing value of WBC, lysozyme, and total protein concentration and increasing cortisol and activities of AST, ALT, ALP, CAT, SOD, and GSH content and also showed insignificant difference in RBC count, albumin, Hb, and glucose content compared with control in juvenile *Paralichthys olivaceus* due to waterborne phenanthrene (Phe). Advaiti et al. (2013) observed the higher anthracene accumulation in the gill, kidney, and liver tissue in *Rasbora daniconius*, in comparison to naphthalene and the higher accumulation of naphthalene in intestinal tissue. It also revealed the maximum toxicity level in intestine tissue due to bioconcentration factors (BCF) for naphthalene exposure, but, on the other hand, for anthracene exposure, *Rasbora daniconius* showed maximum toxicity in the liver tissue. Pampanin and Sydnes (2013) and Wickliffe et al. (2014) revealed that the PAHs are omnipresent pollutants in marine ecosystem coming from different origins like oil-based activities through waste production and leakage, natural oil seeps, fossil fuel burning, smelter industries, marine transportation, and even open environment runoff. Collier et al. (2013), Diamante et al. (2017), and Pampanin (2017) revealed that PAHs have carcinogenic potential to induce contrary effects, namely, cancer, abnormalities in development and respiratory shortcomings, neoplastic disease, and blood.

According to Fanali et al. (2018), B(a)P has potentiality to affect the life cycle of amphibians which has genotoxic effect. It noted the increasing micronucleus frequency and mast cell density, decreased melanin area, and no significant change in leukocyte percentage and little changes in lymphocytes, neutrophils, and eosinophil in *Physalaemus cuvieri* and *Leptodactylus fuscus*. Rahmanpour et al. (2014) assessed the PAH concentration in fish liver of *Alepes djedaba*, carnivore; *Aurigequula fasciata*, omnivore; and *Liza abu* and *Sardinella albella*, phytoplanktivores, obtained from Persian Gulf area and showed that the accumulation of pyrene, acenaphthylene, and naphthalene were high in all fish species than the other constituents of PAHs. It was also recorded that the accumulation of PAH concentration was high in males than the females. In another study Al-Saleh and Al-Doush (2002) reported that B(a)P, naphthalene, and pyrene were accumulated significantly in fish species at the Persian Gulf. Disner et al. (2017) observed no mortality in *Astyanax lacustris* and *Geophagus brasiliensis* when exposed with naphthalene and also showed no significant difference in the liver of *A. lacustris* but increasing GST enzyme activity, and in *G. brasiliensis*, there was no deference in liver tissue and gill cells, but showed increasing DNA damage and GST activity.

Disner et al. (2017) also noticed that naphthalene can be accumulated and absorbed in the gall bladder and highest PAH accumulation was found in *A. lacustris*, whereas in *G. brasiliensis* it was not significant, and it was also revealed that the concentration of naphthalene was not genotoxic for fish sample, whereas, it can potentially be accumulated into the fish body. Van Anholt et al. (2003) postulated that GST activity endorses detoxification and excretion of xenobiotics and attributes to defensive adaptation mechanism against the organic compound and their

metabolites. Shirdel et al. (2016) demonstrated the increasing ALP, AST level, glucose level, and triglyceride and decreasing ALT level, cholesterol level, and albumin in *Cyprinus carpio* due to pyrene exposure. Shirdel et al. (2016) also showed the decreasing thyroid hormones but not affected plasma potassium, calcium, and sodium level. Datta et al. (2007) and Kuzminova et al. (2014) also recorded the decreasing ALT level and hepatocyte death in fish due to higher concentration of pyrene.

Akpoghelie (2018) analyzed the individual PAH concentration on smoked fish and Nigerian suya meat and showed higher PAH value in smoked catfish and suya meat than the smoked fish soaked in boiled water. Akpoghelie (2018) also observed that the mean highest levels of individual PAH consumption by smoked catfish are phenanthrene, naphthalene, fluorene, fluoranthene, and pyrene. Ayoola and Alajabo (2012) reported severe congestion and cytoplasmic vacuolations because of glycolysis phenomenon which ultimately caused mitochondrial and microsomal dysfunction and inflammation in the kidney; the gill showed the highest damages including mild and severe congestion and calcification, and no significant effect was shown in muscle tissues of blackchin tilapia (*Sarotherodon melanotheron*) exposed with engine oil.

