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Analytical Methods for Polycyclic Aromatic Hydrocarbons and their Global Trend of Distribution in Water and Sediment: A Review

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Abstract

Polycyclic aromatic hydrocarbons (PAHs) are major organic pollutants in the environment, which are toxic to humans and biota, given their carcinogenic, mutagenic and teratogenic nature. In this chapter, we carried out an overview of the sources and toxicity of PAHs, their common analytical methods of determination in the water and sediment samples, and also their global trend of distribution, with a view to provide baseline guidance for relevant control authorities. The choice methods for determining these contaminants are high-performance liquid chromatography (HPLC) with UV/fluorescence detectors and GC/MS. Mass spectrometer coupled with GC is preferred because it offers robust identification of the analyte compounds both by retention time and mass spectrum, with additional structural information. Results collated revealed an extensive distribution of PAHs with total mean concentrations ranging from 0.0003 to 42,350 $\mu\text{g/L}$ in water and 0 to $1.266 \times 10^9 \mu\text{g/kg (dw)}$ in the sediment. PAHs in the two environmental matrices were much higher in the regions with intense oil exploration, shipping and industrial activities. It is therefore necessary to regularly monitor their levels in the aquatic environment, so as to provide mitigation options that will prevent risk to humans and aquatic animals.

Keywords: polycyclic aromatic hydrocarbons, carcinogenicity, endocrine system disruption, aquatic environment, bioaccumulation

1. Introduction

Water is the most abundant compound on the surface of the earth and needed in all aspects of life in adequate quantity and quality. However, water in nature picks up some amounts of

chemical impurities, most of which are anthropogenic and that consequentially impact greatly on its quality [1]. There are three major groups of chemical pollutants: stable trace elements, organic materials, and radionuclides. The organic contaminants include persistent organic pollutants (POPs) and some new compounds such as pharmaceuticals, veterinary medicines and hormones [2].

POPs are synthetic chemicals which are either deliberately or unintentionally produced. They are mostly lipophilic, acutely toxic and persistent in the environment with long-range of transport, thereby leading to global pollution. They accumulate in food chain and are found at highest levels in marine mammals [3]. Highly significant and most commonly determined POPs include organochlorine compounds (OCs), e.g. polychlorinated biphenyls (PCBs), pesticides like dichlorodiphenyltrichloroethane (DDT) and its allied metabolic products such as

PAHs	Chemical formula	Molecular weight (g/mol)	CAS number	Ring number	Melting point (°C)	Boiling point (°C)	IARC group	ERL (µg/kg)	ERM µg/kg)
Naphthalene	C ₁₀ H ₈	128	91-20-3	2	80.2	218	2B	160	2100
Acenaphthylene	C ₁₂ H ₈	152	208-96-8	3	92.5	280	NA	44	640
Acenaphthene	C ₁₂ H ₁₀	152	83-32-9	3	93.4	279	3	16	500
Fluorene	C ₁₃ H ₁₀	166	86-73-7	3	115	295	3	19	540
Phenanthrene	C ₁₄ H ₁₀	178	85-01-8	3	99.2	340	3	240	1500
Anthracene	C ₁₄ H ₁₀	178	120-12-7	3	215	340	3	843	1100
Fluoranthene	C ₁₆ H ₁₀	202	206-44-0	4	108	384	3	600	5100
Pyrene	C ₁₆ H ₁₀	202	129-00-0	4	151	404	3	665	2600
Benzo[a]anthracene	C ₁₈ H ₁₂	228	56-55-3	4	167	435	2B	261	1600
Chrysene	C ₁₈ H ₁₂	228	218-01-9	4	258	448	2B	384	2800
Benzo[b]fluoranthene	C ₂₀ H ₁₂	252	205-99-2	5	168	481	2B	NA	NA
Benzo[k]fluoranthene	C ₂₀ H ₁₂	252	207-08-9	5	217	480	2B	NA	NA
Benzo[a]pyrene	C ₂₀ H ₁₂	252	50-32-8	5	177	495	1	430	1600
Dibenzo[a,h]anthracene	C ₂₂ H ₁₄	278	53-70-3	5	270	524	2A	63.4	260
Indeno[1,2,3-cd]pyrene	C ₂₂ H ₁₂	276	193-39-5	6	164	536	2B	NA	NA
Benzo[g,h,i]perylene	C ₂₂ H ₁₂	276	191-24-2	6	278	550	3	NA	NA
ΣPAHs								4000	44,792

NA: not applicable; ERL: effects range low; ERM: effects range median; IARC: International Agency for Research on Cancer; and CAS: chemical abstract services [21–23].

Table 1. Physicochemical properties of the 16 priority PAHs, their toxicity classification and standard pollution criteria concentrations for sediment.

p,p'-DDT, p,p'-DDE, and p,p'-DDD [2]. Others are polycyclic aromatic hydrocarbons (PAHs), phthalate esters, polybrominated diphenyl ethers (PBDEs), polychlorinated naphthalenes (PCNs), BPA (bisphenol A) and alkyl phenols [4, 5].

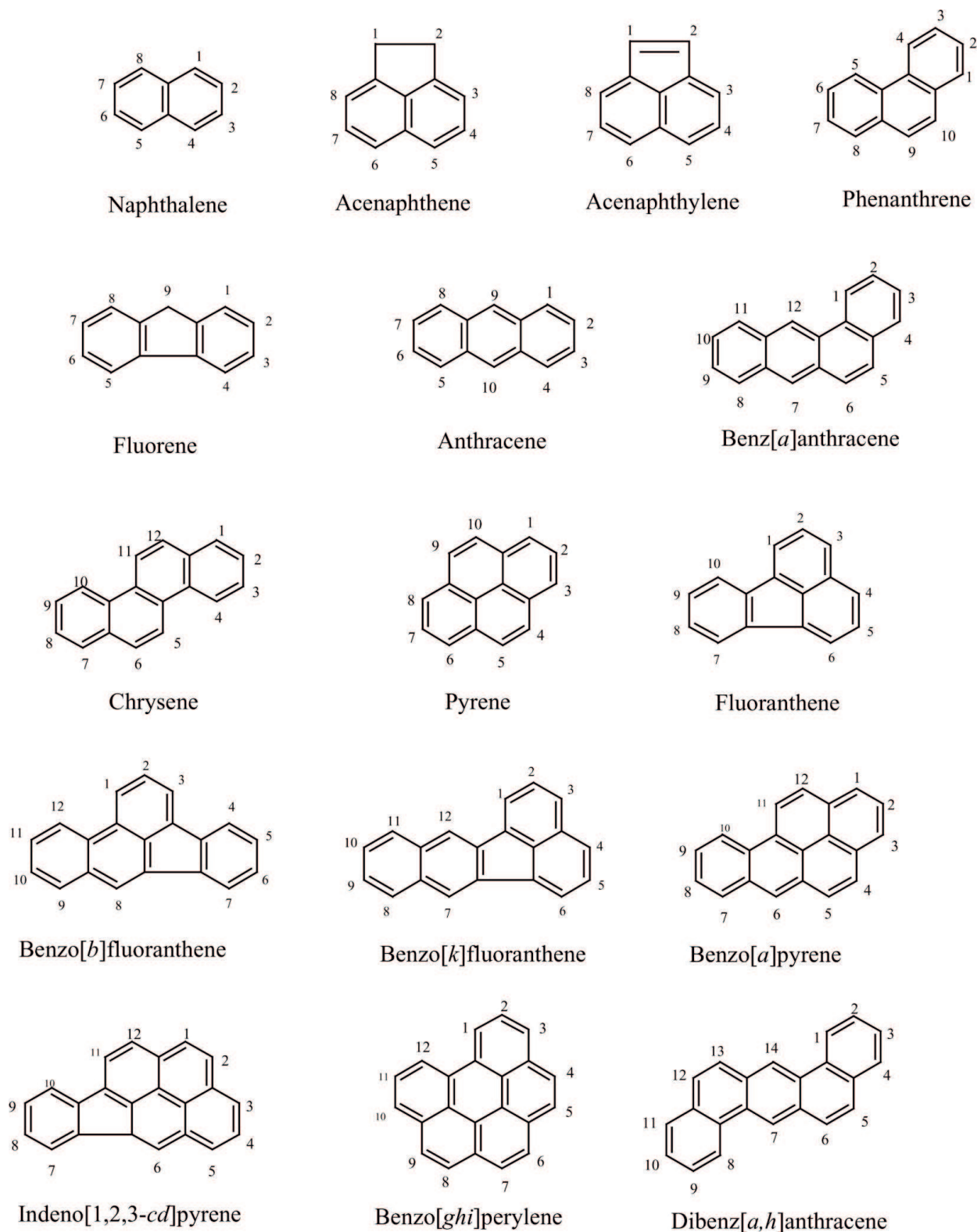


Figure 1. Structures of the 16 priority PAHs [24].

Polycyclic aromatic hydrocarbons (PAHs) are a class of hazardous organic chemicals which can be in linear, angular, and cluster in arrangements. They have two to seven fused carbon rings that can have substituted groups attached, and range from naphthalene ($C_{10}H_8$, two rings) to coronene ($C_{24}H_{12}$, seven rings) with molecular masses ranging from 128 to 278 Da (**Table 1**). They generally have low vapour pressure and are globally distributed in atmospheric, terrestrial and aquatic systems [6–8].

PAHs are basically classified into two: low molecular weight PAHs (LPAHs) and high molecular weight PAHs (HPAHs). LPAHs (e.g. naphthalene, acenaphthene, acenaphthylene, fluorene, anthracene, phenanthrene) tend to have a core structure of two to three benzenoid rings (six-sided aromatic rings of carbon) while HPAHs have molecular structures of four or more benzenoid rings (e.g. fluoranthene, pyrene, benzo[a]pyrene, and benzo[fluoranthenes] (**Figure 1**). The hydrophobicity, bioaccumulation tendency, resistance to biodegradation, and overall environmental persistence of the compounds generally increase with increasing molecular weight [9, 10]. The alkylated PAHs which are formed through diagenetic processes are more toxic than the parent compounds. They usually co-exist with their parent compounds in the environmental matrices [11, 12].

The toxicity of these alkyl substituted PAHs has generated great concerns in the recent times owing to their huge contribution to the total level of PAHs in the crude oils, mineral oils and diesel, compared to their non-alkylated counterparts which are typically from combustion sources. They bioaccumulate to a greater degree and degrade more slowly than their parent homologues. Alkyl substitution may be inducing phototoxicity in exposed organisms after the parent compounds have been broken down. The alkylated PAHs are also more persistent in the environment than the parent PAHs. Although polycyclic aromatic hydrocarbons in the fuels or crude oils spilled into aquatic environments represent a small percentage of the total mass of the volume, the proportion usually increases greatly after a few months of the incidence, thereby constituting a serious health risk to the aquatic biota [13].

Here, we review the analytical techniques for PAHs in water and sediment, as well as the existing data on their sources, toxicity and distribution in aquatic systems around the world.

2. Physicochemical properties of PAHs

2.1. Solubility, structures, melting and boiling points of PAHs

Solubility of PAHs in water generally decreases as the molecular weight increases while their boiling and melting point increases correspondingly [14]. Four-ring and five-ring aromatic hydrocarbons such as chrysene and benzo[a]pyrene are virtually insoluble in water [15]. Solubility also decreases as ring structure increases, as degree of substitution increases, vapour pressure decreases and molecular weight increases [6, 16]. Molecules with a linear arrangement are more likely to be less soluble than the angular or perifused molecules. For example, anthracene is less soluble compared to phenanthrene. Alkyl (i.e. CH_2 — group) substitution of the aromatic ring also results in an overall decrease in the solubility of PAHs, although there are some exceptions, e.g. benz[a]anthracene is less soluble than either methyl- or ethylbenz[a]

anthracene. The solubility of PAHs in water is enhanced three- to fourfold by a rise in temperature from 5 to 30°C. Dissolved and colloidal organic fractions also enhance the solubility of PAHs which are incorporated into micelles [13, 14].

PAHs in aquatic environments rapidly tend to become associated with the particulate matter or organic substances such as biopolymers, humic substances and black carbon ending in sedimentation due to their low solubility in water [8, 16]. Once adsorbed to the sediments, they are much more stable than pure compounds and are resistant to oxidation and nitration reactions to which they would otherwise be quite sensitive due to photochemical processes. Most PAHs are classified as semi-volatile organic compounds because of their low volatility [8]. Some processes such as photo-oxidation, hydrolysis, biotransformation, biodegradation and mineralization in the aquatic system lead to transformation of PAHs to other substances. Likewise, other activities such as bioaccumulation, adsorption, desorption and re-suspension are accountable for the cycling of the compounds all the way through the aquatic environment. High molecular weight PAHs in the aquatic systems are mostly degraded by photo-degradation [17].

2.2. Sorption of PAHs to organic carbon

Total organic carbon (TOC) and black carbon (BC) play an important role in the sequestration of PAHs in soils and sediments despite their relatively low level in the environmental media [14]. Sorption of PAHs to soil and sediments increases with increasing organic carbon content and with increasing surface area of the sorbent particles [10]. Hence, the concentration of PAHs varies largely among different soil size fractions. A particular study reported that the highest total PAH concentration was found in the 250–500 µm size fraction, while the maximum level of individual PAHs was detected in the 250–500 µm or 500–2000 µm size fraction [18].

The organic carbon content depends on geographical location, pollutants entering rivers, pH and layer depth of the tested sediments. Sediment samples with lowest pH recorded the least amount of organic content [19, 20]. The association of PAHs with the solid phase depends on their molecular weight and octanol-water partitioning coefficient (K_{ow}).

Among the EPA 16 priority PAHs, phenanthrene, fluoranthene, benzo[a]anthracene, chrysene, benzo[b&k]fluoranthene, benzo[a]pyrene and indeno[1,2,3-cd]pyrene are the most important contaminants in soil. Furthermore, the high partitioning to organic carbon is the root cause of the high rate of bioconcentration for these compounds and the ease with which they enter the food web [14].