Shi et al. (2005) strongly established that craniofacial skeletal deformities and spinal curvature were found in *Sebastiscus marmoratus*, exposed by pyrene. Jifa et al. (2005) noticed the increasing GPx, SOD, and CAT in Japanese seabass (*Lateolabrax japonicus*) exposed to B(a)P. Ahmad et al. (2004) reported the increasing GST level found in the liver during short-term exposure but decreasing GST level in long-term exposure in *A. anguilla* fish in the presence of naphthalene exposure. Pathiratne and Hemachandra (2010) also reported induced GST level in *O. niloticus* due to fluoranthene and chrysene. Wahidulla and Rajamanickam (2009) examined co-exposure (phenanthrene and nitrite) in *Oreochromis mossambicus* by using electrospray ionization tandem mass spectrometric (ESI-MS/MS) which reported the formation of PAH-DNA adducts in fish, and several adducts were available in the untreated bile samples of that fish. Wahidulla and Rajamanickam (2009) also noticed that mass spectrometry (MS/MS) is very useful for identification and classification of different types of phenanthrene or derivatives of DNA adducts in complex fish bile mixture as well as modified and normal guanosine also available in bile samples which were co-exposed with phenanthrene and nitrite. Oliva et al. (2010) recorded the substantial difference present between CAT, LPO, and glutathione reductase (GR) biomarkers and control fish, and all biomarkers are sensitive toward chronic pollution. Further, GST, CAT, and GPx represent the correlations with liver PAHs and sediments in *Solea senegalensis*. Sturve et al. (2006) noticed increased CAT level in Atlantic North Sea oil-exposed *Gadus morhua*. According to Vieira et al. (2008), although the toxicity and subsequent remedial mechanism of PAHs were not understood clearly, PAH impacts on antioxidant enzymes were significant on a time- and dose-dependent manner. Vieira et al. (2008) also found a statistical variation between control and anthracene-exposed fish (*Pomatoschistus microps*), and anthracene helped to generate O_2, which may transform into H_2O_2 through catalytic activity.

Kerambrun et al. (2012) demonstrated necrosis, lipofuscin, leukocyte abnormalities, blood accumulation, and increasing macrophage numbers due to PAHs metabolized in the liver. Zhou et al. (2011) also demonstrated inflammation and hepatic damage in the liver due to PAH exposure. Horng et al. (2010) reported the disruption in the endocrine system and effects in reproductive function and growth of fish due to PAH exposure. Dessouki et al. (2013) strongly established lamellae mild congestion, moderate atrophy, and epithelial lining shortening in *Tilapia zillii* exposed with crude oil. Incardona et al. (2004) reported the carcinogenicity and immunotoxicity of PAH toxicity in teleost fish as hallmarks, and each PAH compound has specific and distinct developmental effects on early stage of fish after exposure. Dupuy et al. (2014) reported DNA damage, expression of detoxification, and deregulation of the immune system under short-term exposure to PAHs in European flounder juveniles. Xing et al. (2010) recorded the decreasing acetylcholine esterase (AChE) activity and carboxylesterase level in the muscle and brain of *Cyprinus carpio* exposed to chlorpyrifos. Jee et al. (2006) observed increasing ALP activity for cell necrosis in the liver due to 7,12-dimethylbenz(a)anthracene exposure on *Sebastes schlegelii*. Pampanin et al. (2016) demonstrate that higher value of CAT activity, GST activity, and EROD activities were shown in Atlantic cod (*Gadus morhua*) exposed to PAHs.

6.2 Impact on Birds

Both aquatic and land-based bird species are expected to have different lifelong sensitivity levels and types to hydrocarbons. Land-based birds might come into contact with PAH by ambient deposit or dietary food, while aquatic birds, particularly those that live in the water, may do so through major petrochemical spillage episodes, ambient exposure, and feeding. In contrast to several aquatic bird species that are either wingless, discovered in specialized separated surroundings, or in sizable nesting clusters that rely primarily on conventional resettlement and feeding lifestyles, being a terrestrial-dwelling bird species has the advantage of exposing individuals to PAH xenobiotic compounds in a minimally harmful way by allowing them to resettle apart from polluted sites with convenience.

6.3 Impact on Amphibians

Amphibians, particularly toads, are frequently employed as indicator species to assess the state of conservation for wide environmental niche. The majority of frogs start out in stagnate watercourses as embryos and undergo metamorphosis as they grow. The transformation of frog embryos into toads, which ultimately become frogs, serves as a simplification of this process. Environmental pollutants, including

certain PAH xenobiotic compounds, have indeed been utilized as markers for changes in normal metamorphosis timeframes and performance outcomes (such as morphological mutation).