3. Sources of PAHs in the environment

PAHs enter the shallow coastal, estuarine, lake and riverine environments from petroleum spills, treated industrial and municipal waste water discharges, urban and suburban stormwater runoff, chemical refineries, recreational and commercial boats, volcanoes and atmospheric fallout of vehicle exhaust [2, 25]. They are generated from both natural and anthropogenic sources, being ubiquitous.

3.1. Natural sources

These include natural petroleum seeps, forest fires, prairie fires, agricultural burning and post-depositional transformation of biogenic precursors [26]. The actual amount of PAHs and particulates emitted from these sources varies with the type of organic material burned, type of fire, nature of the blaze and intensity of the fire. PAHs from fires tend to sorb to suspended particulates and eventually enter the terrestrial and aquatic environments as atmospheric fall-out. Treated wood has also been recognized as a source of PAHs in water and sediments [14]. Other natural sources include volcanoes, chlorophyllous plants, fungi and bacteria [10].

3.2. Anthropogenic sources

Anthropogenic sources are basically grouped as pyrolytic and petrogenic. Pyrolytic sources include combustion processes (e.g. fossil fuel combustion, electric power generation, refuse incineration, home heating and industrial emissions), while the petrogenic input is closely related to releases from petroleum products (e.g. oil spills, road construction materials such as production of coke, carbon black, coal tar, and asphalt) [7, 9, 10, 27–30].

Some PAH contaminant sources exhibit co-dominance of both pyrogenic and petrogenic types owing to the complex processes involved in the PAH source type. Crankcase and other lubricating oils used in internal combustion engines, for example, contain a variety of petrogenic PAHs. The PAH composition changes, however, as the oil is used, since various combustion-derived PAHs accumulate with the increased use. Coal tar residues from former manufactured gas plant (MGP) sites tend to have a highly complex and highly variable PAH composition, since the coal tar was produced by the heating of PAH containing coal or coke to produce coal gas as a heating and light source prior to the wide-spread availability of natural gas in the mid- to late-twentieth century [9]. Polycyclic aromatic hydrocarbons (PAHs) in water bodies are subject to distribution and accumulation among the water column, suspended particulate matter, bottom sediments, and biota [31], because of their low vapour pressure, non-polarity, lipophilicity and high hydrophobicity [8].

3.3. The use of molecular diagnostic ratios for source identification

Sources of PAHs in the environment are usually identified using several ratios and indices of some particular PAHs on the basis of their composition and distribution pattern [32–34]. An ideal source ratio would be distinctive to a particular source [35, 36]. The molecular ratios are mostly used to distinguish between PAHs from pyrogenic and petrogenic origins [37]. In general, two- to three-ringed and some alkyl-substituted PAHs are good for distinguishing petrogenic contamination [33, 38–40], whereas four- to six-ringed PAHs which are more toxic and thermodynamically stable than those from petrogenic sources are appropriate for identifying those from pyrogenic origins [16, 33, 34, 41], given the high level of non-alkylation in their own composition [32, 33, 42, 43].

The ratio of low molecular weight to high molecular weight PAHs (LMW/HMW) is a measure of weathering process in the aquatic environment. A lower value of this ratio indicates high level of resistance to microbial degradation in the high molecular weight PAHs or a higher

solubility of the low molecular weight PAHs in the water column [33]. However, many diagnostic ratios involving the low molecular weight PAHs (e.g. LMW/HMW, anthracene/Phen, etc.) are very unstable because they are usually influenced by some environmental factors like photodegradation and volatilization; hence, they are very much affected by mobility in the aquatic environment. On the other hand, the higher molecular PAH ratios are relatively more stable and are less affected by such factors [44, 45].

Statistical analysis revealed that the following molecular ratios: Anth/178, BaA/228, Chry/BaA, Flt/Flt + Pyr, Flt/Pyr and Inp/Inp + BghiP are strongly correlated with pyrogenic PAHs. Similarly, Chry/BaA, Inp/BghiP, BaP/BghiP and some other similar ones have shown tendency to provide more useful information needed to differentiate PAHs from several pyrogenic sources such as vehicle emission, coal burning etc. [41, 46]. For instance, BaA/(BaA + Chry) in the range of 0.2–0.35 indicates combustion of coal, grass or wood burning [47] and BaP/BghiP > 0.6 suggests vehicular emission [48]. Although, all the ratios have been found useful in the identification of sources of pollution in the aquatic environment, the information they provide are not very definite but are only rough idea of the origin. The ratios are sometimes inconsistent, as they occasionally offer contradictory information, pointing to different sources of pollution at the same time owing to their instability. Researchers must therefore exercise caution in using them. Cross plot and more ratios can therefore be employed to achieve a robust interpretation of the information provided by these isomeric ratios [33, 39, 41].

The ratios of the alkyl substituted PAHs to their parent compounds have been found appropriate to provide more reliable information for source distinction because the alkylated PAHs decrease in abundance as temperature increases [49]. The formation of these compounds is very distinctive at low temperatures (~100–150°C) than at higher temperatures (~2000°C) because of their thermal instability. Most commonly used of these compounds are the methylated species of phenanthrene, fluoranthene, pyrene, chrysene and benz[a]anthracene (Table 2) [39].

3.4. Toxicity of PAHs and risk of exposure

More than 80% of the total PAH contribution to environmental and health concerns could be attributed to the 16 EPA priority PAHs (Figure 1 and Table 1). Carcinogenic nature of these compounds is a major worry, although not all of them are affected [48]. In water, the toxicity of individual PAHs to plants and animals decreases beyond molecular weight of 202 because solubility drops rapidly afterwards. However, sub-lethal effects can result from exposure to very low concentrations of the high molecular weight (HMW) compounds. In most cases, environmental concentrations of PAHs in water are enormously below levels that are acutely toxic to aquatic organisms except in the vicinity of chemical or petroleum spills. However, concentration of PAHs in the sediment can be much higher, even though their limited bio-availability often reduces their toxic potential to a large extent [6].

PAHs are generally classified into five groups based on their carcinogenic tendencies (Table 1). Group 1 consists of substances with carcinogenic potential for humans and benzo[a]pyrene with sufficient toxicological data is the only member [34, 51]. Group 2A PAHs are those that are probably carcinogenic to humans and a major example in this group is dibenzo(a,h)

Ratio	Petrogenic	Pyrolytic	References
LMW/HMW	>1.0	<1.0	[38]
Phen/anthracene	>15	<10	[32]
Anth/178	<0.1	≥0.1	[41]
BaA/228	<0.2	0.2–0.35	[50]
Chry/BaA	<0.4	>0.9	[44]
Anth/Anth + Phen	<0.1	>0.1	[33]
Flt/Flt + Pyr	<0.4	≥0.5	[37]
Flt/Pyr	<1.0	>1.0	[32]
Inp/Inp + BghiP	<0.2	>0.5	[37]
BaA/BaA + Chry	<0.2	>0.35	[50]
MPhen/Phen	=0.4	<0.4	[39]
MPF/PF	=0.5	<0.5	[39]
MCB/CB	=1.0	<1.0	[39]
MPsp/Psp	=0.8	<0.8	[39]

Phen: phenanthrene; Anth: anthracene; Chry: chrysene; BaA: benzo[a]anthracene; LMW: low molecular weight; HMW: high molecular weight; Flt: fluoranthene; Pyr: pyrene; Inp: indeno(123,cd)pyrene; BghiP: benzo[g,h,i]perylene; MPsp: sum of all the methyl PAH species of phenanthrene, fluoranthene, pyrene, chrysene and benz[a]anthracene; Psp: sum of the parent compounds of the methyl PAH species (i.e. phenanthrene, fluoranthene, pyrene, chrysene and benz[a]anthracene); MPhen/Phen: sum of 3-methylphenanthrene, 2-methylphenanthrene, 9-methylphenanthrene and 1-methylphenanthrene; MPF: sum of three peaks of methylpyrenes/methylfluoranthenes; PF: sum of pyrene and fluoranthene; MCB: sum of five peaks of methylchrysenes/methylbenz[a]anthracenes; and CB: sum of chrysene and benz[a]anthracene.

Table 2. Molecular diagnostic ratios and possible sources of PAHs in the environment.

anthracene. Although, the list contains more PAHs in this category, however, they are not among the EPA priority contaminants. Therefore, the sentence is very correct as far as the 16 priority PAHs are concerned. They are the substances that are possibly carcinogenic to humans. Group 3 compounds are those not classifiable as being carcinogenic to humans and its members include acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene and benzo[g,h,i]perylene. There is another group for those which are probably not carcinogenic to humans but none of the 16 EPA PAHs falls into the category. However, acenaphthylene was not classified into any of the 5 existing groups, probably because there is no sufficient data to decide on where it should belong [22, 24, 37, 52].

Seven of the pyrogenic PAHs (4–7 rings) in the group(s) 1, 2A and/or 2B have been identified by the United States Environmental Protection Agency (USEPA) and the International Agency for Research on Cancer (IARC) to be of high risk to humans and are therefore used to assess the level of pollution in the environment. They are benzo[a]pyrene, dibenzo[a,h]anthracene, benz[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, indeno[1,2,3-cd]pyrene and chrysene [34, 37, 53, 54]. Aside their confirmed carcinogenicity, all the seven PAHs were also found genotoxic alongside benzo[g,h,i]perylene that was not classified as being carcinogenic to humans [24]. The USEPA, therefore, established toxicity equivalency factors (TEFs) for the

PAH congeners	TEF
Benzo[a]anthracene	0.1
Chrysene	0.01
Benzo[b]fluoranthene	0.1
Benzo[k]fluoranthene	0.1
Benzo[a]pyrene	1
Dibenzo[a,h]anthracene	0.1
Indeno[1,2,3-cd]pyrene	0.1

Table 3. Toxicity equivalent factors (TEFs) of the carcinogenic PAHs.

quantification of their level of toxicity. The highest TEF of 1 was assigned to benzo[a]pyrene while lower values as shown in **Table 3** were assigned to other PAHs. Toxicity equivalent concentration (TEC) of individual PAH can be calculated by multiplying the concentration of the congener in the environmental sample with the respective TEF, as shown in Eq. (1). TECs for the seven carcinogenic PAHs (cPAHs) are summed up to obtain the total toxicity equivalent concentration (TTEC) in the chemical mixture or the sample under investigation [37, 55].

$$\text{Total toxicity equivalent concentration (TTEC)} = \sum C_n \cdot \text{TEF}_n \quad (1)$$

where C_n is the concentration of each congener n in the PAH mixture and TEF_n is the toxicity equivalency factor for the specific congener n . Compliance is determined by comparing the TTEC for the sample with the appropriate cleanup level (Method B or C) for benzo[a]pyrene. The Method B and C cleanup levels for the reference substance are 0.137 and 18 mg/kg, respectively, although the estimates are only considered applicable for exposures through the oral route [55, 56].

Some of PAHs can affect health when exposure is at levels higher than the maximum concentration limit (MCL) for relatively short periods of time. The damage can include suppressed immune systems, or red blood cell damage leading to anaemia. Long-term exposure is believed to lead to potential developmental and reproductive effects and some forms of cancer [57]. Occupational exposures to high levels of mixtures containing PAHs have resulted in symptoms such as eye irritation, nausea, vomiting, diarrhoea and confusion. Reactive metabolites of some PAHs, such as epoxides and dihydrodiols, have the ability to bind with cellular proteins and DNA. The resulting biochemical disruptions and cell damage lead to mutations, development of malformations, tumours and cancer. The most common PAH that causes cancer in laboratory animals is benzo[a]pyrene. Ingestion of high levels of these compounds during pregnancy could result in birth defects and decreased body weight of the offspring. Most of the PAHs are not genotoxin by themselves; they need to be metabolized to the diol-epoxides which react with DNA, thus inducing genotoxic damage [10].

Bioconcentration and bioaccumulation of PAHs in organisms occurs through various routes including ingestion, inhalation or dermal contact pathways. PAHs are toxic and their carcinogenicity is initiated by their metabolic conversion to peroxides that bind covalently to cellular

macromolecules, including DNA, causing an increase of elevated levels of DNA adducts and developing errors in DNA replication which cause carcinogenesis in both humans and other organisms [48]. Although unmetabolized PAHs can have toxic effects, the primary concern for animals is the ability of reactive metabolites, such as epoxides and dihydrodiols, of some PAHs to bind to cellular proteins and DNA. The resulting biochemical disruptions and cell damage lead to mutations, mental malformations, tumours, and cancer [6, 9].

3.4.1. *Sediment quality criteria*

The contamination of aquatic sediment by PAHs is evaluated by comparing the PAH concentrations in such sediment sample with the effects-based guideline values like the effects range low (ERL) and effects range median (ERM) established by the United States National Oceanic and Atmospheric Administration (USNOAA) [58, 59]. **Table 1** presents the ERL and ERM values for the 16 priority PAHs. The ERL values suggest a likelihood of serious biological effects on aquatic creatures, while ERM values indicates a great risk of posing damaging biological effects on the aquatic organisms [59]. A lesser PAH concentration than the ERL would guarantee no adverse effects on the benthic invertebrates. However, any concentration between the ERL and ERM suggests the occurrence of such effects occasionally in the aquatic milieu. Meanwhile, higher PAHs concentrations above the ERM value would impact adverse effects on the organisms from time to time [37, 58, 60].

3.5. Extraction methods for PAHs in water and sediment

3.5.1. *Water extraction*

PAHs are usually present in water samples in trace quantity, owing to their low solubility [61]. Therefore, the analytical method to use should be of high enrichment factors for the target compounds and should allow concentrating and increasing the low levels to values that can be detected using analytical instrument [20, 62]. Method validation is very necessary for the recovery of PAHs to show that the extraction procedures for the samples are very effective [63, 64].

Recent techniques for the extraction and concentration of PAHs from environmental water samples include solid-phase extraction (SPE), liquid-liquid extraction (LLE), continuous liquid-liquid extraction (CLLE), solid-phase microextraction (SPME), hollow fibre liquid-phase microextraction (HF-LPME) and stirring bar sorptive extraction (SBSE) [20, 65–68]. The two most commonly used, which were also recommended by the USEPA for pre-concentration of PAHs in drinking water samples are LLE and SPE [63, 69–71].