6.4 Impact on Human

Limited research on xenobiotics in urban ecosystems affecting the human health have been conducted because of the potentiality of these xenobiotic compounds to induce harmful health effects (Dhuldhaj et al. 2022). These xenobiotic compounds are exposed to humans by bioaccumulation of hydrophobic organic xenobiotics that results in its effectiveness can become lipid-rich structures like cell membranes compromise. If the xenobiotic concentration is high, then narcosis happens by impaired function of membrane protein or loss of membrane polarization. Generally, normal method of xenobiotic uptake within the human body is primarily through food chain. Xenobiotic health as well as ecological risks could be evaluated by utilizing different mitigation techniques, thus easing decision-making and risk mitigation activities. This might, in turn, improve the performance of regulators or public health managers to stop the xenobiotic practice globally.

7 Mitigation Strategies

There are many different approaches used for mitigation; some concentrate too extensively on raising consumer and normal citizen knowledge; on the other hand, some involve more loosely organized industry, public environmental administration, nongovernmental organizations (NGOs), and other politicians. Achievements like withdrawal and nitro-masks polycyclic masks are focused on more "expert level" with lower consumer engagement whenever the Sweden country campaign is about eco-labels, medications, washing powder, and others are real examples of regular consumer impact. So, efficacy of mitigating technique can be extremely high involvement in local dependent like national or even regional. For example, high involvement in local dependent likes national or even regional based initiatives like "The Yellow Fish" project, launched by Scottish Environmental Protection Agency and Scottish Water was aimed at cooperating with school children and local normal communities for awareness regarding safe discharge of oil residue and wastes. Finally, this abovementioned approach has been carried out successfully all over Scotland. Go Green is increasingly recognized as one of the most powerful tools and produces more impact on the market and eco-friendly products. Local organization frequently purchases high volume of different products like polybrominated diphenyl ethers (PBDEs) for office purpose, PAHs or nonylphenol in fabrics, that can be a powerful catalyst for changing the perception.

8 Conclusions and Future Perspectives

The present book chapter demonstrated that PAHs are significant pollutants in surface aquatic habitats, and the majority of them exists at comparable to or even above greater than those of the analogous PAHs. PAHs have a propensity to concentrate in aquatic animals; they pose a substantial environmental risk to surface aquatic habitats. Considering this, substantial research on toxicity of specific PAHs to various aquatic invertebrates, especially fish species, have been well-documented. Apart from this the PAH distribution in water and soils of aquatic system documented in this book chapter cannot be overlooked. Anthropogenic activities are directly correlated with PAH distribution in aquatic environment. Accordingly, for achieving the sustainability, it is recommended that PAH levels in aquatic system be continuously monitored and controlled.

Primary obstacles will need to be encountered during study of PAH distribution and toxicity assessment to aquatic invertebrates. The foremost, and perhaps most pressing, is related to the revision of PAH list of priority concern. The said list is utilized extensively in toxicity assessment, but latest evidence has demonstrated that non-included PAHs are potentially more toxic than USEPA PAH priority list at present, which, coupled with their widespread occurrence and higher chemical stability, puts a lot of concern regarding their adverse impacts on the environment. Secondly, more research on benthic toxicity in relation to PAHs is urgently required to close the research gap of aquatic invertebrate toxicity. Thirdly, the PAH toxicity to aquatic invertebrates should not be assessed individually as it is adversely impacted by stressors like climate impact, presence of other compounds, etc. Finally, for an ecologically meaningful evaluation of ecological dangers presented by these chemicals, the PAH toxicity evaluation should consider long-term impacts or chronic toxicity, instead of just merely immediate or short-term impacts. Accordingly, people's understanding of the ecosystem and the use of xenobiotic substances needs to be raised in order to protect the environment from PAH pollution in aquatic ecosystem. Further, shift toward cleaner options like reduced use of fossil fuels and use of alternate energy options should be adopted in order to slow down the entry of petrogenic or pyogenic PAHs for achieving the Sustainable Developmental Goals (SDGs).

Acknowledgments Authors are highly acknowledging the principal of Sukanta Mahavidyalaya for his continuous support and encouragement during the ongoing COVID-19 pandemic. Authors are also thankful to the head of Department of Environmental Science for his continuous support.

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