3.5.2. *Sediment extraction*

Analysis of PAHs in the solid matrices is not simple and therefore requires careful sample pre-treatment such as isolation or extraction, prior to instrumental determination. The extraction procedure may be followed by cleanup if necessary [72].

Extraction methods for PAHs in soils and sediments includes Soxhlet extraction (SE), mechanical shaking or agitation [30, 73], automated Soxhlet extraction, pressurized fluid extraction (PFE), microwave extraction (ME) [74], surfactant promoted extraction, accelerated solvent

extraction (ASE), supercritical fluid extraction (SFE), sub-critical fluid extraction, solvent washing, extraction by vegetable oils and extraction by cyclodextrins [72], ultrasonic extraction [75], microwave dissolution, pressurized liquid extraction (PLE) [76–79], solid phase microextraction (SPME) and micellar solid-phase microextraction (MSPME) [80, 81].

An efficient extraction technique should be able to produce good results within a short time with minimum operator involvement. It should also be cheap, and safe for both the analyst and the environment [82]. The choice of extraction technique depends on several factors including capital cost, operating cost, sample matrix, simplicity of operation, sample throughput and the availability of a standardized method [30, 83].

3.6. Analytical methods for polycyclic aromatic hydrocarbon in water and sediment

Polycyclic aromatic hydrocarbons with their derivatives are globally determined after extraction from food, environmental or biological samples using analytical methods approved by certain agencies and/or organizations such as the United States Environmental Protection Agency (USEPA), International Organization for Standardization (ISO) and National Institute for Occupational Safety and Health (NIOSH). The methods are basically grouped into three: immunoassay, spectrometric and chromatographic methods [57, 84].

Immunoassay methods (EPA 4030 and 4035, Update III) which exist mostly as kits are not very popular because of their tendency to introduce strong biases in the final results. Besides, the precision, accuracy and affinity of the methods for many aromatic compounds are significantly lower than what could be obtained from other standard methods. Hence, they are mostly used for field screening in the analysis of soil and water [84, 85]. Among the spectrometries, ultraviolet (UV) and infrared (IR) methods are the most prominent. However, UV methods (absorption and fluorescence) which are considered being sensitive and selective to aromatic compounds like PAHs are more often affected by interference due to the presence of some other compounds like lipids in the sample matrix. Similarly, the IR spectrometric method which although is fast and cheap, requires the sample to undergo a mandatory cleanup step after extraction before analytical determination and is also poorly selective [57].

Liquid and gas chromatographic methods are the most frequently used for the analysis of PAHs, in spite of being more expensive and time consuming [8, 9, 36]. Available liquid chromatographic (LC) methods include high-performance liquid chromatography (HPLC) with UV and fluorescence (FL) detectors in series (EPA 550, 610 and 8310; NIOSH 5506 and 5800) [74, 86], mass spectrometer [87], photo-diode array detector (PDA) [88], PDA and fluorescence detectors combined [89], or fluorescence detector alone (ISO 17993) [22]. Whereas gas chromatographic (GC) methods could be used after the EPA recommended organic extraction procedures with flame ionization detector (EPA 610 and 8100, NIOSH 5515), Fourier transform-infrared detector (EPA 8410), mass spectrometer (EPA 525, 625 and 8270; ISO 18287; ISO/DTS 28581; ISO/FDIS 28540 and EN 15527), or mass spectrometer with thermal extraction (EPA 8275) [22, 74, 90].

3.6.1. Liquid chromatographic methods

HPLC methods are more patronized because of the ease of determining thermally labile, semi-volatile, less volatile or non-volatile compounds. They are also more sensitive, specific

and reproducible than some GC based methods [8, 63, 91–93]. EPA methods 550, 610 and 8310 require the aqueous samples to be treated prior the instrumental analysis with liquid-liquid or solid phase extraction procedure for isolation of the compounds of interest. Solid samples are extracted using either Soxhlet or sonication devices with suitable solvent(s) [94–96]. The sample extracts are required to be dissolved in any solvent miscible with the one used for extraction before injection into the instrument [84].

However, NIOSH 5506 is limited in that, it can only respond to samples extracted by acetonitrile only and not any other extraction solvent. The performance of the method is also affected negatively by huge presence of extremely adsorptive particulate matter such as fly ash, asphalt fumes, or diesel soot in the sample. But it is sensitive to PAHs and capable to determine them in the mixture of aliphatic compounds, even in trace level. NIOSH 5800 is also different from others because it uses a flow-injection method for the determination of total polycyclic aromatic compounds in the sample at two different sets of fluorescent wavelengths [21]. The HPLC methods (EPA 550, 610, 8310 and NIOSH 5506) determine PAHs in the sample extracts using UV and fluorescence (FL) detectors connected in series. The first four PAHs (naphthalene, acenaphthylene, acenaphthene, and fluorene) in the priority list of USEPA which are not very fluorescent are analysed with the less sensitive ultraviolet detector while the remaining ones are determined using fluorescence detector with better sensitivity [87].

EPA 8310 provides adequate sensitivity at part per billion levels for the detection of PAHs in water samples. The method is also applicable to the analysis of PAHs in the effluent samples [84]. UV and fluorescence detectors are the most extensively used in the liquid chromatographic measurement of PAHs, especially those with high molecular weights. UV/Visible detector can detect almost all the PAHs in the UV range of 190 to 360 nm. The sensitivity and selectivity of fluorescence detector in the quantitation of PAHs in the complex environmental mixture is much higher, particularly when appropriate excitation and emission wavelengths are selected [63, 69, 87, 88]. Photodiode array (PDA) detector which is much more sensitive than UV/Visible detector is sometimes used as an alternative, either alone [8, 70, 88] or with fluorescence detector [89, 97]. Notwithstanding, the latter remains the most sensitive among the modern LC detectors, which is highly recommended for trace determination of PAHs [98].

Another valued detector in liquid chromatography is mass spectrometer (MS). It is very useful for identification and characterization of trace polar components, especially if many compounds of interest are involved [92, 99]. An all-inclusive use of LC/MS for the analysis of aromatic compounds has been reported. It involves the introduction of sample into the chromatograph for separation, after which it passes through a sophisticated interface (such as thermospray, electrospray, moving belt and particle beam) where separation of target compounds from aqueous mobile phase takes place, then finally into the mass spectrometer for characterization [92, 100]. However, there is no particular interface suitable for the separation of all the polycyclic aromatic hydrocarbons in the sample [87].

3.6.2. Gas chromatographic methods

Gas chromatographic methods are used for the separation and detection of non-polar organic compounds that are volatile and thermally stable. It is also used for the analysis of certain

semi-volatile compounds including PAHs [92, 99]. Applicable detectors for the analytical determination of aromatic compounds including PAHs in samples using GC include photoionization detector (PID), flame ionization detector (FID), Fourier transform-infrared (FT-IR) and mass spectrometer (MS) [75, 84, 101, 102]. The technique can offer high resolving power with the use of capillary column. PAHs with molecular weight (MW) above 300 atomic mass unit (amu) are always difficult to analyse with GC because of their low volatilities, tendency to decompose when subjected to high temperature, and possibility of adsorbing to the GC inlet and column [87].

EPA 8021B is a GC method that is majorly used with PID to determine the level of some volatile aromatics such as benzene, toluene, ethylbenzene, and xylenes (BTEX), as well as certain oxygenates (e.g. methyl-t-butyl ether (MTBE)), a number of olefins, cycloalkanes, branched alkanes and some halogenated compounds in so many sample types, including ground water, aqueous sludges, waste solvents, oily wastes, soils and sediments. It has the advantages of being selective and sensitive, although it is easily desensitized and contaminated by compounds with heavy molecular weights [84, 103].

EPA 610 was specifically designed for PAHs determination in wastewater after liquid-liquid extraction (LLE) with methylene chloride. The advantage of the method is that it is available for use as a liquid chromatographic technique with UV and fluorescence detection. It can also be used as a gas chromatographic method with either packed or capillary column coupled with flame ionization detector (GC/FID) [87, 94]. EPA 8100 is another GC/FID method that can be used to determine the target compounds in both water and solid samples. It is a packed column gas chromatographic method. The method allows the water samples to be adjusted to neutral pH and extracted prior to analytical determination using either LLE or continuous LLE, while the extraction of solid samples could be achieved through the use of Soxhlet or ultrasonic extraction set-up. The packed column in the procedures conversely present a major challenge of adequate resolution of four pairs of PAHs, which are anthracene and phenanthrene; chrysene and benzo[a]anthracene; benzo[b]fluoranthene and benzo[k]fluoranthene; and dibenzo[a,h]anthracene and indeno[1,2,3-cd]pyrene, although the listed pairs of compounds can be well resolved if capillary column is used in place of the packed column. Otherwise, the silica gel cleanup is suggested as a necessary component of the methods, except if the sample matrix is relatively clean [87, 90].

NIOSH 5515 which is also a GC/FID method was designed to analyse air sample with capillary column (30 m × 0.32-mm ID, fused silica capillary, 1-μm DB-5) coupled with FID, after being subjected to filter extraction [86, 104]. Even though FID is a sensitive detector for PAHs, the use is limited by its sensitivity to background interferences from some common environmental pollutants like phthalates and other co-extracted non-target compounds from carbonaceous sources. Therefore, cleanup step is very mandatory for appropriate quantification and identification of analytes using this detector [84, 87, 105, 106].

EPA 525, 625, and 8270 are GC/MS methods for identification and quantitation of PAHs and some other contaminants in various environmental media [87]. EPA 525 was designed for the determination of several groups of semi-volatile compounds including PAHs, phthalates, PCBs and adipates in drinking or river water. The pH of the water sample is to be adjusted to <2 using 6 N HCl before a solid phase extraction (SPE) procedure [107]. EPA 625 was, however,

intended for the analysis of the listed classes of contaminants in the wastewater samples. The municipal and/or industrial wastewater samples are recommended for extraction at two different pHs using LLE, followed by GC/MS analysis. The updated version of the method (EPA 625.1) has included the use of SPE as an alternative extraction procedure [108].

Moreover, EPA 8270 can be employed for the quantitative determination of the levels of semi-volatile organic pollutants in water, air, soils, and other solid waste matrices. Recommended sample preparation techniques for aqueous samples in this method include LLE and CLLE. Solid samples are to be prepared by Soxhlet, automated Soxhlet, ultrasonic, supercritical fluid, or solvent extraction device while non-aqueous solvent-soluble wastes are to be made ready for instrumental analysis by solvent dilution. In addition to the listed extraction methods, EPA 8270 also made provision for the isolation of semi-volatile compounds in the leachates obtained from toxicity characteristic leaching procedure (TCLP) by SPE. Aside PAHs, the method can be applied to several other classes of organic compounds, such as chlorinated hydrocarbons, pesticides, aromatic nitro compounds, phenols, phthalate esters, organophosphate esters, nitrosamines, ethers, ketones, anilines, haloethers, aldehydes, pyridines, and quinolones [109].

EPA 8272, another GC/MS technique is used for the analysis of ten parent PAHs and two alkylated PAHs (naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, chrysene, 2-methylnaphthalene and 1-methylnaphthalene) in the pore water recovered from sediments, groundwater, and any other water sample (e.g. seawater, tap water) [110, 111]. The target compounds determinable with the method are those that are very soluble in the environmental waters. The interstitial water is usually removed from the sediment by centrifugation, followed by supernatant collection, while other sample types are prepared for analysis by removal of colloid with flocculation using aluminium potassium sulphate (alum) and sodium hydroxide. The flocculation step is repeated, followed by centrifugation, supernatant collection and solid phase microextraction (SPME). The PAHs in the extract are thereafter determined using GC/MS operated in the selected ion monitoring (SIM) mode [112].

GC/MS is the most frequently used technique for the analytical determination of many organic compounds, including PAHs because it identifies analytes not only by retention time but also by mass spectrum, providing structural information and high sensitivity needed for quantification in selected ion monitoring (SIM) mode [8, 66]. It is more expensive than the non-selective procedures like GC/FID and GC/PID and is often employed to determine the concentrations of target volatile and semi-volatile constituents of petroleum. However, the identification of unknown compounds with MS is limited using electron ionization (EI) because mass spectra only are not sufficient for suitable identification of substances. Chemical ionization (CI) or high resolution mass spectrometry if available can provide additional information needed for exhaustive elucidation [57, 84, 99].

EPA 8410 and 8275 are other GC based methods for PAHs. EPA 8410 uses Fourier transform-infrared spectrometer (FTIR) for detection and quantitation of the compounds of interest in the sample extract. The method is considered a valuable complement to EPA 8270 because it enables proper identification of certain isomers that are ordinarily difficult to be differentiated

using GC/MS. The capillary GC procedure is applicable to the analysis of many semi-volatile organic compounds in wastewater, soils, sediments, and solid wastes. It requires compulsory cleanup of extract before injection into the gas chromatograph [113]. EPA 8275 is another capillary GC/MS procedure with an online thermal extraction for quantitative analysis of specific PCBs and the 16 EPA priority PAHs in soils, sludges, and solid wastes [87]. It involves the extraction of the analyte compounds from the sample matrix by heating to 340°C in the extraction chamber, where the extract is held for about three minutes before being swept into the column by split injection in the ratio ~35:1 or ~400:1, depending on the concentration of the sample. The injected extract is concentrated on the head of the GC column. The analytes are appropriately separated in the column and are qualitatively and quantitatively determined using mass spectrometer [114].

Of all the methods discussed, the most prevalent for the determination of PAHs in environmental media are the GC/MS and HPLC with UV/fluorescence detectors. The choice of the two is based on their major advantages of high sensitivity and selectivity, in addition to the ability of mass spectrometer to provide additional structural information when used as detector [115].

3.7. Levels of PAHs in some waters and sediments across the world

3.7.1. Levels in water

The levels of PAHs in some environmental waters across the globe are presented in **Table 4**. The reported concentrations varied from 0.0003 to 42,350 µg/L. The minimum and maximum values were both recorded in the Asian continent, precisely from the Kor River water, Iran [16] and major rivers of Southern Thailand, respectively. Foremost rivers in the southernmost part of Thailand were categorized as natural inland water Class II, implying that the water must be made to pass through a number of treatment steps before it can be considered for reuse, given their level of pollution. The most abundant PAHs in the water samples from these rivers were the 4 and 5 rings congeners, which suggest discharge of anthropogenic wastes as major source of contaminants in the water bodies [116].

Other higher levels published emanated from African continent. For instance, Edokpayi et al. [117] reported PAH concentration in the range of 126–7510 µg/L for Mvudi River water and BDL–7805 µg/L for Nzhelele River water, both in South Africa. The elevated concentrations of the organic contaminants in the two rivers were linked to contamination by the wastewater treatment facilities in the study area. Similarly, rivers from Mutshundudi and Nzhelele areas of Limpopo, South Africa were reportedly polluted up to 137 µg/L by high degree of refuse dumping, organic waste burning, activities of the roadside mechanics and traffic density in the area, with HPAHs predominating in the rainy season [64]. Gorleku et al. [102] also accounted for total PAHs as high as 84.50 µg/L in the water column of Tema Harbour, Ghana. The levels determined at the inner fishing harbour (e.g. canoe landing site and some locations in the main harbour) were higher than at the outer fishing harbour. Canoe landing site recorded significantly high values because of possible leakage of petroleum products from the two-stroke engines of the fishing canoes, industrial effluent discharge into the sea through Chemu Lagoon [118], smoking of fish and other anthropogenic activities in the vicinity.

Sample source	Obtained concentration (µg/L)	% LPAHs	Reference
Europe			
Evoikos Gulf Water, Greece (Shipyards)	0.0009–0.14	68.6	[70]
Malliakos Gulf Water, Greece (Ag. Marina)	0.002–0.05	75.0	[70]
Malliakos River Water, Greece (Sperchios)	0.001–0.07	96.3	[70]
Surface Waters of Northern Greece	0.001–0.68	85.2	[127]
Asia			
Kor River Water, Iran	0.0003–0.24	81.6	[16]
Surface waters in Hangzhou, China	0.99–9.66	–	[128]
Gao-ping River, Taiwan	0.01–9.40	–	[129]
Xiamen Harbour, China	0.11–0.95	–	[130]
Water Resources in Mahasarakham University, Thailand	0.001–0.009	13.4	[123]
Major Rivers of Southern Thailand	2250–42,350	–	[116]
Well Water and River Water, Xuanwei and Fuyuan, China	0.0009–0.06	–	[131]
Mumbai Harbour Line, India	0.009–0.047	–	[132]
Reclaimed and Surface Water of Tianjin, China	1.80–35	95.9	[121]
Africa			
Suez Canal, Egypt	0.01–0.5	16.2	[124]
Shallow Lake, Zeekoevlei, South Africa	0.00001–0.01 (individual)	95.0	[133]
Mvudi River water, South Africa	126–7510	25.3	[117]
Nzhelele River water, South Africa	BDL – 7805	23.1	[117]
Surface Water in Nigerian Coastal Communities – Eleme, Nigeria (highly industrialized)	22.10 (total)	–	[97]
Surface Water in Nigerian Coastal Communities – Eleme, Nigeria (less industrialized)	8.39 (total)	–	[97]
Lakes and Rivers around Johannesburg/Pretoria in South Africa	0.021–0.62	86.6	[20]
Tema Harbour Water, Ghana	33.20–84.50	–	[102]
Rivers Water, Limpopo, South Africa	0.10–137	–	[64]
Hartbeespoort Dam, South Africa	0.030–0.05	–	[134]
America			
Paraíba do Sul River, Brazil	0.255 (benzo[a]pyrene only)	–	[135]
Mississippi river, USA	0.06–0.15	–	[136]
Chesapeake Bay, USA	0.02–0.09	–	[137]

Sample source	Obtained concentration (µg/L)	% LPAHs	Reference
York river, USA	0.002–0.12	–	[138]
Petroleum Produced Water, Sergipe, Brazil	3.50–44.30	52.4	[67]
San Francisco Estuary, USA	0.007–0.12	–	[139]

BDL: below detection limit.

Table 4. Levels of PAHs in waters around the world.

The EU Directive 98/83/EC gave a permissible level of 0.1 µg/L for PAHs in water intended for consumption by humans [119, 120]. Unfortunately, the target limit was found exceeded in many regions of the world as shown in **Table 4**; this may be attributed to the increased urbanization, industrialization and incessant discharge of untreated or partially treated effluents into the water bodies. Other possible sources of high PAHs in the water phase of the aquatic systems include vehicular exhaust emission, intense shipping activities [121], and run-off from petroleum filling stations [97]. The results compiled revealed that pollution due to PAHs in water is more pronounced in the Asian and African continents than other parts of the globe. Hence, there is need for strict compliance.

Table 4 indicated that LPAHs are more soluble in the water phase than the sediments, as they recorded large percentages in most of the water samples analysed [16, 63], although their solubility is usually reduced significantly in the marine water [122]. Two- and three-ring PAHs which are referred to as low molecular weight PAHs account for between 52.4 and 96.3% in the water column, except in few studies conducted in Thailand, South Africa and Egypt [117, 123, 124].

3.7.2. Levels in sediment

The global distribution of PAHs in the sediments as shown in **Table 5** revealed that the total concentrations of the contaminants ranged between 0 and 1.266×10^9 µg/kg. The highest levels of these organic pollutants were reported from Taylor Creek, Bayelsa State in the Southern part of Nigeria, an environment known for oil exploration. The extremely high level of PAHs in the area can be associated with the activities of the Etelebou flow station that discharges liquid effluents into the tributary of Taylor Creek. The contaminant levels were particularly high at Ogboloma, Koroama and Okolobiri of the community. This could be very injurious to the health of humans in the locality and also affect the metabolic and behavioural systems of the aquatic organisms adversely [125].

Similarly, PAHs in the range of 310–528,000 µg/kg dry weight was recorded in the surficial marine sediments obtained from Kitimat Harbour, Canada. The pollution reported in the harbour sediments could principally come from an aluminium smelter at the head of Kitimat Arm through atmospheric deposition, run-off water and effluent discharge. Remarkably high PAH levels (1×10^7 µg/kg) were even obtained from one of the settling ponds at Alcan aluminium smelter site. The outfall from the site reportedly flows directly into the harbour while

Sample source	Obtained concentration ($\mu\text{g/kg}$ dry weight)	% HPAHs	Reference
Europe			
West Mediterranean Sea (French Riviera, Corsica, Sardinia)	1.5–20,440	–	[141, 142]
The Czech Republic (Industrial)	3500–61,700	–	[143, 144]
Inshore coastal areas around Malta	0–14,990	–	[145]
Asia			
Gulf and the Gulf of Oman, UAE	0.6–9.4	–	[146]
Coastal of Bushehr, Persian Gulf	41.7–227.5	–	[25]
Industrial Port Area of Southern Kaohsiung Harbour	4425–51,261	56.3	[75]
Mumbai Harbour Line, India	17–134,134	–	[132]
Gulf and the Gulf of Oman, Qatar	0.55–92	–	[146]
Khure-Musa Estuarine, Persian Gulf	703–3302 (total)	80.9	[140]
Gulf and the Gulf of Oman, Bahrain	13–6600	–	[146]
Marine Environment, Korea	8.80–18,500	–	[147]
Coastal and Estuarine Areas of the Northern Bohai and Yellow Seas, China	52.3–1871	78.3	[148]
Gulf and the Gulf of Oman, Oman	1.6–30	–	[146]
Delhi, India	920–19,321 (total)	62.4	[8]
Kor River, Iran	167.4–530.3	82.5	[16]
Kyeonggi Bay, Korea	10–1400	–	[58]
Middle of Muggah Creek Estuary, Sydney (Australia)	142 (total)	–	[149, 150]
America			
South San Francisco Bay	~120 to 9560 (total)	–	[151]
Gulf of Naples and nearby Coastal Areas, US	0.34–31.77	–	[2, 152, 153]
Casco Bay, Maine, Texas	16–20,798 (total)	93.6	[154]
Kitimat Harbour, Canada	310–528,000	–	[126]
Fore River and Portland Harbor, Maine	2953–278,300	69	[122]
San Francisco Bay, California	36–6273 (total)	87.5	[155]
Todos Santos Bay, Mexico	7.6–813	–	[156]
Bagnoli Surface Sediment (industrial side of the Gulf of Naples)	0.1–2947	–	[2, 157, 158]
Tabasco state, Mexico	454–3120	–	[159]
Northwest Coast Mediterranean Sea	86.5–48,090	–	[160]
Africa			
Suez Canal, Egypt	103.41–238.76	76.2	[124]

Sample source	Obtained concentration ($\mu\text{g/kg}$ dry weight)	% HPAHs	Reference
Central South Africa (Industrial, Residential and Agricultural)	44–39,000 (total)	–	[144, 161]
Lakes and Rivers around Johannesburg/Pretoria in South Africa	61–45,281	52.3	[20]
Rivers in Thohoyandou, Limpopo Province, South Africa	111.6–61,764 (total)	–	[64]
Taylor Creek, Southern Nigeria (non-tidal freshwater-Bayelsa)	1.781×10^8 – 1.266×10^9	–	[125]
Mvudi River water, South Africa	266–21,600	55.3	[117]
Nzhelele River water, South Africa	206–13,710	87.4	[117]
Tema Harbour, Ghana	28,600–190,300	–	[102]

Table 5. Levels of PAHs in sediments around the world.

surface run-off from the northern part of the site and effluent from the anode plant wet scrubbers in the area enter through the lagoon, raising the concentration of PAHs in the harbour sediments [126]. Another elevated PAH levels from American sediments were reported from Fore River and Portland Harbour, Maine. The total PAHs at most of the sampling locations were high. For instance, levels detected at the Gas Works/China Clay Docks, Maine State Pier and Casco Bay Ferry Terminal were 278,300, 161,990 and 63,533 $\mu\text{g/kg}$, respectively. High concentrations at these sites were possibly from combustion-related sources because the ratio of LPAHs to the total PAHs in all the study sites were very low, signifying they are less likely to have come from petrogenic origins [122].

The study conducted in 2011 at the Suez Canal, Port Said in Egypt also revealed the effects of heavy shipment, sewage outfalls, highest traffic density of oil tanker, and discharge of industrial effluents on the health status of the marine sediment at the sites. The total PAHs at Port Said and Suez Harbours were up to 239 $\mu\text{g/kg}$ [124]. Likewise, Gorleku et al. [102] and Dhananjayan et al. [132] reported concentration ranges of 28,600–190,300 $\mu\text{g/kg}$ and 17–134,134 $\mu\text{g/kg}$ in the Tema Harbour, Ghana and Mumbai Harbour Line, India, respectively. Reasons for these levels of PAHs include oil spillage, coastal and river run-off, industrial and domestic wastes discharges. Diagnostic analysis suggested that the PAH assemblages in the Mumbai Harbour Line could have originated from combustion of fossil materials, while the results from Tema Harbour indicated a possible contamination from both petrogenic and pyrogenic sources [102, 132].

Generally, the extremely high levels of PAHs in the freshwater and marine sediments globally were mostly from oil exploration areas, harbours/shipping yards and industrial locations. The compiled results showed that the effects of pollution due to industrial growth were not as high as those from the two other sources. PAHs occurred well above the ERL (4000 $\mu\text{g/kg}$) in most of the areas where the studies were carried out, and not less than 25% of the sites exceeded the ERM value of 44,792 $\mu\text{g/kg}$. This implies there is possibility of high biological risk to the aquatic creatures in the freshwater and marine environments discussed if not curtailed within a reasonable period of time [37, 58, 59].

Table 5 revealed that the ratio of high molecular weight PAHs to the total PAHs (expressed in percentage) in the sediments ranges generally from 56.3 to 93.6%, corroborating previously reported works [16, 63, 102, 140] and suggesting sources associated with run-off, air deposition and combustion of fossil materials [122].

4. Conclusion

PAHs are among the major organic pollutants found in the aquatic systems. They are mostly generated from both natural and anthropogenic sources. Many of them are highly carcinogenic in nature and are also linked with endocrine system disruption at levels higher than the maximum concentration limit within a short period of time. Hence, they are frequently determined in the environmental samples. Liquid and gas chromatography remain the most commonly used analytical methods for the qualitative and quantitative determination of the organic contaminants, owing to their several advantages, which include better resolution, high sensitivity and selectivity. HPLC with UV/fluorescence detectors in series and GC/MS have proven to be the best techniques amongst others. GC/MS is the most frequently used because of the advantages of identification using both retention time and mass spectrum, providing added information on the chemical structures of the analyte compounds. It also offers high sensitivity required for quantification in selected ion monitoring (SIM) mode. Although, LC/MS can offer similar advantages, it is limited in that, there is no specific interface suitable for the separation of all the PAHs at the same time.

The results collated revealed that fresh and marine waters in many parts of the world are polluted with PAHs, possibly due to increased urbanization, industrialization, incessant discharge of untreated or partially treated effluents into the water bodies and intense shipping activities, amongst many other inputs. The pollution was more pronounced in the Asian and African continents than other parts of the globe. Similarly, the levels reported for the sediments were in most cases above the ERL, signifying the likelihood of serious biological effects on aquatic organisms worldwide. Particularly high concentrations of PAHs in the sediment compartment were generally from areas characterized with intense oil exploration, shipping and industrial activities. LPAHs which are more soluble in the water phase recorded high percentage in most of the water samples and conversely, HPAHs were found generally higher in the sediment samples with percentage ranging from 56.3 to 93.6%. Therefore, there is need for strict compliance with environmental laws, in order to achieve a very safe environment for humans and biota.

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Conflict of interest

We declare that there is no conflict of interest concerning the publication of this paper.

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